

Trapped gold, flashy dyes: Taking advantage of zeolitic imidazolate framework-8's weakness

Gevangen goud, felle kleurstoffen: Voordeel halen uit
zeolitic imidazolate framework-8's zwakke punt

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Preface

Even though theses have a reputation for being a kind of academic torture device, I genuinely had fun making mine. Between the inevitable setbacks and the little wins, I found myself actually enjoying the process. Of course, this was largely because I had the chance to work with fantastic supervisors, Jorid and Rajesh, whose support and guidance have shaped this work in more ways than I can count. Over the past year, you didn't just help me, you taught me. You taught me through troubleshooting experiments and designing setups, tweaking posters and presentations, academic writing, and even trying to make sense of my data management (which is still a bit of a mess, sorry). I've learned a lot! More importantly, you've helped me start developing the mindset and habits needed to grow in research. I am aware that I've still a lot to learn, but your guidance has given me a strong foundation to build on. For that, I'm truly grateful. Thank you for your patience, your wisdom, and for somehow managing to supervise without ever making it feel like I was being supervised. That's a talent.

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A wise man and woman once said: "*Nooit gedacht da gij op 't unief zou geraken!*" And honestly, mom and dad, six years ago, I didn't either. But hey, miracles happen. That being said, if it weren't for the two of you, I wouldn't be sitting here writing this. I'll never forget the look you gave Mrs. Wens back in high school when she suggested I drop math and science and go for social sciences. If looks could kill, we'd

have had an empty teacher's lounge. And then there were the times I forgot my student dorm key... and you drove all the way from Antwerp to bring it. Not all heroes wear capes. Some drive down the E19 with a spare key and a sigh. I also want to thank you for showing interest in my thesis, and for nodding enthusiastically at the right moments. Your support is a major reason I've made it this far. So for all that (and for the countless other things I've probably taken for granted): thank you.

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Thank you everyone!

Abstract

This work exploits the acid-responsive behavior of zeolitic imidazolate framework-8 (ZIF-8) for two distinct applications. In application one, gold nanoparticles (AuNPs) are encapsulated within ZIF-8 to address purification, aggregation, and dosing challenges of AuNP suspensions. The resulting AuNP@ZIF-8 powders enable easy handling, efficient purification through centrifugation at low g-forces, and demonstrate excellent redispersibility upon acid-triggered ZIF-8 degradation. The encapsulation strategy in ZIF-8 proved highly effective, achieving gold retention efficiencies above 80% after three purification cycles. In contrast, the gold retention efficiency for non-encapsulated AuNPs was less than 25% after three purification cycles. Embedment in ZIF-8 converted non-purified colloids into even more robust, dispersible solids, enhancing their suitability for transport and long-term storage.

Secondly, ZIF-8's acid response is used as a trigger for fluorescence activation of encapsulated fluorescent dyes, enabling acid vapor detection. Upon exposure to acid vapors, ZIF-8 degrades, restoring the quenched fluorescence of the dye. Rhodamine B was identified as the most promising candidate because of its robust and reproducible fluorescence behavior in ZIF-8. A simplified optical setup using LED excitation and camera-based detection successfully demonstrated acid vapor sensing at single-digit ppmv levels. Finally, the technology was further translated into films, facilitating device integration.

Together, these studies demonstrate that ZIF-8's acid sensitivity can be strategically used to improve gold nanoparticle processing and enable the development of practical, portable acid-sensing materials.

Samenvatting

In dit werk wordt het zuurgevoelige gedrag van *zeolitic imidazolate framework-8* (ZIF-8) onderzocht en benut voor twee verschillende toepassingen. In toepassing één worden goudnanodeeltjes (AuNPs) ingekapseld in ZIF-8 om uitdagingen aan te pakken met betrekking tot zuivering, aggregatie en dosering van AuNP-suspensies. De resulterende AuNP@ZIF-8 poeders vergemakkelijken het werken met AuNPs, maken efficiënte zuivering mogelijk via centrifugatie bij lage g-krachten, en tonen uitstekende resuspensie na zuur-geïnduceerde afbraak van ZIF-8. Deze inkapselingsstrategie bleek zeer effectief, met goudretentie boven de 80% na drie zuiveringscycli terwijl dit maar 25% was voor niet-ingekapselde AuNPs. Daarnaast maakt inkapseling het mogelijk om ongezuiverde colloïdale systemen om te zetten in meer robuuste, resuspendeerbare poeders die geschikt zijn voor transport en langdurige opslag.

In toepassing twee wordt de zuurgevoeligheid van ZIF-8 benut voor de fluorescentieactivering van ingekapselde fluorescerende kleurstoffen, waarmee detectie van zure dampen mogelijk wordt. Bij blootstelling aan zure dampen degradeert ZIF-8, waardoor de onderdrukte fluorescentie van de kleurstof wordt hersteld. Rhodamine B bleek de meest geschikte kandidaat vanwege zijn robuuste en reproduceerbare fluorescentiegedrag. Een eenvoudige optische opstelling met LED-excitatie en cameradetectie toonde met succes aan dat zure dampen al bij lage ppmv-waarden kunnen worden waargenomen. De technologie werd bovendien vertaald naar dunne films, waardoor integratie op vaste oppervlakken mogelijk werd.

Gezamenlijk tonen deze studies aan dat de zuurgevoeligheid van ZIF-8 strategisch kan worden ingezet om zuivering van goud nanopartikels te verbeteren en de ontwikkeling van praktische, draagbare sensormaterialen voor zuurdetectie mogelijk te maken.

List of Abbreviations and Symbols

AuNP(s)	Gold nanoparticle(s)
AuNP@ZIF-8	Umbrella term for all different types of AuNPs in ZIF-8
C343	Coumarin 343
Cit-AuNP(s)	Citrate-capped gold nanoparticle(s)
Cys-AuNP(s)	Cysteine-capped gold nanoparticle(s)
Cys-PAH-AuNP(s)	Cysteine-PAH-capped gold nanoparticle(s)
Dye@ZIF-8	Umbrella term for all different types of dye in ZIF-8 materials
EM	Electromagnetic
F	Fluorescein
FA	Formic acid
HmIM	2-methylimidazole
HmIM:Zn ratio	2-methylimidazole to zinc ratio
LAL	Laser ablation in liquid
LSPR	Localized surface plasmon resonance
mDye@ZIF-8	Fluorescent dyes in large ZIF-8 crystals
MOF	Metal–organic framework
Na ₃ Ct	Tri-sodium citrate
nDye@ZIF-8	Fluorescent dyes in nano-sized ZIF-8 crystals
NP(s)	Nanoparticle(s)
PAH	Poly(allylamine) hydrochloride
PAH-AuNP(s)	Polly(allylamine) hydrochloride-capped gold nanoparticle(s)
pMNP(s)	Plasmonic metal nanoparticle(s)
PVP	Polyvinyl pyrrolidone
PVP-AuNP(s)	Polyvinyl pyrrolidone-capped gold nanoparticle(s)
Rh6G	Rhodamine 6G
RhB	Rhodamine B
RI	Refractive index
SC(s)	Semiconductor(s)
SERS	Surface enhanced Raman spectroscopy
SSA(s)	Specific surface area(s)
UV-Vis	Ultraviolet-visible light
ZIF	Zeolitic imidazolate framework

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1 Context and Objectives

Metal-organic frameworks (MOFs) are a class of porous, crystalline materials known for their high specific surface area (SSA), tunable structure, and molecular sieving capabilities. Among the different types of MOFs, zeolitic imidazolate framework-8 (ZIF-8) stands out for its high porosity and crystalline structure thereby providing a robust platform for integrating functional components. Its acid sensitivity causes the lattice to degrade when exposed to an acid environment. This acid-responsive behavior will be used for two distinct applications.

In the first application, the objective is to improve the purification, handling, and dosing of gold nanoparticles (AuNPs). AuNPs are valued for their optical properties, but their purification involves significant AuNP losses during centrifugation due to aggregation and incomplete redispersion. Additionally, the long-term stability of AuNP suspensions and purification of large volumes pose challenges. To address these limitations, AuNPs are immobilized within ZIF-8 forming a hybrid powder that enables centrifugation and washing without aggregation or losses. Furthermore, the acid-responsive behavior of ZIF-8 can be exploited to dissolve ZIF-8 after processing, allowing even redispersion of the AuNPs. This hybrid powder also permits precise weighing for accurate AuNP dosing, crucial for reproducible catalyst preparation.

In the second application, the objective is to exploit ZIF-8's acid-responsive behavior to develop a low-cost, fluorescence-based acid vapor sensing system. In this approach, fluorescent dyes are encapsulated within the MOF. Upon acid-triggered decomposition of ZIF-8, the fluorescence of the dyes is restored, offering a distinct and irreversible signal. This mechanism provides an advantage over adsorption-based methods, which are reversible and depend on subtle material property changes that can be difficult to detect, particularly at low concentration ranges. To translate this concept into a practical sensing platform, acid-sensing films will be fabricated by airbrushing ZIF-8-dye composites onto substrates. Furthermore, the intrinsic fluorescence behavior dyes will be studied.

2 Literature

2.1 Metal-organic frameworks

Metal-organic frameworks (MOFs) are a class of porous crystalline materials made from organic ligands (linkers) coordinated to metal ions or clusters (nodes), forming highly structured, hybrid networks (**Figure 2-1**). MOFs are widely used in applications such as gas storage, separation, catalysis, and drug delivery^{1–4}. Compared to traditional materials like zeolites, a subclass of aluminosilicates, they provide large SSAs, tunable and uniform porosity, selective interactions, and modularity for tailoring chemical properties. These features make MOFs more versatile than (alumino)silicates, which have rigid and less adjustable pore structures^{5–9}.

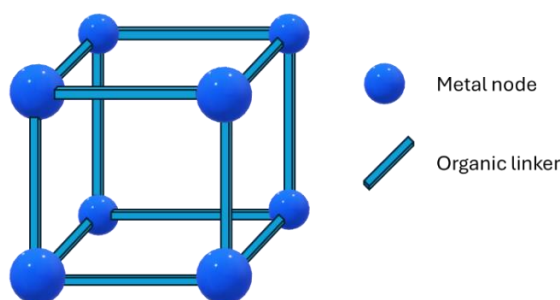


Figure 2-1: General representation of a MOF. The metal nodes function as joints keeping the structure together yet flexible. These may include metal clusters or metal ions of Cu, Zn, Fe, Co, ... The linker length allows for tailoring the porosity. Common examples of organic linkers include polyamines, carboxylates, crown ethers and phosphonates⁹.

2.1.1 Zeolitic imidazolate framework-8

ZIF-8, a prominent MOF, has attracted attention for its unique architecture, reported stability, and broad applications^{10–14}. Structurally, ZIF-8 consists of zinc ions (Zn^{2+}) tetrahedrally coordinated to nitrogen atoms from 2-methylimidazolate linkers, forming a crystalline framework with a sodalite-type topology. This structure includes large cavities accessible via windows measuring approximately 3.4 Å (**Figure 2-2**)^{4,15–17}. ZIF-8 is a hydrophobic material, making the framework resilient in aqueous environments. Its thermal stability depends on the environment. Under inert environments (N_2) ZIF-8 is stable up to 550 – 600°C, while this is only around 440°C in air^{18–21}.

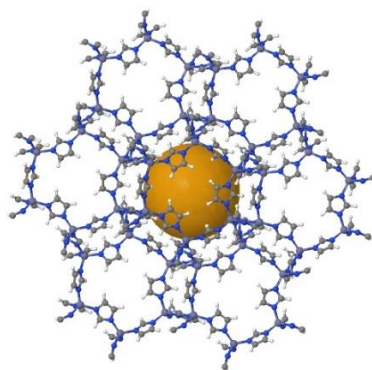


Figure 2-2: ZIF-8 structure. The yellow sphere indicates the cavity of a sodalite cage which has a diameter of approximately 11.6 Å. Blue spheres represent nitrogen, grey spheres are carbon, white spheres are hydrogen and purple spheres are zinc. From ChemTube3D, (2022)²².

ZIF-8 has high porosity, with SSAs often exceeding 1600 m²/g and a micropore volume of ~0.64 cm³/g, which facilitates efficient adsorption of gases and liquids^{11,23–25}. The uniform pore structure ensures consistent molecular sieving. Additionally, the modularity of its linkers allows functionalization for specific uses^{26–28}. ZIF-8 is a leading material for gas storage, and chemical sensing^{11,23–25}. It is widely applied in environmental remediation, gas separation, excelling in adsorption, catalytic degradation, and detection sensitivity^{1,4,29–31}.

ZIF-8 synthesis has been extensively studied, using methods such as solvothermal, microwave-assisted, ultrasonic, and aqueous approaches^{32–34}. Aqueous synthesis is particularly appealing for its environmental sustainability, avoiding toxic solvents like DMF^{15,16,34}. In this method, a zinc salt reacts with 2-methylimidazole (HmIM) in water, often producing high-crystallinity ZIF-8, though the degree of crystallinity depends on the linker-to-metal (HmIM:Zn) ratio. Other parameters influencing the crystal morphology are the pH, reactant concentration, and temperature control^{15,35}.

Despite its remarkable advantages, ZIF-8 presents certain challenges. The aqueous synthesis method, while environmentally advantageous, often requires careful optimization to achieve high yields and uniformity^{21,36,37}. Scaling up ZIF-8 production for industrial use also remains a key area of investigation³⁸. Additionally, ZIF-8 suffers from destabilization in acid environments leading to a change in material properties such as porosity and density^{16,39–41}.

2.1.2 Acid sensitivity of ZIF-8

When exposed to acid environments, the porous framework of ZIF-8 collapses (**Figure 2-3**)^{16,39–41}. Under acid conditions, protonation of the nitrogen atoms in 2-methylimidazolate linkers breaks the Zn-N coordination bonds, leading to hydrolysis and structural disassembly⁴². To optimize ZIF-8's acid-responsive properties, functional modifications of the imidazolate linkers have been employed to fine-tune degradation rates and pH sensitivity^{41,43}. Incorporating ZIF-8 into hybrid materials, such as polymer or graphene oxide composites, enhances structural integrity while retaining its pH-responsive disassembly^{16,44}.

The acid-responsive behavior of ZIF-8 enables its use in various pH-sensitive applications, particularly in acid environments where its controlled degradation occurs^{16,42}. For example, in drug delivery, ZIF-8 can encapsulate therapeutic agents and release them selectively in acid microenvironments, such as generated by tumors, allowing site-selective drug delivery^{43,45}. ZIF-8 functions as a controlled-release system in soil remediation, discharging catalytic agents under acid conditions to facilitate targeted pollutant breakdown and cleanup⁴⁶. ZIF-8's acid responsiveness also supports pH-sensitive catalysis, where encapsulated NPs or reactive species are released under acid conditions to drive chemical reactions^{14,47}. Lastly, in food packaging, ZIF-8 composites can release antimicrobial agents in response to spoilage-induced acidity, extending shelf life^{39,40,48}.

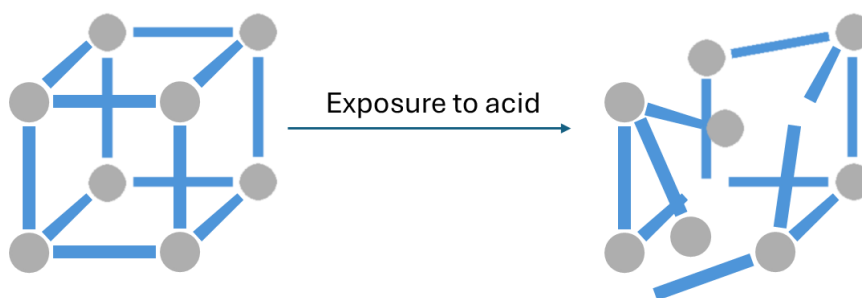


Figure 2-3: Illustration of ZIF-8 collapse upon exposure to acid. The blue rods represent the organic linker (2-methylimidazolate) and the grey spheres represent the Zn^{2+} -node.

It is important to note that other ZIFs display diverse behaviors under similar conditions, depending on their metal-linker framework and topology. For instance, ZIF-71, incorporating 4,5-dichloroimidazolate linkers, demonstrates enhanced acid resistance compared to ZIF-8. The chlorinated linkers increase hydrophobicity and

reduce susceptibility to protonation, slowing the breakdown of Zn-N coordination bonds in acid conditions^{39,49,50}. ZIF-67, a cobalt-based counterpart to ZIF-8, shows intermediate acid stability. The Co-N coordination bonds are slightly stronger than Zn-N, providing increased resistance to acid hydrolysis. However, like ZIF-8, ZIF-67 still degrades in highly acid aqueous environments, albeit at a slower rate⁴⁹. Another example is ZIF-90, which features an aldehyde-functionalized imidazolate linker. ZIF-90 exhibits enhanced acid sensitivity because of the electrophilic nature of its functional group, which facilitates hydrolysis⁴⁹. Environmental factors also play a critical role in determining ZIF stability. ZIFs tend to be more robust in dry acid vapors (e.g., SO₂ and CO₂), where hydrolysis is minimal, compared to aqueous or humid acid environments, where water accelerates proton transfer and facilitates degradation^{39,49}.

In this work, the acid sensitivity of ZIF-8 is exploited for two distinct applications: improving the handling, purification and storage of AuNP suspensions, and enabling fluorescence-based acid vapor sensing.

2.2 Gold nanoparticles: A brief review

2.2.1 Relevance of plasmonic metal nanoparticles

For centuries, humanity has been using plasmonic metal nanoparticles (pMNPs) to create visual effects, such as the captivating glow of the 4th century Lycurgus Cup and the vibrant colors of medieval stained glass (**Figure 2-4**)^{51–54}. In both cases, the presence of gold and silver nanoparticles (NPs) in ceramics or glass played a critical role, though mainly served aesthetic purposes. Yet, despite their early usage, the full potential of pMNPs remained unknown for ages due to a limited understanding^{52,53}.

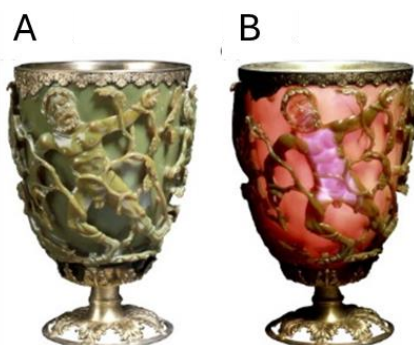


Figure 2-4: Lycurgus Cup, consisting of a gold and silver NPs infused glass, displaying the dichroic filter effect. Reflected light A) resonates differently than transmitted light B) hence showing different colors. At the basis of this phenomenon lies surface plasmon resonance⁵². Photo from Loos *et al.* (2015)⁵⁴.

Today, pMNPs have been widely adopted by scientists across several fields and play a crucial role in advancing a plethora of applications thanks to their distinct physicochemical properties at the nanoscale (**Table 2-1**)^{55–57}. For example in sensing applications, some pMNPs exhibit localized surface plasmon resonance (LSPR), which enhances sensor sensitivity by amplifying electromagnetic (EM) fields near the NP surface^{4,29,58–60}. This amplification strengthens interactions between the sensor and target analytes, enabling the detection of trace concentrations of pollutants, toxins, or biological markers such as in pregnancy or rapid COVID tests^{58,59}. LSPR-induced shifts in resonance wavelength or intensity allow for highly sensitive and specific detection^{61–64}. In photocatalysis, pMNPs, especially noble metals like platinum, silver, and gold, function primarily as co-catalysts or electron reservoirs, thereby improving photocatalytic efficiency⁶⁵. They enhance light absorption, promote charge carrier generation and separation, and inhibit the recombination of electron-hole pairs in semiconductor (SC) photocatalysts, such as TiO₂. As a result, catalytic processes like pollutant degradation, water splitting for hydrogen production, and CO₂ reduction become more efficient, thereby supporting sustainable environmental applications and green chemistry initiatives^{65–67}.

2.2.2 Localized surface plasmon resonance

A: General mechanism

LSPR occurs when the collective oscillations of conduction electrons in metal nanostructures, particularly in noble metals like gold and silver, are excited by incident light^{66,68–73}. These metals, because of their high density of free electrons, allow plasmon resonance when the frequency of the incoming light matches the natural oscillation frequency of the electrons (**Figure 2-5**)^{68,69,74}. Several parameters, including material type, dielectric environment, morphology of the NP, and the distance between them, influence the resonance conditions at which a pMNP exhibits maximal resonance^{67,71,72,75}. LSPR leads to a strong enhancement of the local EM field at the metal surface, near-field enhancement, which is highly localized, decreases exponentially with distance from the NP surface, and becomes negligible beyond ~5 nm, depending on nanoparticle morphology and material characteristics^{69,72,76}.

Table 2-1: Properties and applications of different pMNPs.

Properties / Applications	Gold NPs ^{56,58,65,74,77–79}	Silver NPs ^{55,59,75,80–84}	Platinum NPs ^{65,85–88}	Palladium NPs ^{65,85,89–91}	Copper NPs ^{92–95}
Sensing Applications	Biosensors (glucose, proteins, DNA)	SERS-based sensors	Electrochemical sensors (glucose, H ₂ O ₂)	Hydrogen sensors	Electrochemical sensors
	SERS-based sensors	Gas sensors (NH ₃ , H ₂ S)	Gas sensors (H ₂ , O ₂)	Electrochemical sensors	Gas sensors (CO, NO _x)
	Colorimetric sensors (e.g., pregnancy test)	Environmental sensors (pesticides, heavy metals)			
Catalysis Applications	CO oxidation	Antibacterial	Hydrogen evolution & Oxygen reduction	Hydrogenation	CO ₂ reduction
	Photocatalysis	Photocatalysis	Photocatalysis	Carbon-carbon coupling (Suzuki)	Photocatalysis
	Electrocatalysis (methanol oxidation)		Fuel Cells	Methanol oxidation	Ullmann reaction
					Water splitting
Advantages	Chemically inert	Superior LSPR	High catalytic activity	High hydrogen adsorption	Low cost
	Most studied	High SERS sensitivity	Stability under harsh conditions	Efficient catalysis	Good plasmonic effects
Limitations	Expensive	Prone to oxidation	Expensive	Expensive	Prone to oxidation
	Often catalytically outperformed by Pt	Stability issues & Cytotoxicity risks	Very weak LSPR	Weak LSPR	Lower stability
				High chemical reactivity	

Surface enhanced Raman spectroscopy (SERS)

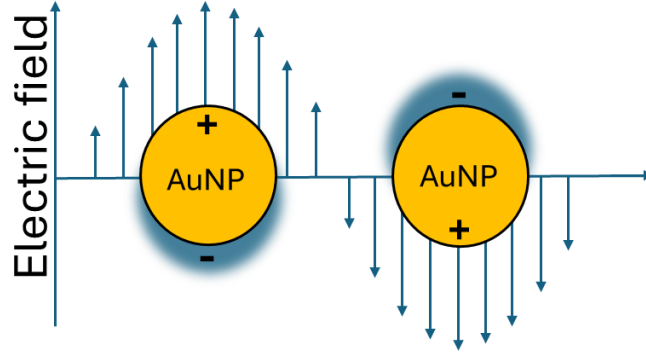


Figure 2-5: Simplified diagram of LSPR. The oscillating electron gas is excited by the evanescent fluctuating electric field. Since the particle size is considerable smaller than the wavelength, the electrons oscillate coherently. Adapted from Willets *et al.* (2007)⁷³.

B: Influence of material type and refractive index on LSPR

According to Mie theory and Drudes model, the resonance frequency for LSPR is sensitive to the refractive index (RI) of both the NP and its surroundings since the medium can offer resistance to the electron oscillation. The resonance condition can be expressed as:⁹⁶

$$\omega_{res} \approx \frac{\omega_p}{\sqrt{2\varepsilon_m + 1}} \quad 1$$

$$n = \sqrt{\varepsilon_{eff}} \quad 2$$

Where ω_p is the plasma frequency of the metal and ε_m is the dielectric constant of the surrounding medium. This equation shows the general trend, though it is not accurate for noble metals when the wavelength is smaller than $1 \mu\text{m}$ ⁶⁷. As the RI (n) of the surrounding medium changes, it modifies the effective dielectric constant experienced by the NP (**Eq. 2**). A higher RI offers more resistance to the oscillating electrons, meaning the electrons take longer to complete an oscillation, hence corresponding to lower frequency resonance and leading to a redshift. Conversely, a lower RI environment leads to a blueshift^{67,97}. Such a shift in RI can be used in sensing applications.

The metal's dielectric function (ε_m) determines the electron response to external EM fields (**Eq. 1**). Its real part governs the LSPR condition, while the imaginary part accounts for energy losses through damping, absorption, and scattering. These losses are critical in applications like photocatalysis (absorption-driven) and sensing

(scattering-driven). Silver, with lower energy losses, produces sharp, intense LSPR peaks. Gold, by contrast, has higher damping due to interband transitions near 1.7 eV, causing a redshift and broadening of its LSPR peak. Although gold and silver have similar plasma frequencies because of comparable electron densities, these interband effects make silver's plasmon peaks sharper and shifted toward the blue/UV region^{67,96–99}.

C: Plasmon coupling and anisotropy in gold nanostructures

When two AuNPs are brought into proximity (< 5 nm), their collective optical properties undergo changes because of strong plasmon coupling between neighboring NPs, which results from the overlap of their near-fields. This overlap results in very strong near-field enhancements between the NPs termed hotspots (**Figure 2-6A**)^{67,100,101}. In anisotropic arrangements, such as side-by-side dimers, plasmon coupling can result in the appearance of two distinct LSPR peaks corresponding to transverse and longitudinal modes (**Figure 2-6A**). The relative positions of these peaks are influenced by factors such as the orientation and size of the NP ensemble, as well as the polarization of the incident light^{67,100}.

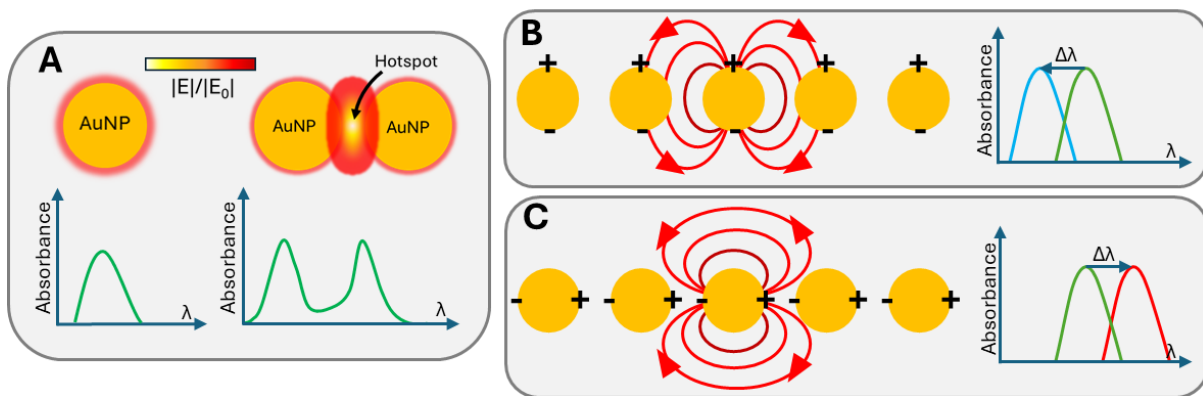


Figure 2-6: Effect of AuNP clustering on absorption spectrum. A) Example of how clustering changes the bulk absorbance spectra. The color bar represents the electric field strength, white being the strongest enhancement. **B)** Transversal mode plasmon excitation of a 1D array of AuNPs resulting in a blue-shift. **C)** Longitudinal mode plasmon excitation of a one-dimensional array of AuNPs resulting in a red-shift. Adapted from Zhang *et al.* (2013)⁶⁷.

In the case of a one-dimensional array of pMNPs exposed to EM waves polarized perpendicular to the array's long axis, the transverse mode is excited. In this mode, the electrons of all NPs oscillate in phase, which increases the restoring force of the dipole within each particle because of the repulsive charge distribution of neighboring particles. Consequently, the resonant wavelength is blue-shifted relative to that of an

isolated NP (**Figure 2-6B**). Conversely, when the longitudinal mode is excited (*i.e.*, along the short axis of the pMNP array), the dipole is attracted by the surface charges of adjacent particles, leading to a reduction in the restoring force (**Figure 2-6C**). This results in a red-shift of the longitudinal resonance. Although far-field coupling also occurs, its effect is negligible compared to near-field coupling. Near-field coupling can be analogized to molecular orbital theory, where linear combinations of atomic orbitals form new molecular orbitals. In the case of near-field coupling, the plasmons of neighboring particles hybridize into bonding and antibonding modes^{66,67,76,100}.

Unlike spherical pMNPs, anisotropic particles, such as gold nanorods (GNRs), inherently exhibit multiple LSPR peaks because of their geometry supporting different plasmon modes (**Figure 2-7**). GNRs have a transverse LSPR along the short axis, producing a higher-frequency resonance, and a longitudinal LSPR along the long axis, resonating at a lower frequency. The longitudinal peak shifts toward the infrared as the aspect ratio increases. This shape also allows multipolar modes, such as quadrupoles, which resonate at lower frequencies due to slower charge oscillations, further contributing to additional LSPR peaks^{39,67,100,102,103}.

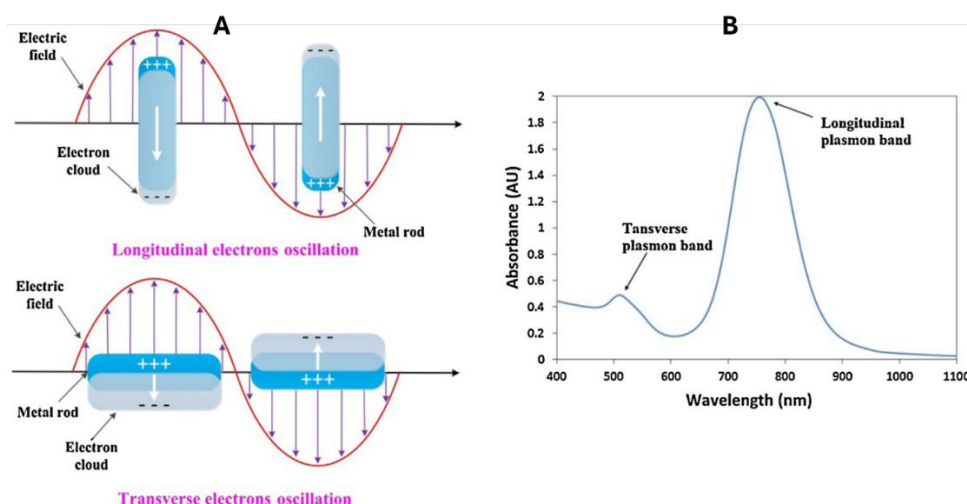


Figure 2-7: Longitudinal and transversal plasmon modes of an ideal GNR. A) Schematic illustration of LSPR excitation for GNRs and **B)** LSPR absorption bands of GNRs. From Cao *et al.* (2014)¹⁰⁴.

2.2.3 A textbook application of pMNPs: Plasmonic photocatalysis

Plasmonic photocatalysis refers to the enhancement of photocatalytic processes through the integration of pMNPs into SC systems. These NPs play an active role in light-driven reactions by improving both the absorption of light and the generation and

separation of charge carriers. When combined with wide-bandgap SCs such as TiO_2 , plasmonic NPs expand the active spectral range of the photocatalyst, enabling the use of visible light that would otherwise be largely unutilized^{66,67}. One of the primary advantages lies in their capacity to improve charge dynamics. Upon illumination, photoexcited charges in the SC tend to recombine rapidly, particularly when diffusion paths to the surface are long. Metal–semiconductor interfaces, such as those formed between AuNPs and TiO_2 , can create a Schottky junction (**Figure 2-8**). This junction introduces an internal electric field that spatially separates photogenerated electrons hole pairs (e/h), thereby reducing recombination losses. Additionally, the energetic alignment across the junction allows for directional movement of charge carriers: electrons can be driven from the metal into the semiconductor conduction band, while holes accumulate on the metal side to participate in oxidation reactions⁶⁷. Beyond charge separation, plasmonic NPs also serve as active energy mediators through the generation of hot carriers. These hot carriers, if not rapidly thermalized, can be injected into the conduction band of adjacent semiconductors, where they can contribute directly to chemical transformations. This hot carrier pathway provides a means to drive reactions that would otherwise require more energetic photons^{66,67,105,106}. Another critical contribution of plasmonic particles is localized heating. The non-radiative decay of plasmonic excitations leads to nanoscale temperature increases. This localized heat enhances molecular diffusion, increases adsorption-desorption dynamics, and accelerates the kinetics of thermally activated surface reactions. Although previously thought to be limited, thermal contributions are increasingly recognized as a dominant factor in plasmon-enhanced catalysis¹⁰⁷. Plasmonic NPs, particularly those larger than ~60 nm, enhance light scattering and optical pathlength, improving absorption in thin-film photocatalytic systems without increasing SC thickness^{67,98}.

Despite these benefits, plasmonic photocatalysis is not without challenges. Noble metals such as gold and silver are expensive and can reduce the available surface area for adsorption when they block SC active sites. Improper design of the metal–semiconductor interface can also lead to defect formation or increased recombination⁶⁷. Nevertheless, by overcoming spectral limitations, improving charge utilization, and introducing new activation pathways, plasmonic NPs offer a powerful

toolkit to enhance photocatalytic performance in both environmental and energy applications^{66,67,108}.

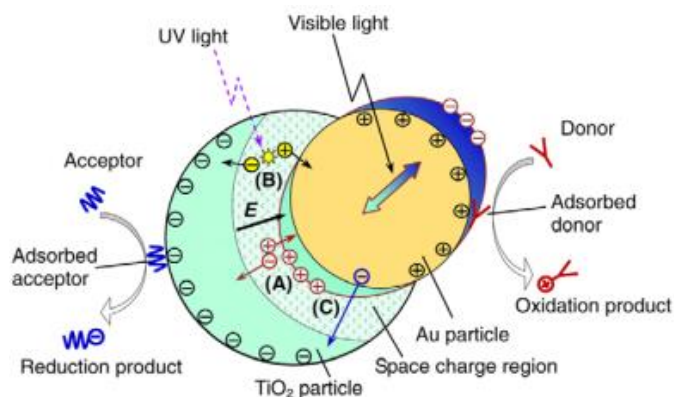


Figure 2-8: Basic mechanisms of plasmonic photocatalysis. Pathways during plasmonic photocatalysis (TiO₂-Au system) depicting LSPR driven generation of e/h pairs (A), UV driven e/h generation (B), the internal electric field (E) facilitating charge separation and spontaneous charge transfer of high energy electrons over the space-charge region into the TiO₂ conduction band (C). From Zhang *et al.* (2013)¹⁹.

2.3 Handling gold using AuNP@ZIF-8 hybrid materials

2.3.1 Methodologies for the synthesis of spherical gold nanoparticles

Many procedures exist to synthesize AuNPs. These can be classified into chemical and physical techniques. Chemical methodologies typically use a gold precursor such as tetrachloroauric acid (HAuCl₄) and a reducing agent such as citric or oxalic acids, borohydride, aminoboranes, and many other to form AuNPs. In special occasions this reducing agent also functions as a stabilization agent for the AuNP suspension^{102,109–112}. Physical techniques produce AuNPs by using energy-based processes to transform bulk gold or atomic vapor into NPs^{102,113–115}. A comparison between chemical and physical techniques is made in **Table 2-2**.

The Turkevich method is a well-known wet-chemical technique for forming a monodisperse AuNP suspension^{52,76,77,102,109,110,112,116–121}. In this form of seed-mediated growth, NPs in a range between 16 – 147 nm can be produced^{102,109,110}. Typically, HAuCl₄ is boiled under reflux and the Au³⁺-cations are reduced upon addition of a reducing agent. The seed-mediated growth comprises 4 steps: partial reduction of the gold precursor, seed formation, adsorption of Au³⁺ on the seeds, and reduction of the adsorbed species (**Figure 2-9**)^{109,122,123}. When using tri-sodium citrate (Na₃Ct) as a reducing agent, the pH of the solution increases shifting the equilibrium

Table 2-2: Physical and chemical techniques for AuNP synthesis.

Aspect	Physical Techniques ^{102,113–115,124}	Chemical Techniques ^{102,109,112,119,121,123,125}
Purity	Produces high-purity NP, typically surfactant-free, suitable for clean surface applications.	May involve chemical stabilizers or surfactants, requiring additional purification steps for biomedical or catalytic applications.
Cost	High due to specialized equipment.	Lower as it relies on simpler chemical reactions, though precursor is expensive. Scalability may involve additional costs.
Size Distribution	Often broad size distributions, requiring post-processing for uniformity.	Better control over size and shape through chemical or biological tuning, though crystallinity might vary.
Scalability	Highly scalable, particularly LAL, suitable for industrial-level production.	Scalable but requires optimization for consistent results at larger volumes.
Environmental Impact	Environmentally friendly as no toxic reagents are used, especially in LAL.	Depends on the chemicals used. Biological methods are greener but can lack control over size and shape.
Surface Functionalization	Limited flexibility for in-situ functionalization but produces clean surfaces ideal for post-synthesis modification.	High flexibility for in-situ functionalization during synthesis.

Laser ablation in liquid (LAL)

between various gold species. At lower pH, $[\text{AuCl}_4]^-$ is more prevalent, but as the pH rises, it shifts towards less reactive hydrolyzed species like $[\text{AuCl}_3(\text{OH})]^-$ and $[\text{AuCl}_2(\text{OH})_2]^-$. This limits the concentration of $[\text{AuCl}_4]^-$, capping the amount of Au^0 that can form. The rapid reduction of $[\text{AuCl}_4]^-$ generates Au^0 atoms, which quickly aggregate into small clusters. These clusters coalesce into stable seed particles, with citrate also stabilizing the seeds by binding to their surfaces. This stabilization prevents further aggregation or dissolution of seeds^{102,109,110,119,122,123}.

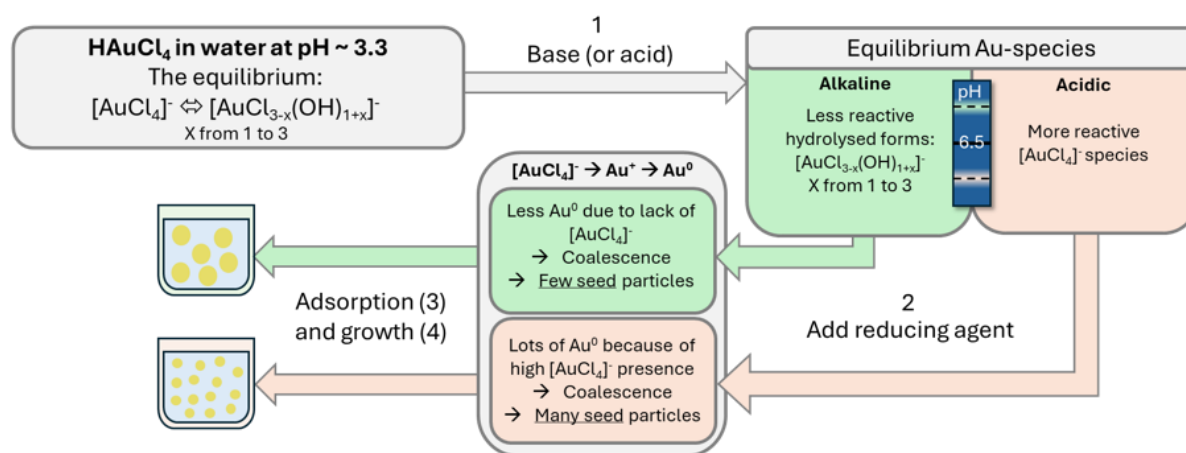


Figure 2-9: The reduction mechanism in the Turkevich synthesis of AuNPs. 1) The pH of the synthesis mixture dictates the equilibrium between HAuCl_4 and its hydrolyzed forms ($[\text{AuCl}_{3-x}(\text{OH})_{1+x}]^-$, x from 1 to 3). 2) A partial reduction reaction transforms the $[\text{AuCl}_4]^-$ species into metallic gold (Au^0). 3) The non-reduced hydrolyzed Au-species adsorb on the metallic gold seeds and 4) are further reduced by the reducing agent. Based on Kettemann *et al.* (2016), Zhao *et al.* (2013), Wuthschick *et al.* (2015), Bartosewicz *et al.* (2018) and Turkevich *et al.* (1951)^{102,109,119,122,123}.

From this point, the remaining gold ions, in the form of $[\text{AuCl}_{3-x}(\text{OH})_{1+x}]^-$, are deposited onto the seed particles. This growth phase is controlled by the electrostatic double layer formed around each seed particle, where citrate contributes by attracting gold ions that reduce directly onto the seed surfaces. This process leads to the formation of monodisperse NPs, as no new particles are introduced after the nucleation stage^{102,109,110,119,121–123}. Thus, increasing citrate initially leads to smaller and more numerous AuNPs due to faster nucleation, but at very high citrate concentrations, pH effects can dominate, leading to fewer or larger particles. Further influencing this mechanism are the temperature and ionic strength of the solution. Elevated temperatures accelerate the reduction rates and shift the equilibrium of gold species, thereby affecting the number of seeds and thus the final size of the AuNPs¹²⁶. Similarly,

ionic strength impacts the colloidal stability of the seeds, with higher ionic strength potentially leading to larger particles because of decreased stabilization^{102,109,127}.

To form an AuNP suspension using physical methods, two common techniques are laser ablation in liquid (LAL) and ultrasonic machining (**Table 2-3**). Together, all these techniques allow for the synthesis of a broad range of AuNPs with varying sizes.

Table 2-3: Aspects of common physical technologies for AuNP synthesis.

Aspect	Laser Ablation in Liquid ^{102,113,114,128,129}	Ultrasonic Machining ^{102,130}
Mechanism	Pulsed laser ablates a gold target in liquid, creating plasma plumes that condense into NPs.	High-frequency ultrasonic waves generate cavitation bubbles that collapse, fragmenting gold into NPs.
Purity	Produces surfactant-free, high-purity NPs.	Produces high-purity NPs but with less precision than LAL.
Cost	High due to energy-intensive processes and expensive laser equipment.	Lower compared to LAL, as ultrasonic devices are less complex.
Size Distribution	Size can be controlled by laser parameters but often requires post-processing for uniformity.	Broad size distribution with less precise control.
Scalability	Scalable and suitable for industrial applications like diagnostics and remediation.	Moderate scalability, mainly suitable for small- to medium-scale synthesis.
Environmental Impact	Environmentally friendly. Avoids toxic chemicals and surfactants.	Also environmentally friendly, does not use toxic reagents.
Surface Functionalization	Limited flexibility because of the clean, surfactant-free surfaces.	Similar limitations to LAL.

Laser ablation in liquid (LAL)

2.3.2 Post-synthesis modifications for gold nanoparticles

To maintain the stability of an AuNP suspension, a protecting agent is typically used to coat the surface of the NPs (**Table 2-4**). While citrate serves this role during the Turkevich synthesis, it is not always sufficient because it forms weak electrostatic interactions with the NP surface^{131–133}. These interactions are easily disrupted in the presence of cations, which neutralize the repulsive forces and can lead to particle clustering. Especially multivalent cations can form bridging species when coordinated

to the citrate carboxyl functional groups^{132,134,135}. By employing capping agents, the stability of the colloidal suspension can be improved via three main mechanisms: electrostatic stabilization, steric hindrance, and strong binding to the surface³⁹.

Table 2-4: Typical capping agents and their interaction with AuNPs.

Property	PVP ^{77,136–138}	PAH ^{33,110,139,140}	Thiols ^{131,141,142}	Amines ^{143–146}
Stabilization medium	Steric	Electrostatic	Covalent bond	Electrostatic and mild covalent
Interaction strength	Van der Waals forces and mild ionic interactions	Moderate ionic binding	Strong covalent interaction	Moderate, through lone pair of electrons on N
Ligand exchange feasibility in water	Feasible in water	Moderate, water exchange possible under controlled pH conditions	Difficult, requires harsh chemical exchange	Feasible in water, though lower binding affinity
Research extent	Extensively researched for biomedical and catalytic uses	Fairly well-explored, especially in layer-by-layer assembly	Highly researched, stable and ideal for biofunctionalization	Moderately explored, especially in simple AuNPs for catalysis

Polyvinyl pyrrolidone (PVP), poly(allylamine) hydrochloride (PAH)

These capping agents not only enhance stability but also alter key properties like solubility, surface charge, and reactivity¹⁴⁷.

However, to perform a capping agent exchange the NP suspension needs a washing step to remove excess of reducing agent or capping agent after AuNP synthesis. This is commonly done by centrifugation^{82,102,119,131,148}. While this step helps purify the suspension, it also introduces certain challenges. The high centrifugal forces applied during this process often result in a reduction of the interparticle distances as particles are concentrated into a pellet. This closer proximity enhances van der Waals attractions, which can overwhelm the electrostatic repulsion provided by stabilizing agents such as citrate, leading to irreversible aggregation. This effect has been clearly demonstrated in studies where centrifuged samples showed greater aggregation than non-centrifuged controls, often resulting in visible clustering and a loss of monodispersity^{139,148–150}.

Another issue arises from the disruption of the electrical double layer that surrounds AuNPs. Under strong centrifugal forces, the differential movement of ions relative to NPs can polarize the double layer. This polarization destabilizes the colloidal suspension, reducing the repulsive forces that prevented aggregation. Such destabilization has been observed to promote clustering of NPs in subsequent steps, especially when the AuNPs were exposed to large centrifugal forces^{148,149}.

Centrifugation can also result in the loss of NPs due to incomplete redispersion. Pellets formed at the bottom of the centrifuge tube are often difficult to redisperse effectively, leading to physical losses and reduced recovery efficiency. This problem is exacerbated when NPs adhere to centrifuge tube walls or remain in aggregated states that resist redispersion^{139,148,150}. Moreover, coating polymers may also interact with the polymeric material of Eppendorf tubes through electrostatic interactions, promoting adhesion to the walls. Changes in solvent composition or ionic strength during redispersion, particularly when stabilizing agents are partially removed, can further destabilize the suspension and enhance aggregation tendencies^{148,149,151}.

Addressing these challenges requires the development of compounds or molecular frameworks capable of stabilizing NPs during centrifugation, preserving their colloidal properties, and enhancing recovery efficiency.

2.3.3 AuNP@ZIF-8 hybrid materials: State of the art

The integration of AuNPs into ZIF-8 has emerged as a compelling strategy to combine the plasmonic and catalytic properties of AuNPs with the porosity and chemical versatility of ZIF-8^{4,11,12,23,29,34,47,138,152–154}.

A: Synthesis

One common approach to form of AuNP@ZIF-8 hybrids involves embedding pre-synthesized AuNPs within ZIF-8. In this approach, AuNPs, coated with PVP (PVP-AuNPs), are mixed with ZIF-8 precursors such as zinc nitrate and 2-methylimidazole in water or methanol^{23,154}. The pyrrolidone groups of PVP coordinate with zinc ions, initiating the nucleation and growth of ZIF-8 around the NPs. Excess PVP can hinder encapsulation by competing with AuNP-bound PVP for zinc ions, leaving NPs unincorporated. Therefore, the PVP-AuNP suspension is typically purified to remove excess PVP molecules. The timing of AuNP introduction to the ZIF-8 precursor mixture also influences their spatial distribution: early addition promotes central embedding

within ZIF-8 crystals (**Figure 2-10**), while delayed addition results in stratified arrangements. Electrostatic interactions further enhance the encapsulation process, as the negative zeta potential of PVP-coated AuNPs attracts positively charged ZIF-8 precursors^{23,154}. A study by Ma *et al.* (2019) supports the understanding of how PVP mediates the interaction between AuNPs and ZIF-8. In their approach, AuNPs were formed *in-situ* on the surface of pre-synthesized ZIF-8 using PVP as a stabilizing and anchoring agent, ensuring uniform distribution of AuNPs on the ZIF-8 surface¹⁵⁵. These observations underscore the dual role of PVP in controlling PVP-AuNP stability and facilitating their integration into or onto ZIF-8 structures through coordination-driven assembly.

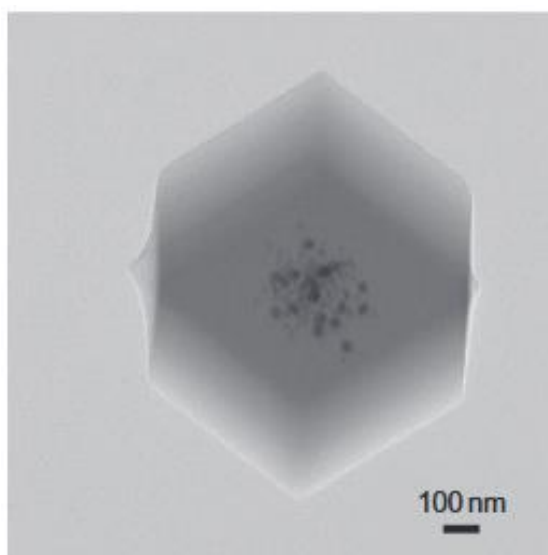


Figure 2-10: TEM image of 13 nm and 34 nm sized PVP-AuNPs, evenly distributed in a central area in a ZIF-8 crystal. The NPs were added at the start of the ZIF-8 nucleation reaction. From Lu *et al.* (2012)²³.

Cysteine, an amino acid, can be used instead of PVP to incorporate functional particles such as biomacromolecules. In this context, the carboxyl group of cysteine faces the macromolecular surface, while the thiol group remains available to bind metals. This strong thiol–metal interaction forms the basis for successful encapsulation¹⁵⁶. However, when cysteine is used to stabilize AuNPs instead of citrate, its orientation is reversed: the thiol group binds tightly to the gold surface, leaving the carboxyl group exposed. This free carboxyl group then dictates the interaction with ZIF-8, in a manner similar to citrate-stabilized AuNPs^{141,157}.

An alternative method involves *in-situ* growth of AuNPs within the ZIF-8 matrix¹⁵⁸. In this process $[\text{AuCl}_4]^-$ ions diffuse into pre-formed ZIF-8 crystals and are reduced by sodium borohydride, forming AuNPs directly within the porous structure. Although this approach ensures uniform NP distribution, it depends heavily on reaction conditions such as precursor concentration and reduction time. Both methods underscore the importance of optimizing interactions between NPs and ZIF-8 precursors to achieve desired hybrid properties^{102,124,158}.

B: Applications and challenges

AuNP@ZIF-8 hybrids show great promise in catalysis and sensing, combining the plasmonic properties of AuNPs with the porosity and mechanical stability of ZIF-8. In catalysis, the molecular sieving of ZIF-8 enables selective reactions, while embedded AuNPs enhance reaction rates through LSPR effects. These hybrids demonstrate high efficiency in photocatalytic applications such as dye degradation and CO oxidation, where the synergy between molecular confinement and plasmonic energy transfer boosts both activity and selectivity^{47,152}. In sensing, the high surface area and tunable adsorption properties of ZIF-8 facilitate selective analyte interactions, while AuNPs amplify detection signals, particularly in techniques like surface-enhanced Raman scattering. Studies highlight their effectiveness in trace detection of pollutants and biomolecules^{10,29}.

The synthesis of AuNP@ZIF-8 hybrids relies heavily on the centrifugation of pre-synthesized AuNPs to remove excess stabilizers or reducing agents, a critical step for achieving clean surfaces and efficient encapsulation within ZIF-8^{23,29,138,154}. As mentioned previously, this step faces several complications (see section 2.3.2). Scaling up remains challenging due to the reproducibility of the centrifugation step and the cost of gold precursors, while uneven NP distribution can limit plasmonic coupling and catalytic efficiency¹⁵². Furthermore, weakly bound AuNPs may leach under harsh conditions, compromising stability¹³⁸.

2.4 Acid vapor sensing using fluorescent dyes in ZIF-8

2.4.1 General concepts of fluorescence

Fluorescence, a type of luminescence, is a photophysical phenomenon characterized by the emission of light by a substance that has absorbed EM radiation, typically in the ultraviolet – visible (UV-Vis) range^{159,160}. The fluorescence mechanism

is well-established (**Figure 2-11**). A fluorophore absorbs a photon, causing an electron within the molecule to transition to an excited state. This ultrafast process ($\sim 10^{-15}$ s) is followed by non-radiative relaxation mechanisms, such as vibrational relaxation, through which the electron settles into the lowest vibrational level of the first electronic excited state. The electron then returns to the ground state via the emission of a

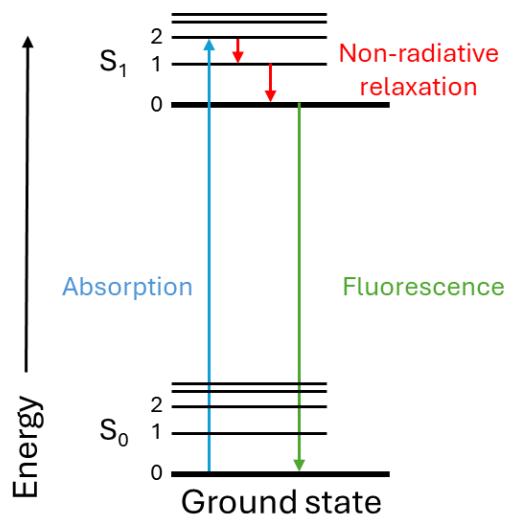


Figure 2-11: A Jablonski diagram illustrating the fluorescence phenomenon.

photon. Due to the energy lost during the non-radiative relaxation, the emitted photon has a longer wavelength than the absorbed one. This wavelength difference is well-known as the Stokes shift^{159,160}. Fluorescence finds a myriad of applications ranging from bioimaging to pollutant detection to authentication purposes^{159–162}. The fluorophores come from a wide range of chemicals such as organic molecules, protein-based fluorophores, inorganic nanomaterials (quantum dots) and fluorescent dyes^{159,160,163}.

An important aspect of fluorescence is the quantum efficiency ϕ ^{159,162,164}. This parameter is defined as the ratio of emitted to absorbed photons. For imaging and sensing applications, a quantum efficiency close to unity is desired. Also, the pH serves a prominent role. For example, the fluorescence of fluorescein (F) is highly pH-dependent due to its multiple ionizable groups, including phenolic hydroxyl groups (pKa ~ 6.4 and ~ 4.4) and a carboxylic acid group (pKa ~ 2.1), which alter its electronic structure and fluorescence efficiency (**Figure 2-12A**). At acid pH, fluorescein exists in its non-fluorescent lactone form, while at neutral to slightly basic pH, it transitions to its highly fluorescent di-anionic form, resulting in a strong increase in quantum yield^{163,165,166}. In contrast, rhodamine 6G (Rh6G) shows much less pH sensitivity

(pKa ~6.13) because it predominantly exists in a stable cationic form across a wide pH range, maintaining its electronic structure and fluorescence properties regardless of environmental pH changes. This difference makes Rh6G more robust for applications in varying pH conditions^{163,166,167}.

2.4.2 Rhodamine 6G as fluorescent dye

A good example of a fluorescent molecule is Rh6G (**Figure 2-12B**). Rh6G is highly fluorescent because of its conjugated π -electron system in the xanthene core, which lowers the energy gap between ground and excited states, enabling efficient absorption of visible light (525 – 550 nm)^{161,164}. The delocalized π -electrons stabilize the excited state by evenly distributing excitation energy, minimizing non-radiative decay and maximizing fluorescence. Additionally, amino groups enhance electron donation and strengthen the conjugation, while the quaternary ammonium group stabilizes the molecule in polar environments, boosting photostability and fluorescence efficiency. These structural features collectively give Rh6G its high quantum yield and exceptional brightness, making it a widely used fluorophore^{161,164,167}.

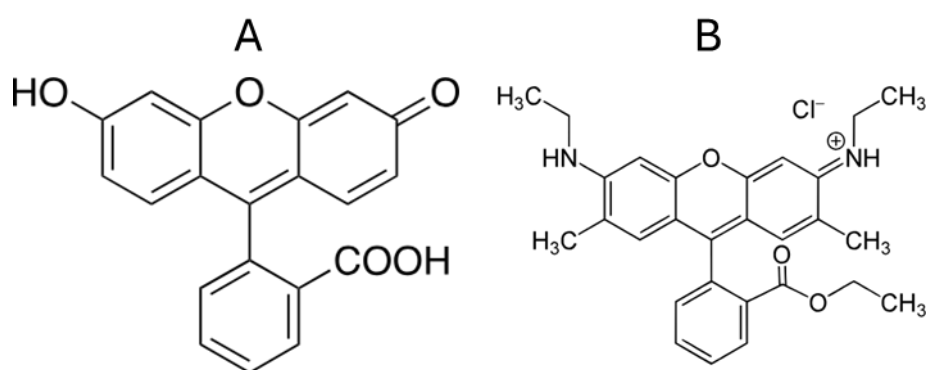


Figure 2-12: Molecular structures of fluorescein and Rh6G. A) Structure of fluorescein, highlighting its ionizable groups. From Song *et al.* (2000)¹⁶⁸. **B)** Structure of Rh6G with a conjugated π -electron system in the xanthene ring. From Ogunsipe (2018)¹⁶⁷.

2.4.3 Dye – ZIF-8 hybrid materials

Fluorescent dyes are crucial in sensing technologies, with MOFs like ZIF-8 serving as ideal hosts due to their high porosity and large SSA, which enhance sensitivity and improve dye stability^{169–171}. These systems often rely on fluorescence modulation, either enhancement or quenching, in response to target analytes^{172,173}. Fluorescence quenching refers to any process that decreases the intensity of a fluorophore, which can be reversible or irreversible, depending on the

interaction^{159,161,169,174}. For many fluorophores, it is argued that fluorescence is quenched through complex formation, with metals for example. However, as shown in **Figure 2-13**, this is not the case for RhB and Rh6G. Even more interesting, for the latter, an enhancement is observed. Therefore, aggregation-induced quenching is a possible explanation for the quenching mechanism of fluorescent dyes in MOFs. In this quenching phenomenon, close packing of fluorophores leads to non-radiative energy dissipation, primarily due to the formation of non-emissive H-aggregates driven by π - π stacking interactions. This effect is particularly pronounced in solid-state systems where, because of high dye loading, the proximity of dye molecules results in significant reductions in fluorescence quantum yield and photon output^{175,176}.

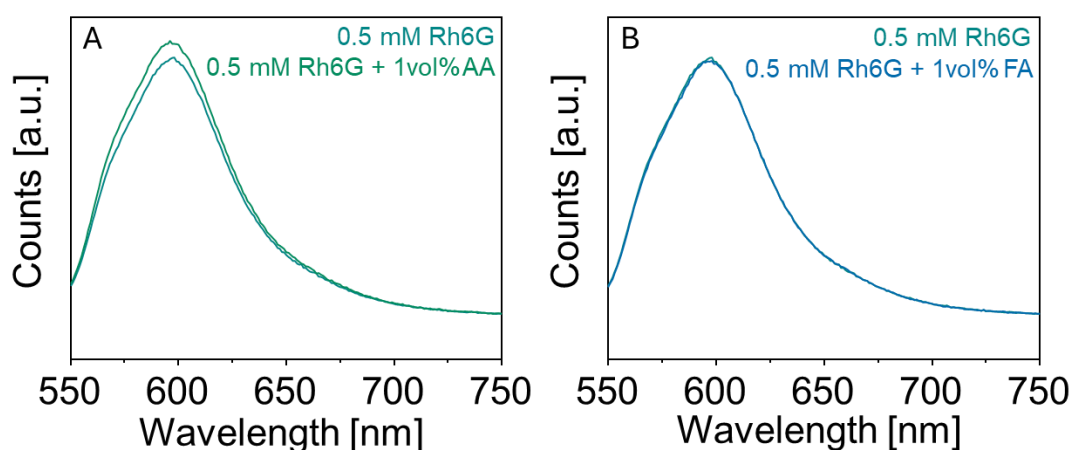


Figure 2-13: Fluorescence spectra demonstrating that quenching is not due to complex formation with Zn^{2+} . A) Rhodamine B, B) Rhodamine 6G.

Recent approaches incorporate fluorescent dyes during MOF synthesis to allow controlled degradation in acid vapor conditions, releasing the dye and enabling acid-sensitive detection (**Figure 2-14A**). A study by Smets *et al.* (2024) highlights the development of a low-cost, fluorescence-based system for detecting acid vapors using dye-containing ZIF-8 materials (Dye@ZIF-8). These dyes, including F, coumarin 343 (C343), and rhodamine B (RhB), were chosen for their fluorescent properties, affordability, and safety. This approach achieves impressive sensitivity, up to single-digit ppmv under extended exposure, and relies on the degradation of ZIF-8 upon acid exposure to release encapsulated dyes and alleviate aggregation-induced quenching. Among the tested dyes, RhB@ZIF-8 exhibited the most distinct fluorescence response, particularly between 10 and 41 ppmv acetic acid (**Figure 2-14B**), while

F@ZIF-8 and C343@ZIF-8 faced challenges due to protonation, decreasing their fluorescence intensity³⁹.

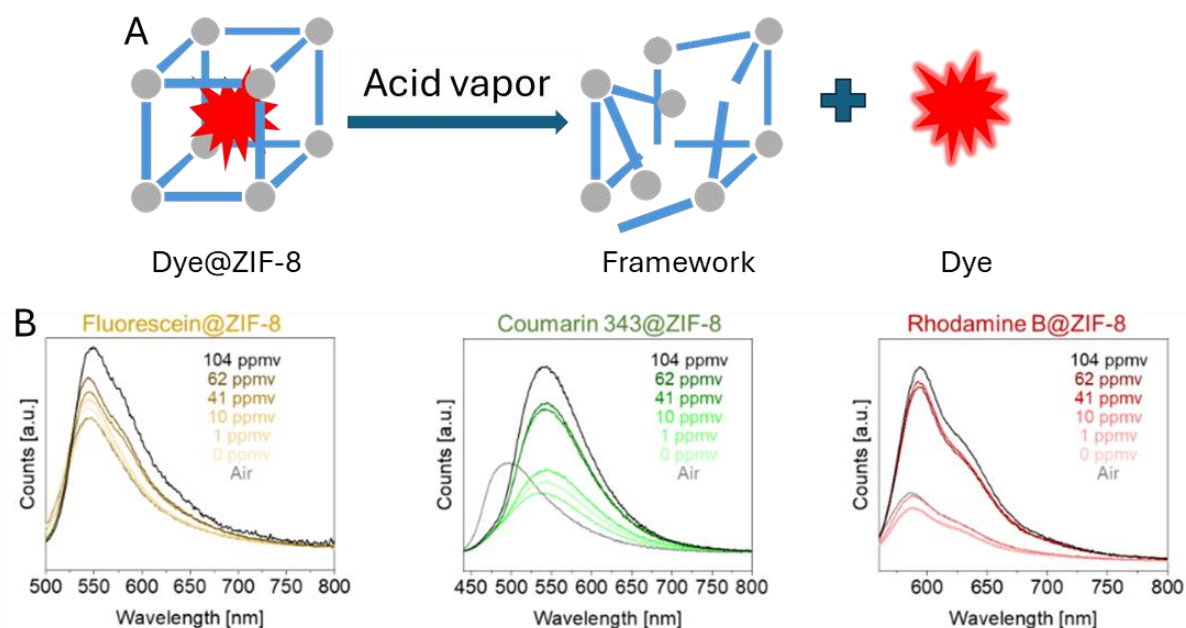


Figure 2-14: Acid-triggered fluorescence activation of Dye@ZIF-8. **A)** Acid-induced degradation of ZIF-8, leading to the release of encapsulated dye molecules, restoring the fluorescence. **B)** Emission spectra during acetic acid concentration screening. An excitation wavelength of 485 nm, 430 nm, and 550 nm was used for fluorescein@ZIF-8, coumarin 343@ZIF-8, and rhodamine B@ZIF-8 respectively. From Smets *et al.* (2024)³⁹.

Furthermore, their system uses a simple 385 nm LED and a camera module for detection, demonstrating the feasibility of low-tech, cost-effective setups. Fluorescence-based sensing allows tuning of performance by selecting dyes with optimal excitation wavelengths, exemplified by C343's stronger response due to its wavelength compatibility with the LED. These qualities, combined with simplicity, sensitivity, and adaptability, make fluorescence-based sensing a highly effective method for chemical detection compared to adsorption-based sensors where often complex readout methods are necessary^{39,177}.

Degradation of ZIF-8 was confirmed, even at low vapor concentrations, using ellipsometry on an 80 nm-thin ZIF-8 film (**Figure 2-15**). A distinct shift in the optical signal occurs around 2.5 ppmv, indicating the onset of degradation. However, following acid exposure, the ZIF-8 layer is no longer a continuous, homogeneous film, and the extracted Δn values can no longer be interpreted as true refractive indices. Instead, they should be viewed qualitatively as indicators of structural changes. Comparable trends were observed for other acid vapors (**Figure 7-1**). The degradation kinetics are

influenced by ambient humidity, as water serves as the medium through which protons diffuse into ZIF-8³⁹.

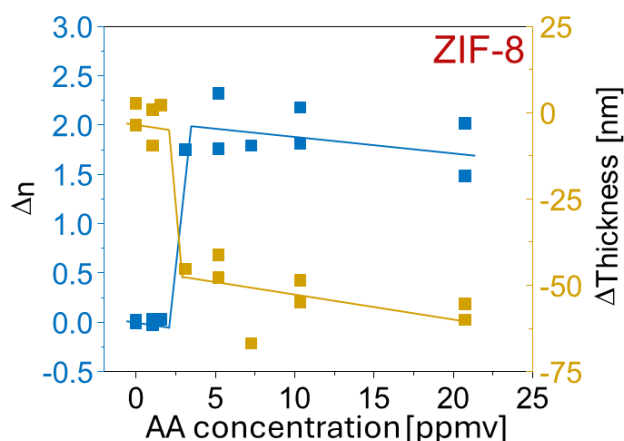


Figure 2-15: Ellipsometry measurements on a thin ZIF-8 film exposed to acetic acid vapor. From Smets *et al.* (2024).

2.5 Bridging gaps in current knowledge

This work will study two separate applications. In part 4 “Trapping gold”, ZIF-8 is utilized to improve AuNP handling and yield during purification. Despite the significant advancements in the synthesis and application of AuNP suspensions, their practical limitations during purification and dosing limit use. We target the encapsulation of AuNPs within ZIF-8, particularly in balancing strong stabilization of AuNPs during synthesis with facile redispersibility after drying. Addressing these issues is critical for developing AuNP@ZIF-8 powders that maintain catalytic and plasmonic properties after redispersion. Most existing studies focus on in-solution synthesis and applications, leaving the effects of drying and rehydration largely unexplored. Additionally, scaling up AuNP synthesis presents a bottleneck. Centrifugation – a key step for NP purification – often leads to major losses and aggregation, which can compromise cost, reproducibility, and catalytic efficiency.

In part 5 “Flashy dyes”, fluorescent dyes are encapsulated instead of AuNPs to make an acid vapor sensor. The degradation of MOFs has been demonstrated as a promising approach for detecting volatile acids. Though commonly, expensive lab-based equipment that requires experienced users are used to study these phenomena. This thesis contributes to a valorization project in which fluorescent dyes are incorporated in MOFs, of which, upon degradation, the fluorescence is enhanced. This

approach is compatible with low-tech read-out electronics, facilitating robust and low-cost sensor device integration. This project incorporates a new fluorescent dye in ZIF-8 aiming to minimize dye-intrinsic pH sensitivities and further characterizes the Dye@ZIF-8 structures.

What both applications have in common is that the acid sensitivity of ZIF-8 is used as an opportunity to achieve the desired outcome.

3 Materials and Methods

3.1 Synthesis of AuNP@ZIF-8 hybrids

3.1.1 Synthesis of gold nanoparticles

A: Chemicals

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%, Thermo Fisher), tri-sodium citrate dihydrate (> 99%, Chem-lab), deionized water

B: Methodology

AuNPs were synthesized following a modified Turkevich method (**Figure 3-1**), as outlined by Turkevich *et al.* (1951)^{121,122}. All glassware was cleaned with aqua regia, thoroughly rinsed with deionized (DI) water, and dried prior to use. A solution of 1 mL of 0.01 M HAuCl_4 was mixed with 98 mL of DI water in a 250 mL round-bottom flask. The mixture was heated to reflux under constant stirring. Upon reaching boiling, 1 mL of a 1 wt% tri-sodium citrate solution was added to initiate the reduction and nanoparticle formation. The reaction proceeded for 30 minutes before rapid quenching in an ice bath to stop further reaction. The citrate-capped AuNP suspension (Cit-AuNP) was stored at 4°C in a dark environment to minimize photodegradation. The optical properties of the citrate-capped AuNPs and concentration were assessed by UV-Vis spectroscopy and spectroquant™ gold test respectively.

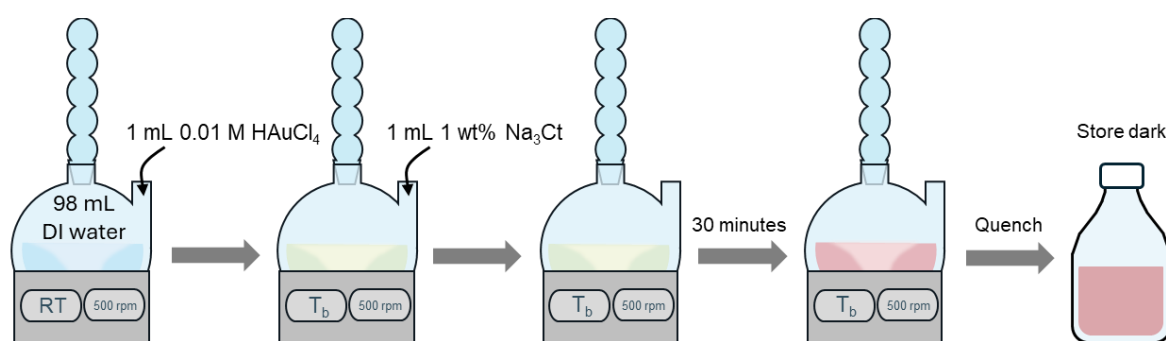


Figure 3-1: Schematic of the AuNP synthesis via the modified Turkevich method. Room temperature (RT), boiling point of the solution (T_b)

3.1.2 Stabilizing agent exchange

A: Chemicals

Poly(allylamine) hydrochloride (PAH, MW 17500, Sigma-Aldrich), PAH (MW 15000, 97.9%, BLDpharm), polyvinyl pyrrolidone (PVP, MW 10000, Alfa Aesar), L-Cysteine (Sigma-Aldrich), AuNP suspension

B: Methodology

Typically, 5 mg of PAH in 1 mL DI water was added to 10 mL of Cit-AuNP colloid. The ligand exchange process was allowed to proceed for at least 2 hours (**Figure 3-2**). For ligand exchange using PVP, a ratio of 0.5 mg of PVP per 10 mL of AuNP suspension was maintained. These polymer-to-AuNP ratios were selected to ensure sufficient surface coverage while minimizing excess polymer in solution (**Figure 7-4**). The PVP-capped AuNP suspension (PVP-AuNP) and PAH-capped AuNP suspension (PAH-AuNP) were stored at 4°C in a dark environment to minimize photodegradation.

In another approach, a (second) coating of cysteine was used by adding 100 µL or 500 µL of a 40 mM cysteine solution to the PAH-AuNPs or AuNPs formed by laser ablation in liquid (LAL-AuNPs). This mixture was stirred for at least 30 minutes. The formed Cys-PAH-AuNP (double coating) or Cys-AuNP (single coating) suspensions were stored at 4°C in a dark environment to minimize photodegradation. Successful ligand exchange was monitored by shifts in the UV-Vis absorption spectrum.

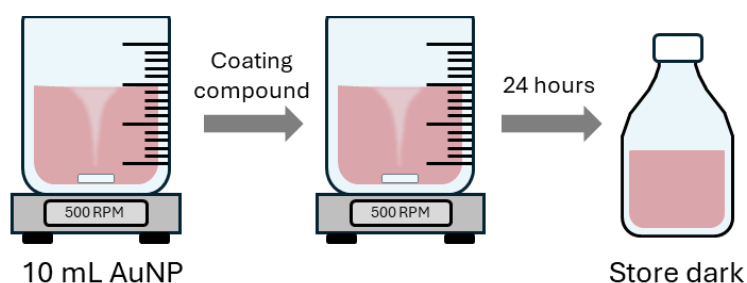


Figure 3-2: Ligand exchange of citrate-capped AuNPs with PAH, PVP, or cysteine.

3.1.3 Synthesis of ZIF-8**A: Chemicals**

2-methylimidazole (HmIM, 99%, Sigma-Aldrich), zinc precursor ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Thermo Fisher), DI water

B: Methodology

Based on works by Kida *et al.* (2013) and Jian *et al.* (2015), ZIF-8 was synthesized using different HmIM:Zn ratios^{15,35}. In the case of a 1:1 ratio, 22.8 mg of linker was dissolved in 10 mL of DI water and stirred for 1 minute, followed by the addition of 82.6 mg zinc nitrate hexahydrate. For higher ratios, the linker quantity was adjusted. The reaction time depends on this ratio, longer reaction times are required for lower ratios while ensuring reaction completion. The resulting white precipitate was

collected by centrifugation (Eppendorf centrifuge 5804) in a 10 mL Falcon tube for 15 minutes at 1110 x g and washed twice with 10 mL DI water. The product was dried overnight in a vacuum oven at 40°C (Thermo Fisher Scientific, VacuTherm) (Figure 3-3). This methodology was followed throughout this work unless otherwise specified. Phase purity and crystallinity of the synthesized ZIF-8 were confirmed by PXRD.

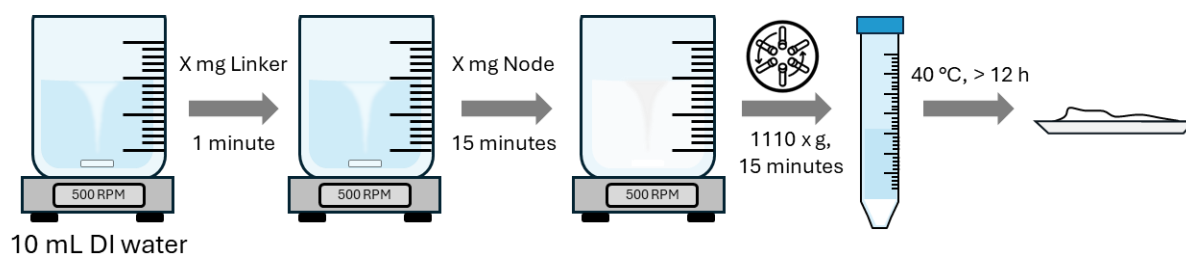


Figure 3-3: Synthesis of ZIF-8.

3.1.4 Synthesis of AuNP@ZIF-8

A: Chemicals

2-methylimidazole (HmIM, 99%, Sigma-Aldrich), zinc precursor ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Thermo Fisher), AuNP suspension

B: Methodology

The synthesis methodology will be screened throughout this work based on works by Lu *et al.* (2012), Li *et al.* (2014), and Xie *et al.* (2023)^{23,34,154}. Typically, the linker was added to 10 mL of AuNPs suspension. After stirring for 1 minute, the zinc precursor was mixed in. The time to let the ZIF-8 form was adjusted to the HmIM:Zn ratio. Lower ratios (1:1 – 5:1) were allowed to stir overnight, while for higher ratios (10:1 – 40:1) shorter times sufficed. The exact conditions will be further specified below. In most cases, the linker and metal precursor were stirred in the AuNP suspension as a powder, but occasionally, pre-dissolved linker and metal node solutions were preferred. Following each synthesis, 10 mL of the newly formed AuNP@ZIF-8 material was collected via centrifugation (Eppendorf centrifuge 5804) in a 10 mL Falcon tube for 15 minutes at 2740 x g and washed twice with 10 mL DI water. The supernatant was discarded, and the precipitate was dried in a vacuum oven (Thermo Fisher Scientific, VacuTherm) overnight at 40°C (Figure 3-4). ZIF-8 formation was confirmed by PXRD and FTIR, while the successful encapsulation of AuNPs within ZIF-8 was

verified by SEM. The distribution of AuNPs inside the ZIF-8 crystals was further analyzed using HAADF-STEM imaging.

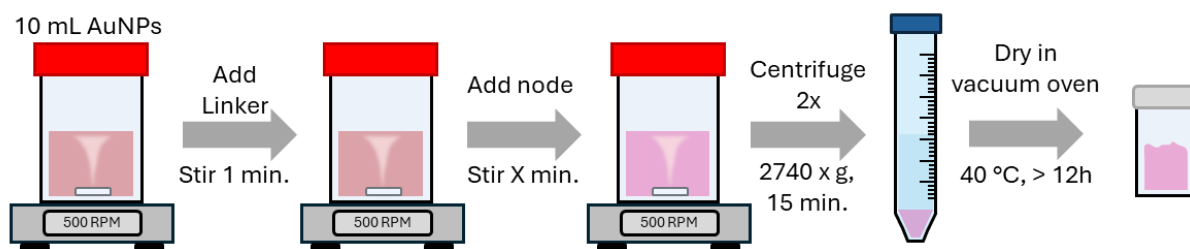


Figure 3-4: Synthesis protocol of AuNP@ZIF-8. Depending on the type of AuNP to be encapsulated, another gold suspension was used.

3.1.5 *In-situ* reduction of HAuCl_4 in ZIF-8

A: Chemicals

2-methylimidazole (HmIM, 99%, Sigma-Aldrich), zinc precursor ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Thermo Fisher), tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%, Thermo Fisher), sodium borohydride (NaBH_4 , Sigma-Aldrich, $\geq 98.0\%$), DI water

B: Methodology

Based on a paper by Liao *et al.* (2016)¹⁷⁸. 5.67 g of 2-methylimidazole was dissolved in 20 mL of DI water. In parallel, 0.29 g of the zinc precursor was dissolved in 2 mL of a 10 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution. Once both precursors were fully dissolved, the zinc–gold mixture was added dropwise to the linker solution under constant stirring. After 20 minutes of reaction, the resulting precipitate was collected at once by centrifugation (Eppendorf Centrifuge 5804) in a 50 mL Falcon tube at $10000 \times g$ for 5 minutes and washed three times with DI water. Following the final wash, the pellet was resuspended in 5 mL of DI water in a clean vial, and a stir bar was added. To initiate the *in-situ* reduction, 205 μL of a freshly prepared 10 mM NaBH_4 solution was introduced to the suspension. The mixture was stirred for 3 hours in the dark to complete the reduction process. Finally, the product was recovered by centrifugation,

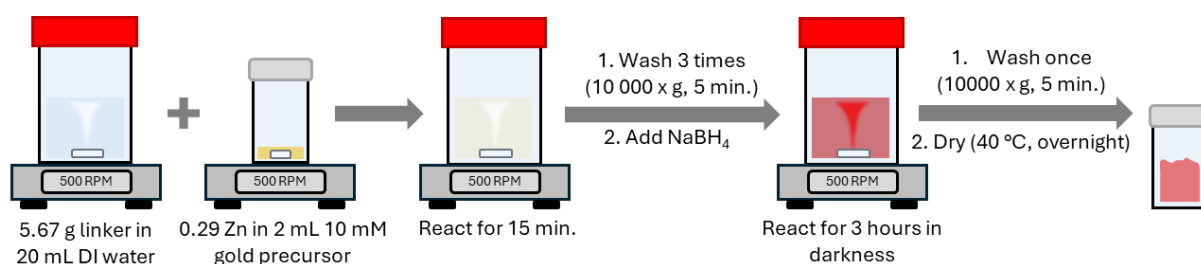


Figure 3-5: Synthesis protocol *in-situ* reduction.

washed once to remove residual reagents, and dried to a powder (**Figure 3-5**). The powders' crystallinity was verified by PXRD, and the internal nanoparticle formation was observed by HAADF-STEM.

3.2 Resuspending AuNP@ZIF-8 hybrids

A: Chemicals

AuNP@ZIF-8 powder, acetic acid (AA, glacial acetic acid, VWR chemicals), hydrochloric acid (HCl, VWR chemicals, 37%), DI water

B: Methodology

To resuspend to AuNPs, an arbitrary amount of AuNP@ZIF-8 powder was resuspended in 3 mL of DI water. To facilitate resuspension, the powder was sonicated until all visible aggregates were gone. Subsequently, an acid solution (1 M AA or HCl) was added in small portions (~50 μ L per portion) while sonicating (**Figure 3-6**). The addition of acid was stopped when the suspension transitioned from opaque to transparent. The resuspension behavior and optical properties of the released AuNPs were evaluated by UV-Vis spectroscopy and HAADF-STEM imaging.

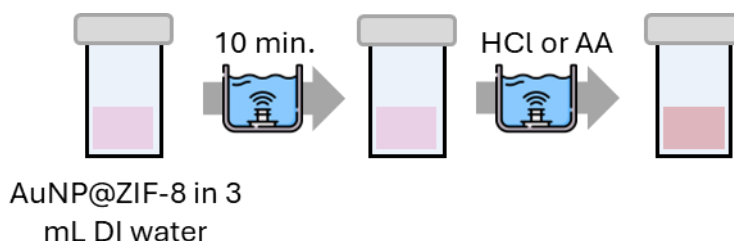


Figure 3-6: Protocol for degradation of ZIF-8 and resuspending AuNPs

3.3 Yield test of AuNP@ZIF-8 washing

A: Chemicals

AuNP suspension, AuNP@ZIF-8, hydrochloric acid (HCl, VWR chemicals, 37%), DI water

B: Methodology

10 mL of AuNP colloid suspension was evenly distributed over 5 microcentrifuge tubes. One tube was used to determine the initial gold content and optical properties using a photometric gold assay and UV-Vis spectroscopy, respectively. The remaining four tubes were centrifuged at 6000 $\times$ g for 15 minutes using a FastGene high-speed minicentrifuge (Nippon genetics). After this, 1.8 mL of the supernatant was removed

and replaced by DI water. The pellets were resuspended by vigorous shaking. One tube was then analyzed again for gold content and optical properties, while the remaining three underwent two additional identical washing steps, resulting in a total of three washing cycles.

A similar procedure was applied to AuNPs encapsulated in ZIF-8. However, centrifugation was performed at $3000 \times g$. Following resuspension, ZIF-8 was degraded using 1 M HCl under sonication before recording the UV-Vis spectrum (**Figure 3-7**). The gold content and LSPR after resuspension were quantified using the spectroquant™ gold assay and UV-Vis spectroscopy respectively.

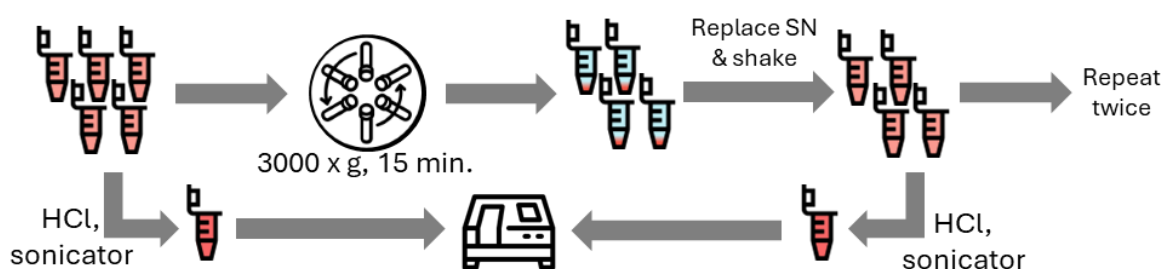


Figure 3-7: Protocol for assessing the yield of multiple washing cycles. The depicted diagram is for AuNP@ZIF-8 species. For unembedded AuNPs there was no HCl added before quantification.

3.4 Acid vapor detection with Dye@ZIF-8 hybrids

3.4.1 Synthesis of macro-sized Dye@ZIF-8 hybrids

A: Chemicals

2-methylimidazole (HmIM, Sigma-Aldrich, 99%), zinc precursor ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Thermo Fisher), Rh6G (TCI, > 95%), RhB (Sigma-Aldrich, > 99.8%), DI water, ethanol (EtOH, Fischer Scientific, > 99.8%)

B: Methodology

As described by Smets *et al.* (2024), 0.2 g zinc nitrate hexahydrate was dissolved in 0.8 mL DI water³⁹. Separately, 17.3 mg of either RhB or Rh6G was dissolved in 4 mL of DI water and mixed into the zinc solution. Meanwhile, 2 g of the linker was dissolved in 8 mL water. This linker solution was then added dropwise to the zinc-dye mixture while stirring. After reacting for 15 minutes, the resulting dye in macro-sized ZIF-8 (mDye@ZIF-8) material was collected using centrifugation (Eppendorf Centrifuge 5804, $2100 \times g$, 8 min.) and washed three times with a 1:1 (v/v) water/ethanol mixture. Finally, the powder was dried overnight in a vacuum oven (Yamato, ADP310C) at 60°C .

(Figure 3-8). Successful dye encapsulation and ZIF-8 formation were confirmed by HPLC analysis and PXRD and FTIR.

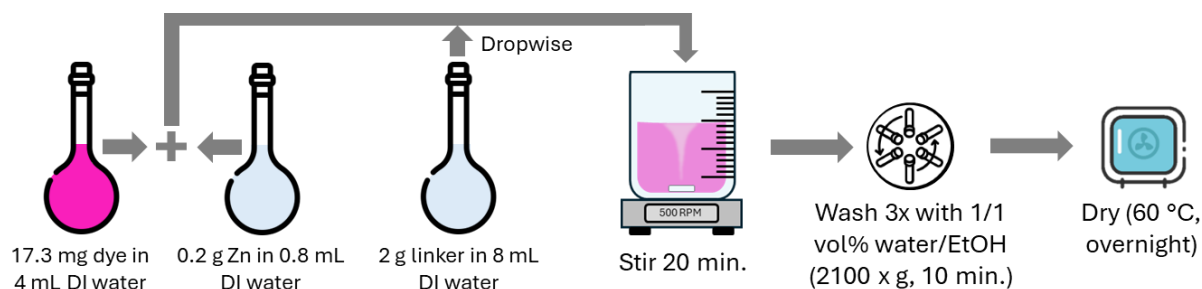


Figure 3-8: Diagram for the synthesis of mDye@ZIF-8. The synthesis could also be scaled up by multiplying all quantities with the desired factor.

3.4.2 Synthesis of nano-sized RhB@ZIF-8 hybrids

A: Chemicals

RhB (Sigma-Aldrich, > 99.8%), methanol (MeOH, Fischer chemicals, ≥ 99.9%), 2-methylimidazole (HmIM, Sigma-Aldrich, 99%), zinc precursor ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ hexahydrate, 99%, Thermo Fisher Scientific), DI water, triethylamine (Thermo Scientific, > 99%)

B: Methodology

Based on by Xiong *et al.*¹⁷⁹, RhB was dissolved in methanol (solution A) at concentrations of 10 mM. In parallel, 892.5 mg of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL MeOH (solution B), and a separate solution (C) was made by dissolving 492.6 mg of 2-methylimidazole and 0.837 mL of triethylamine in 10 mL MeOH. Solutions A, B, and C were immediately combined in a 25:10:10 volume ratio and stirred for 5 minutes to complete the crystallization (**Figure 3-9**). The resulting dye in nano-sized ZIF-8 (nDye@ZIF-8) suspension was centrifuged at 9,062 x g for 10 minutes (Eppendorf Centrifuge 5804). The supernatant was discarded, and the solid was washed with 40 mL MeOH, sonicated for 5 minutes, and centrifuged again. This

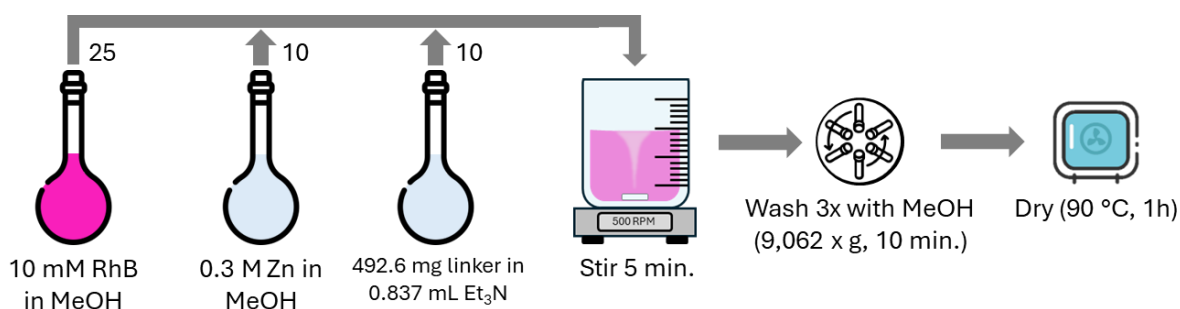


Figure 3-9: Synthesis of RhB in nano-sized ZIF-8 crystals.

washing step was repeated 3 times in total. Finally, the product was dried in a vacuum oven (Yamato, ADP310C) at 90°C for 1 hour. ZIF-8 formation was assessed by PXRD.

3.4.3 Synthesis of RhB@ZIF-8 films on silicon wafers

A: Chemicals

Isopropyl alcohol (IPA, Sigma-Aldrich, ≥99.8%), RhB@ZIF-8 powder

B: Methodology

A 5 wt% macro or nano RhB@ZIF-8 suspension in IPA was sonicated for 60 minutes to ensure complete resuspension of the powder. The resulting suspension was transferred to a spray cup and applied to the non-polished side of a 2 × 2 cm² silicon wafer in several coatings using a Harder & Steenbeck Colani 1.2 mm airbrush with a Sparmax compressor (**Figure 3-10**). Finally, the wafers were dried in a vacuum oven (Yamato, ADP310C) at 60°C. Film uniformity was evaluated using optical profilometry and digital microscopy.

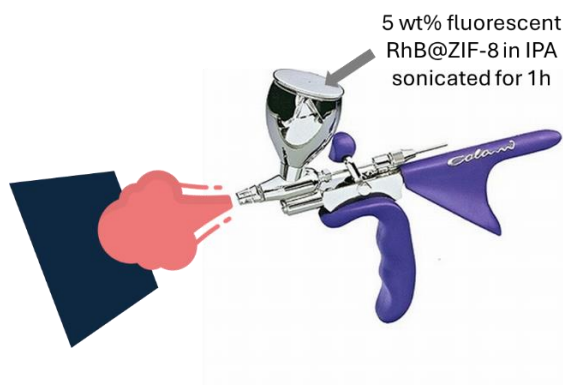


Figure 3-10: Procedure for coating a silicon wafer. A compressor was provided along with the spray gun to supply the required pressure. Multiple layers could be applied as needed.

3.4.4 Acid vapor degradation of Dye@ZIF-8

A: Chemicals

Acetic acid (AA, Fischer chemicals, ≥ 99.7%), DI water, Dye@ZIF-8 (as a powder or coated on a wafer)

B: Methodology

Prior to exposure, all samples were activated in an oven at 80°C for 1 hour. Dye@ZIF-8 powders were placed in glass vials and positioned inside Schott bottles for acid vapor exposure. For wafer experiments, the wafers were directly placed in the Schott bottles. To generate the desired acetic acid vapor concentration, a vial with an

acetic acid solution with a defined molar concentration was added to the bottle. The resulting vapor pressure establishes the correct concentration inside the closed system, as determined by Henry's law¹⁸⁰. Samples named 'air' have no AA-containing vial. Samples named '0 ppmv' had vial filled with DI water. Unless specified otherwise, samples were exposed to acid vapor overnight (*i.e.*, 19 h). After exposure, fluorescence was measured either via a standard fluorescence spectrometer or using an in-house built setup without prior activation. This setup used LEDs for excitation and a camera to capture fluorescence intensity (**Figure 3-11**).

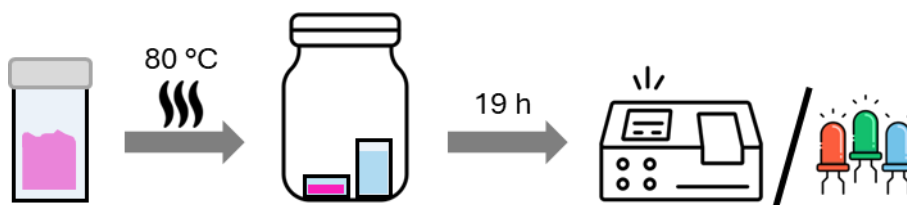


Figure 3-11: Acid vapor exposure and measurement of Dye@ZIF-8 species.

3.5 Characterization techniques

UV-Vis spectrophotometry (Shimadzu UV-2600): Assess the optical properties of AuNP suspensions and confirm surface capping or coating via light absorption and monitor ZIF degradation through changes in light scattering.

Spectroquant™ gold test (Merck NOVA 60): Measure gold concentrations

PXRD (Malvern PANalytical Empyrean diffractometer, Cu K α 1: 1.5406 Å and Cu K α 2: 1.5444 Å, PIXcel 3D solid-state detector): Verify crystal phase of ZIFs.

SEM (FEG-ESEM-EDX, Thermo Fisher Scientific Quanta 250 at an accelerating voltage of 20 kV): Study ZIF morphology and interaction between ZIFs and AuNPs

HAADF-STEM (Thermo Fischer Tecnai Osiris microscope operated at an accelerating voltage 200 kV. 50 pA current was used for HAADF-STEM imaging. A nanoparticle solution (5 μ L) was drop-cast on a Cu TEM grid with a carbon layer and left to dry in ambient air): Study ZIF morphology and interaction between ZIFs and AuNPs

FTIR (Thermo Scientific, Nicolet iS10): Verify formation of ZIF-8

HPLC (Agilent 1200 Series SL quaternary system equipped with a G1322A degasser, a G1311A quaternary pump, a G1367A automated sample injector, a G1316A thermostatted column compartment, and a G1314A variable wavelength detector): Assess the loading of dye in ZIF-8.

Optical profilometry (Sensofar S lynx with Nikon 50x interferometric lens. Processing software: Gwyddion): Study the homogeneity of with Dye@ZIF-8 coated silicon wafers.

Fluorescence spectroscopy (Horiba, Fluorolog-3): Measure fluorescence signal after acid vapor exposure of Dye@ZIF-8 materials.

Custom-built setup (excitation at 385 nm or 450 nm, filter 495 nm. ImageJ was used for intensity analysis): Measure fluorescence signal after acid vapor exposure of Dye@ZIF-8 materials.

Digital microscopy (Tagarno FHD Prestige, 3 times magnified. Before particle analysis with ImageJ, the image brightness was set to 210): Study homogeneity of films.

3.6 Data normalization

Two types of normalization are applied to the UV-Vis data. For analyzing relative intensity, **Eq. 3** is used. This method, labeled as $A/A_{\max}$ (normalized), preserves the relative intensities between data points and is indicated by a numbered y-axis ranging from 0 to 1, though the lowest datapoint is not necessarily 0. In contrast, when only the shape of the UV-Vis peaks is compared **Eq. 4** is employed, labeled as A_{strict} (strictly normalized). This normalization scales all values strictly between 0 and 1, 0 corresponding to the lowest datapoint and 1 to the highest, enabling better comparison of spectral peak features. In such cases, the y-axis is left unnumbered.

$$x_{\text{norm}} = \frac{x}{x_{\max}} \quad 3$$

$$x_{\text{norm}} = \frac{x - x_{\min}}{x_{\max} - x_{\min}} \quad 4$$

4 Results and Discussion: Trapped gold

4.1 From fragile colloids to robust powders: Handling gold at scale

Centrifugation is widely used for the purification of AuNPs. However, it often results in a significant loss of material (**Figure 7-2**). Another major complication is the lack of standardized centrifugation protocols. Reported RPM's, duration, and number of purification cycles vary widely and seem to be chosen arbitrarily, even for nanoparticles of similar sizes and with the same surface functionalization^{149–151,181,182}.

Purification efficiency can be defined as the percentage of retained AuNPs after centrifugation and resuspension, relative to the starting concentration. A high efficiency indicates minimal loss of AuNPs during the washing steps. **Figure 4-1A** illustrates purification efficiency for 10 mL Cit-AuNP. These 15 nm-sized Cit-AuNPs were centrifuged at $7342 \times g$ for 20 minutes. The purification parameters are based on a study by Balasubramanian *et al.* (2010), who found that $7000 \times g$ for 20 minutes provides an optimum of ~80% recovery of 20 nm-sized citrate-capped AuNPs¹⁵¹. Even though these conditions fall well within the commonly reported centrifugation rates, a loss of 52% occurred after the first purification step, significantly higher than the reported values. However, a critical parameter for purification yield by centrifugation is the washed volume and in this experiment, 10 mL of Cit-AuNP suspension was washed

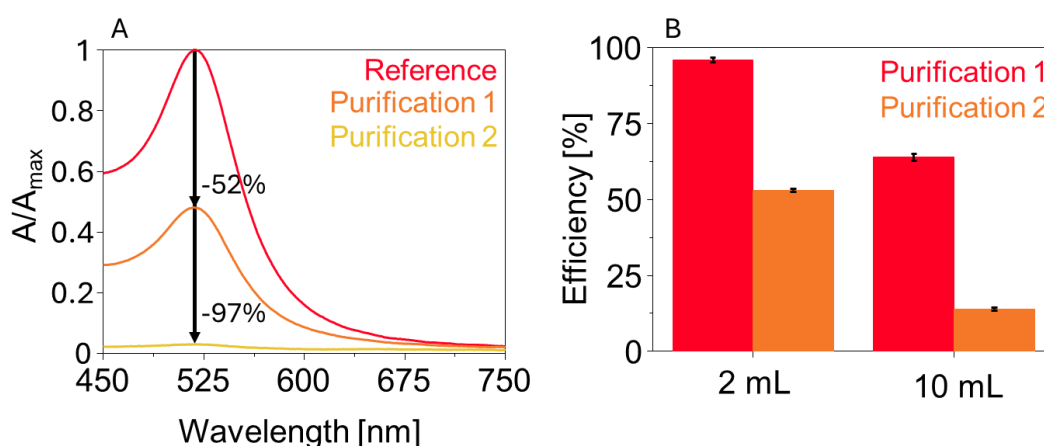


Figure 4-1: Cit-AuNP loss during purification by centrifugation. A) Normalized UV-Vis spectra showing Cit-AuNP losses after purification of 10 mL Cit-AuNP colloid. Each purification cycle comprises centrifugation, replacing supernatant with DI water, and resuspension of the pellet. The black arrows indicate the cumulative Cit-AuNP loss after each cycle. Eppendorf Centrifuge 5804. **B)** Difference in purification efficiency between centrifugation of 2 mL Cit-AuNP or 10 mL Cit-AuNPs. For the 10 mL an Eppendorf Centrifuge 5804 was used. For the 2 mL volume this was a FastGene high-speed minicentrifuge (Nippon genetics). Both centrifugation experiments were performed at $6000 \times g$ for 15 minutes.

in a single centrifugation tube, whereas 2 mL tubes are more common. **Figure 4-1B** shows the increase in yield by transitioning to smaller volumes. Normally, gentle pipetting is sufficient to resuspend the pellets, which is important when dealing with small or delicate materials that could be damaged by vigorous agitation. This approach is effective because the pellets are loosely packed and more easily dispersed. However, more compact pellets, which are often formed by centrifuging larger volumes, present a greater challenge. As described by Voo and Jacobsen (1998), resuspension can be dramatically impeded as pellet density increases¹⁸³. Denser pellets exhibit stronger cohesion and less internal fluid, reducing the surface area exposed to the washing solution and limiting its ability to disperse the pellet. Therefore, the volume of suspension, plays a key role in determining the ease of resuspension.

The purification efficiency for a single wash cycle of 2 mL Cit-AuNPs maintaining small volumes is quite good (96%, **Figure 4-1B**). However, a study by Schneider *et al.* (2004) found that the quantity of free sodium citrate is reduced by a factor of about 50-100 after one purification cycle when centrifuging 1.5 mL Cit-AuNP suspension for 3h at 3300 x g. As a result, employing multiple washing cycles is common to ensure a highly purified AuNP suspension^{150,151}.

To summarize – the three major setbacks when purifying citrate-capped AuNPs by means of centrifugation are 1) significant material loss, 2) the lack of standardized centrifugation protocols, and 3) the limitation of washing only small volumes at once.

4.2 Not all gold shines: How capping agents make or break stability

4.2.1 Ion-mediated cluster formation and acid stability of citrate capped AuNPs

In this work, the terms coated and capped refer to surface modifications of AuNPs. Capping typically involves small molecules such as citrate, while coating is more often used in the context of polymers, including PVP or PAH. In contrast, encapsulation or embedding refers to the incorporation of NPs into a larger host structure, such as the porous framework of ZIF-8. For example, ZIF-8 encapsulated Cit-AuNPs describes gold nanoparticles functionalized with citrate on their surface and embedded within ZIF-8. Clustering or cluster formation and aggregation also refer to two separate phenomena. Clustering is the formation of an unstructured group of NPs that are separated by only a few nm. These structures are still optically active in the UV-Vis and the process is reversible. Aggregation is a more extensive form of

clustering in which visible NP clumps are formed due to irreversible interactions. These clumps display limited intensity and broad spectral features in the UV-Vis range.

At first, the ZIF-8 precursors were added to a Cit-AuNP suspension targeting AuNP encapsulation. However, upon addition of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a color change from red to blue indicated cluster formation (**Figure 4-2A**). This observation is consistent with the UV-Vis spectra of the same suspension (light green curve) showing a second peak appearing around 675 nm as a result of plasmon coupling between closely spaced NPs (**Figure 4-2B**). Two phenomena can occur due to zinc ion interaction: the formation of bridging species and surface charge compensation resulting in diminishing shielding effects^{120,132,134}. The negatively charged carboxylic groups of the citrate ligands can interact with the positively charged zinc ions. These zinc ions can form bridging species with the citrate ligands from neighboring AuNPs (**Figure 7-3**). Furthermore, binding positively charged zinc ions to a colloid suspension that is

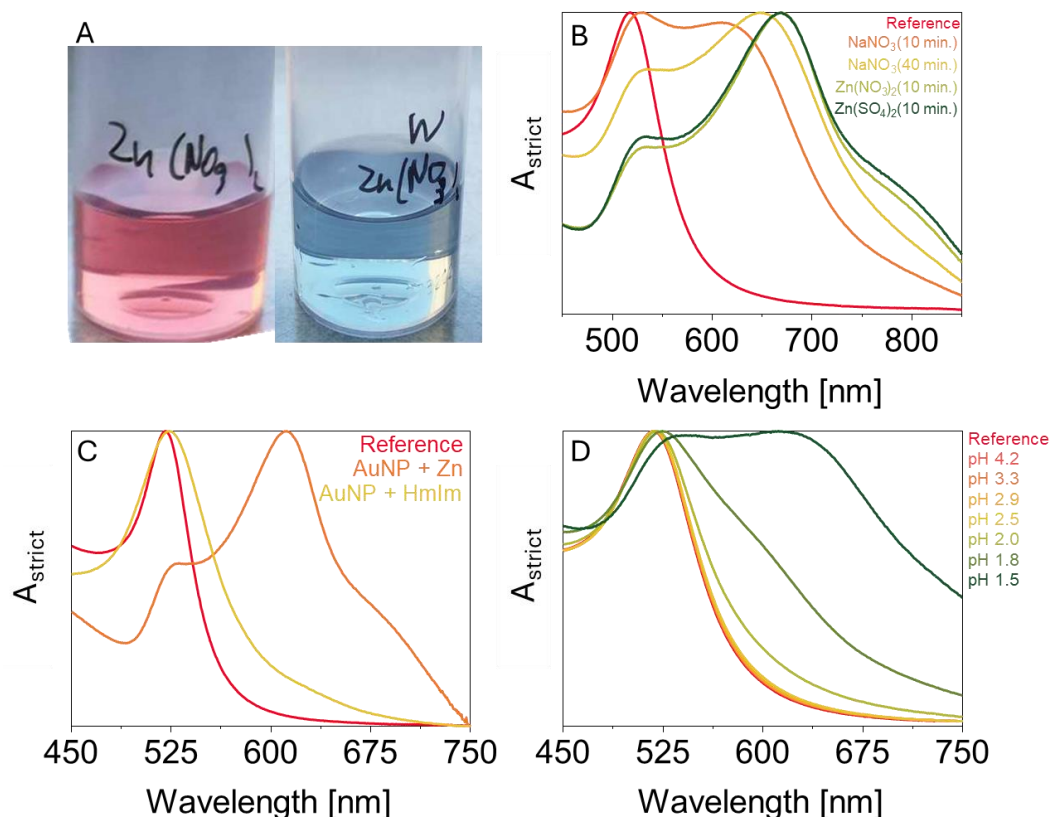


Figure 4-2: Stability of citrate-capped AuNPs. **A)** Visual color change of the suspension before (left) and after (right) adding $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a final concentration of 28 mM. **B)** UV-Vis spectra showing the effect on NP clustering when adding different salts to the gold suspension. Concentration of each salt was around 28 mM. **C)** Effect of ZIF-8 precursors on AuNP clustering. Concentration of zinc is 29 mM and concentration of the linker is 555 mM. **D)** Acid stability of the gold suspension when adding 0.1 M HNO_3 . References are Cit-AuNP suspensions and all spectra are strictly normalized.

negatively electrostatically stabilized will reduce the efficiency of the stabilization, therefore allowing cluster formation¹³². This proximity allows plasmon coupling resulting in the observed color shift and additional absorption band in the UV-Vis spectrum. Cluster formation highly depends on the type of salt that is added to the AuNP suspension, as indicated in **Figure 4-2B** which shows UV-Vis spectra of a Cit-AuNP suspension after adding the various salts. All salts resulted in clustering, but less noticeably for NaNO_3 after 10 minutes, likely related to the monovalent nature of the cations. Divalent Zn^{2+} ions interact more strongly with citrate's carboxyl groups, leading to faster cluster formation relative to Na^+ . The NaNO_3 -treated sample spectrum after 40 minutes shows an increased clustering by approaching that of $\text{Zn}(\text{NO}_3)_2$ and ZnSO_4 . The anion (NO_3^- or SO_4^{2-}) does not seem to influence cluster formation.

To avoid clustering, the synthesis of Cit-AuNP@ZIF-8 is not feasible when first adding the metal precursor to the Cit-AuNP suspension. **Figure 4-2C** demonstrates that the citrate-capped AuNP suspension is stable in the presence of 2-methylimidazole, a weak base. The pH increase upon addition enhances the electrostatic repulsion between the citrate ligands even further. Therefore, Cit-AuNP@ZIF-8 can be synthesized by first adding the linker and subsequently the metal precursor.

Since the AuNPs will be exposed to an acid environment for ZIF-8 degradation, this regime should be taken into account. When decreasing the pH of a citrate-stabilized gold colloid, the carboxylic groups are protonated ($\text{pK}_{\text{a}1} \sim 3.13$, $\text{pK}_{\text{a}2} \sim 4.76$, $\text{pK}_{\text{a}3} \sim 5.41$, free citrate) decreasing electrostatic repulsion, thereby destabilizing the suspension. **Figure 4-2D** shows the pH-dependent clustering when adding 0.1 M HNO_3 in small portions. The onset of clustering starts around pH 2.5. However, studies typically report cluster formation starting at pH 3.0¹⁸⁴. For this reason, a more prudent limit of pH 3.0 is considered as the limit for stability of Cit-AuNPs.

4.2.2 Increasing suspension stability using PVP or PAH coatings

As mentioned in the literature (section 2.3.2) polyvinyl pyrrolidone (PVP) or poly(allylamine) hydrochloride (PAH) are employed to enhance colloid stability in harsher environments^{40,72,108,137,140,150}. To see if coating the NPs with a polymer affects the yield during purification without further processing, 10 mL of a PAH-AuNP colloid and 10 mL of a PVP-AuNP colloid were purified by centrifugation while maintaining the

parameters from Cit-AuNPs study. A key mechanism driving NP clustering during centrifugation, as proposed by Roca *et al.* (2010), is the temporary polarization of the electrical double layer¹⁴⁹. Under high centrifugal forces, the double layer becomes polarized, forming a dipole that enhances attractive interactions between AuNPs. This effect appears to be strongest for citrate-capped AuNPs, because when citrate on the AuNP surface is coated or exchanged with PAH or PVP, the yield after centrifugation increases (**Figure 4-3**), suggesting reduced clustering. The polymer shell may limit NP interaction within the pellet, leading to looser packing and easier redispersion. This effect is especially pronounced for PVP, which provides steric stabilization through a physical barrier that likely inhibits cluster formation. In contrast, PAH, like citrate, stabilizes AuNPs via electrostatic repulsion, though with a positive charge. However, this repulsion may be less effective at preventing clustering than the steric hindrance offered by PVP.

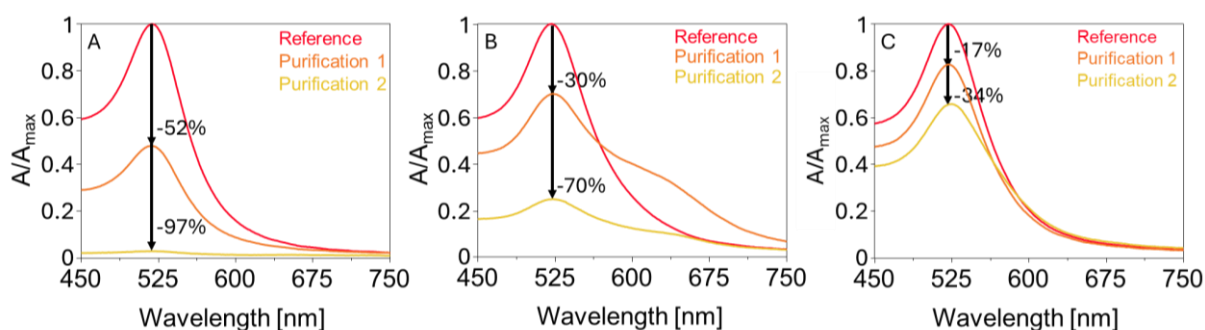


Figure 4-3: Comparison of purification efficiency for A) Cit-AuNPs, B) PAH-AuNPs, and C) PVP-AuNPs. Each sample was washed in a 10 mL volume, and centrifugation was performed at $7342 \times g$ for 20 minutes. The purification process was repeated twice. The references are non-centrifuged suspension of each AuNP-type. All normalized spectra.

Although alternative stabilizing agents already show improvements, this work aims to maximize the yield by embedding AuNPs in ZIF-8. This approach should simultaneously improve AuNP handling, long-term stability, and allow for washing larger volumes as well.

4.3 Getting the gold inside: Three approaches to AuNP encapsulation

To form AuNP@ZIF-8, three distinct strategies were explored, each involving NPs with different surface characteristics. In the first approach, coated AuNPs were used, offering high colloid stability but requiring careful control to ensure efficient encapsulation in ZIF-8. In another method the gold precursor is reduced directly in the

pores of ZIF-8. This *in-situ* approach minimizes synthesis complexity, ensures better encapsulation, but limits AuNP morphology control. Finally, uncapped AuNPs are produced by laser ablation in liquid, combining tunable NP size with clean surfaces, but requiring precise addition timing to avoid AuNP clustering during encapsulation in ZIF-8.

4.3.1 Coated AuNPs

AuNPs coated with PVP or PAH show good stability in acid environments. Up to a pH of 2.0 for PVP-AuNPs and as low as 1.5 for PAH-AuNPs^{137,185}. The stability is also better maintained in the presence of ZIF-8 precursors (**Figure 4-4A and B**), compared to citrate-capped AuNPs. The lack of functional surface groups and increased stability of the NPs might be a reason for this.

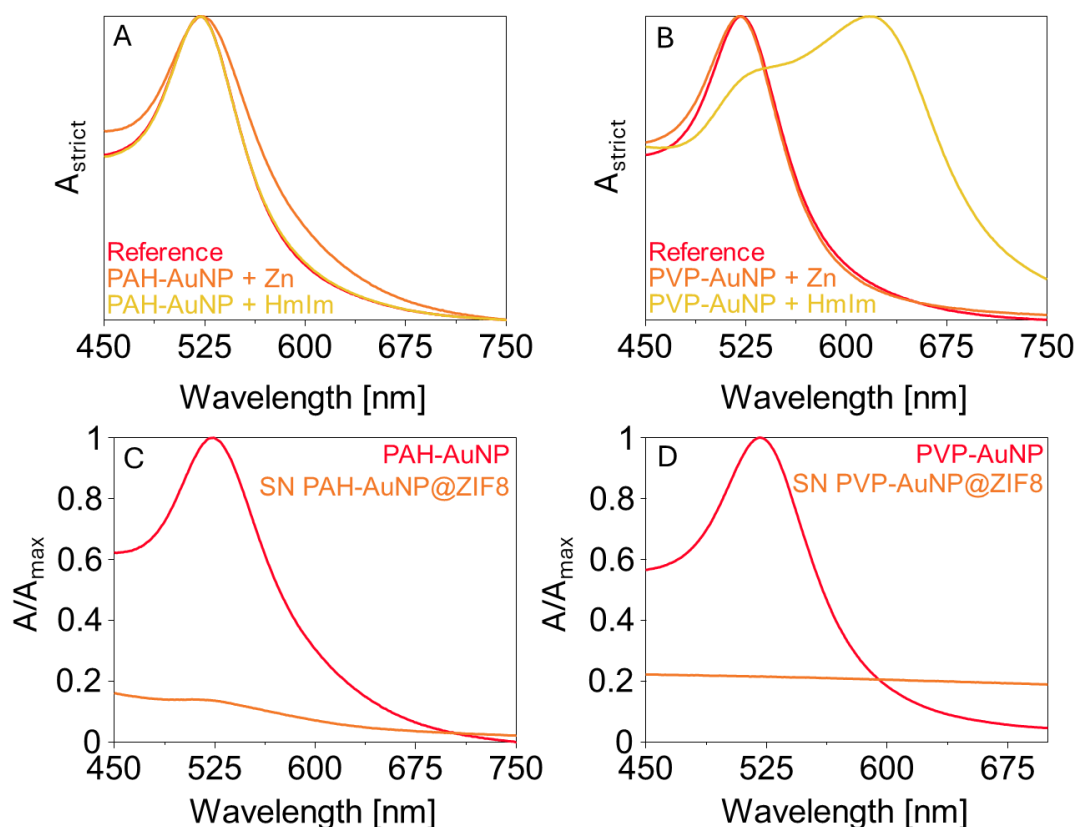


Figure 4-4: Stability of coated AuNPs towards ZIF-8 precursors and their removal efficiency. **A)** Stability of PAH-AuNPs in a 28 mM zinc nitrate solution and a 28 mM Hmlm. Reference is a PAH-AuNP suspension. **B)** Stability of PVP-AuNPs in a 28 mM zinc nitrate solution and a 28 mM Hmlm. Reference is a PVP-AuNP suspension. **C)** Removal of PAH-AuNP@ZIF-8, **D)** Removal of PVP-AuNP@ZIF-8. A and B are strictly normalized. C and D are normalized.

Before encapsulation of the AuNPs in ZIF-8, an optimization experiment (**Figure 7-4**) was conducted to minimize the excess of polymer after ligand exchange.

An excess of ligand molecules can inhibit the interaction between PVP-modified nanoparticles and growing ZIF-8 crystals due to the competitive adsorption of free PVP²³. Furthermore, in many optical applications, close proximity to the AuNPs is required for efficient use, since the nearfield enhancement is generally confined to a distance of a few nanometers from the particle's surface^{66,67,108,124}. By coating the particles with a thick inert polymer shell, their usability is therefore reduced. Hence, minimizing the amount of polymer added, while maintaining suspension stability is needed.

Next, the AuNPs are encapsulated in ZIF-8 (**Figure 7-5**) and the material is centrifuged. The residual bump in the supernatant spectrum in **Figure 4-4C** indicates that not all PAH-AuNPs were removed from suspension, likely because of weak electrostatic repulsion between the positively charged PAH-AuNPs and ZIF-8 particles, which possess a positive zeta potential¹⁸⁶. Abdelhamid (2020) discusses that negatively charged species, such as PVP-AuNPs, are more prone to being embedded because of the strong interaction with Zn^{2+} ¹⁸⁷ (**Figure 4-4D**). To support this statement, a separate experiment was conducted in which PVP-AuNPs were mixed with pre-synthesized ZIF-8 (20:1 HmIM:Zn ratio) powder. In this case, the only way for the NPs to precipitate out of solution is to adsorb onto the ZIF-8 crystal surface, hence revealing an interaction between weakly negatively charged PVP-AuNPs and ZIF-8. Indeed, the absence of a LSPR peak in the supernatant spectrum (**Figure 4-5**) indicates complete removal of PVP-AuNPs. However, an elevated baseline is measured, which is attributed to light scattering as no additional absorbing species are present to account

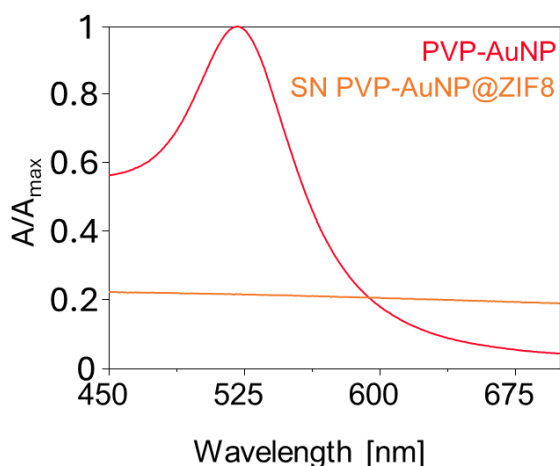


Figure 4-5: Good removal of PVP-AuNP@ZIF-8 after purification. Pre-made ZIF-8 was mixed with PVP-AuNPs. Normalized spectra.

for changes in absorbance apart from the NPs themselves. This observation suggests the presence of residual ZIF-8 particles remaining in suspension.

To investigate the structural nature of the powders after purification, FTIR and PXRD analyses were performed. While FTIR shows characteristic ZIF-8 peaks (**Figure 7-6**), the PXRD diffraction pattern does not match, indicating that other crystalline materials have formed (**Figure 4-6A**). Notably, small bright features corresponding to AuNPs can be observed on the external surfaces of the crystals in both samples (**Figure 4-6B, C, and D**). This association between AuNP and MOF reduces the AuNP-AuNP interactions, and facilitates settling. Although the amount of AuNPs is low and primarily located on the surface, this does not pose a significant issue. The interaction with ZIF-8 is sufficiently strong to remove most NPs from the suspension.

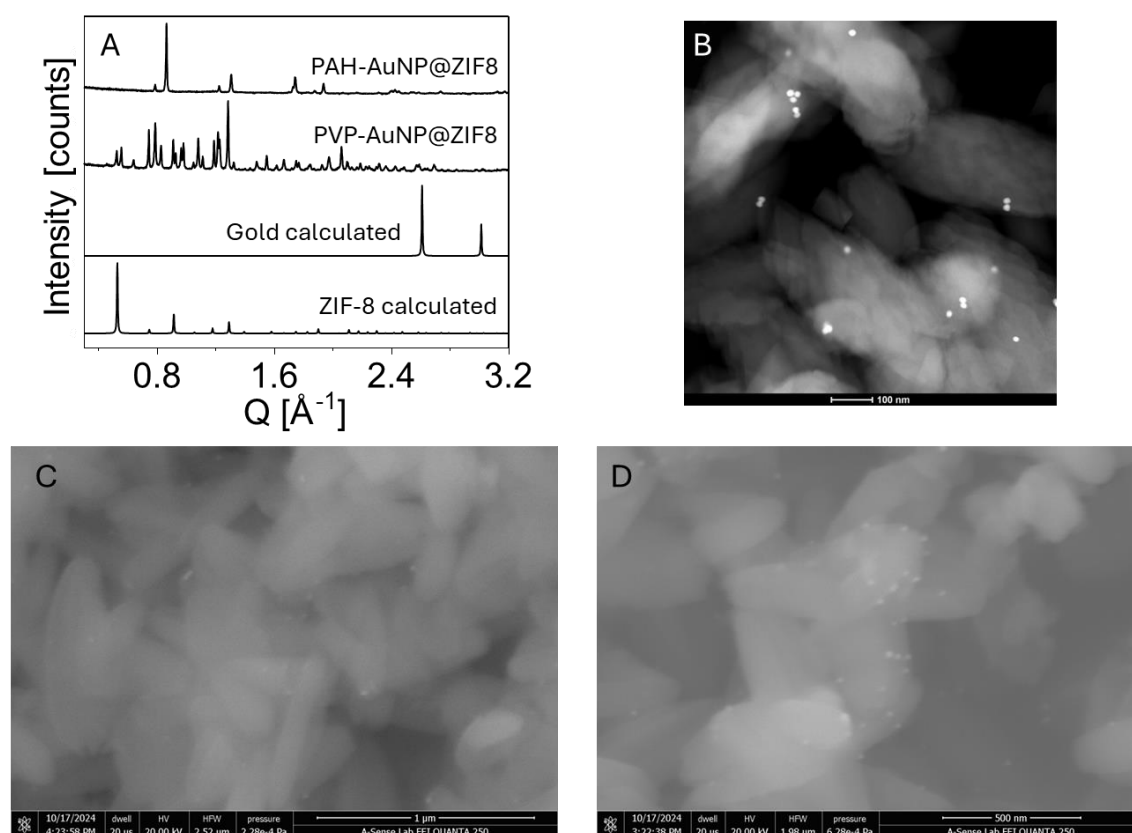


Figure 4-6: Morphology and crystallinity of PAH- and PVP-AuNP@ZIF-8 materials. A) PXRD pattern of both samples with reference diffractograms for gold and ZIF-8. B) HAADF-STEM image of PAH-AuNP@ZIF-8, C) SEM image of PAH-AuNP@ZIF-8. D) SEM image of PVP-AuNP@ZIF-8. PAH-AuNP@ZIF-8 was synthesized using a 2:1 HmIM:Zn ratio. PVP-AuNP@ZIF-8 was synthesized using a 20:1 HmIM:Zn ratio.

As will be further discussed in section 4.4.2, the acid-induced degradation of PVP-AuNP@ZIF-8 showed undesirable behavior. Consequently, the focus shifted to PAH-AuNPs. As the settling with PAH-AuNPs using ZIF-8 was less efficient (**Figure 4-4C**), the affinity of PAH for the MOF needs to be improved. Literature reports commonly address this challenge by introducing an affinity layer using the amino acid L-cysteine, which can facilitate the interaction with ZIF-8¹⁵⁶.

Therefore, both Cys-AuNPs and Cys-PAH-AuNPs were studied. When cysteine is used as a primary capping agent, it binds to gold through its thiol group, leaving the carboxyl group exposed for interaction with ZIF-8¹⁵⁷. However, when cysteine is used as a secondary capping agent around PAH-AuNPs, its orientation is likely reversed¹⁴¹. The negative charged carboxyl group interacts with the positively charged PAH-AuNPs. This leaves the thiol group free, enabling coordination with zinc ions during ZIF-8 growth. As shown in **Figure 4-7A**, Cys-AuNPs remained stable in the presence of the organic linker but aggregated upon addition of zinc ions, likely due to bridging interactions between cysteine's carboxyl group and zinc ions, similar to what happens with Cit-AuNPs.

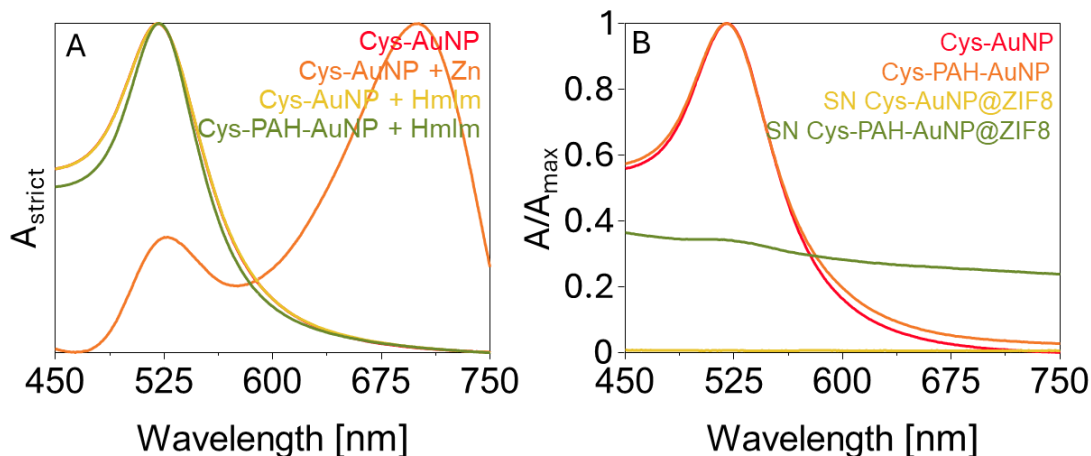


Figure 4-7: Interaction of cysteine-capped AuNPs with ZIF-8 precursors and their removal from suspension.

A) Stability of cysteine- and cysteine-PAH-capped AuNPs in the presence of Zn^{2+} and 2-methylimidazole, 28 mM for both precursors. Strictly normalized. **B)** Removal efficiency of ZIF-8-encapsulated Cys-AuNPs and Cys-PAH-AuNPs after centrifugation. Normalized.

Interestingly, following purification, Cys-PAH-AuNP samples showed residual AuNPs in suspension, similar to what was observed for PAH-AuNP@ZIF-8 (**Figure 4-7B**). This suggests that the addition of cysteine does not significantly enhance the interaction between PAH-AuNPs and ZIF-8. The limited removal of Cys-

PAH-AuNPs from suspension implies a weak or negligible interaction between PAH and cysteine, with the NPs behaving similarly to unmodified PAH-AuNPs. In contrast, Cys-AuNP@ZIF-8 exhibited efficient removal, likely due to the negative surface charge imparted by the carboxyl groups of the cysteine layer. This behavior is similar as observed for citrate-capped AuNPs²³.

4.3.2 *In-situ* reduction

To achieve AuNPs effectively embedded into ZIF-8, a protocol was employed where the AuNPs are formed inside ZIF-8's pores. A major advantage is that no expensive ligands or coatings are needed, reducing the complexity of the synthesis mixture. Furthermore, by first synthesizing ZIF-8 without any other interfering reactions, crystalline phase control is simplified. However, a key limitation of this method is the inability to tune the size and shape of the NPs, as the morphology is limited by the pore size of ZIF-8. Therefore, this method cannot be used to settle a random AuNP suspension. However, the *in-situ* generated AuNPs can serve as a model to assess the system's behavior with uncapped NPs. To achieve a stable AuNP suspension after redispersion, the nanoparticles need to be capped. Although they are initially uncapped, free HmIM likely stabilizes the AuNPs upon acid-induced resuspension.

Since the AuNPs are formed inside the MOF, no encapsulation efficiency can be determined. HAADF-STEM shows that *in-situ* reduction of the gold precursor likely results in the formation of AuNPs within ZIF-8, as evidenced by the uniform distribution of nanoparticles throughout the MOF structure (**Figure 4-8A**). The gold loading of this

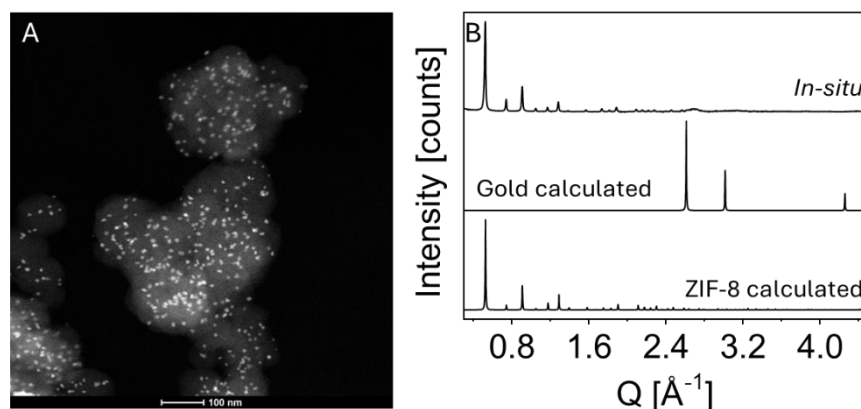


Figure 4-8: Characterization of AuNP@ZIF-8 synthesized via an *in-situ* reduction method. A) HAADF-STEM image showing the distribution of gold nanoparticles within ZIF-8. **B)** PXRD pattern of the same material with calculated references for gold and ZIF-8.

material is about 1.73 wt%, assuming no gold losses during synthesis or purification. The corresponding PXRD pattern confirms the presence of well-formed ZIF-8, which is attributed to the high HmIM:Zn ratio (~ 256) used during synthesis (**Figure 4-8B**).

4.3.3 Laser ablation in liquid particles

In laser ablation in liquid, a laser pulse ejects material from a metal target forming a hot metal plasma, which rapidly condenses into NPs. Two major advantages are combined in this final approach: tunable NP morphology and no use of AuNP suspension-stabilizing ligands. 20-30 nm-sized LAL-AuNPs were kindly shared by the group of Dr. Sven Reichenberger (Duisburg-Essen) (**Figure 7-7**). This colloidal suspension was stabilized in a 100 μM NaCl solution.

Since this suspension is only weakly stabilized by adsorbed sodium or chlorine ions, even small perturbations can cause clustering. This is shown in **Figure 4-9A** where addition of ZIF-8 precursors results in clustering of AuNPs. However, the material could be synthesized by adding the AuNPs quickly after the ZIF-8 precursors were combined in a high HmIM:Zn ratio (~ 256). This causes the NPs to be caught in the fast-growing ZIF-8 network, minimizing the time to form clusters. Good removal from suspension also indicates successful encapsulation of these species (**Figure 4-9B** and **Figure 7-8**). Since the material was produced using high HmIM:Zn ratio, a crystalline ZIF-8 phase can be detected with PXRD (**Figure 4-9C**).

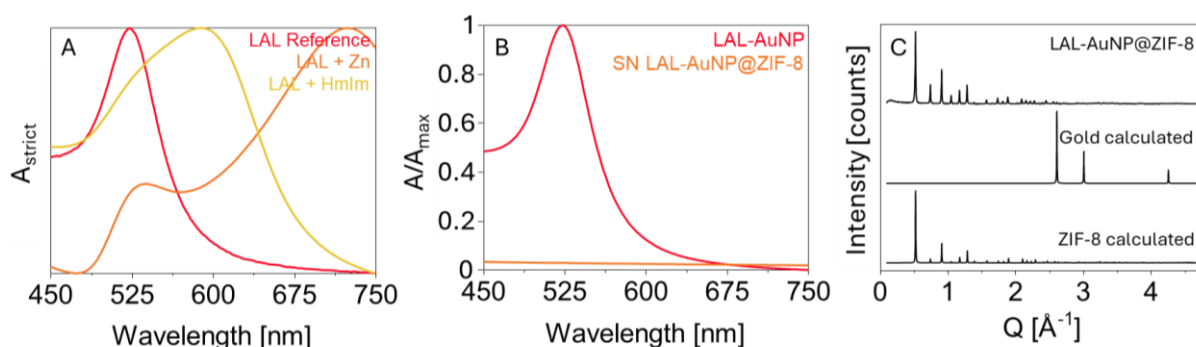


Figure 4-9: Evaluation of LAL-AuNP interactions with ZIF-8 precursors and their encapsulation performance. A) Stability of LAL-AuNPs in the presence of ZIF-8 precursors (Zn^{2+} and HmIM). Strictly normalized. **B)** Removal of LAL-AuNP@ZIF-8 from suspension after centrifugation. Normalized. **C)** PXRD pattern of LAL-AuNP@ZIF-8 with reference patterns for gold and ZIF-8.

4.3.4 Influence of linker-to-metal ratio on encapsulation

The HmIM:Zn ratio was systematically varied, ranging from 1 up to 256. While this ratio is known to influence the crystalline structure of ZIF-8^{15,35}, it also affects the

encapsulation efficiency of AuNPs. To investigate this, PAH-AuNPs were encapsulated using different HmIM:Zn ratios. After 24 hours of mixing, the suspensions were centrifuged (Eppendorf Centrifuge 5804, 2740 x g, 15 min, 10 mL) and the supernatants were analyzed by UV-Vis spectroscopy to detect residual AuNPs (**Figure 4-10A**). At a ratio of 1, no PAH-AuNPs remain in the supernatant, and the absence of background scattering suggests that ZIF-8 is not present either. This suggests that all material has settled out of suspension. However, the formation of crystalline ZIF-8 is unlikely under these sub-stoichiometric conditions. It is more plausible that at this HmIM:Zn ratio an amorphous or polymeric ZIF-like phase formed¹⁸⁸, which effectively encapsulated the AuNPs (**Figure 4-10B**).

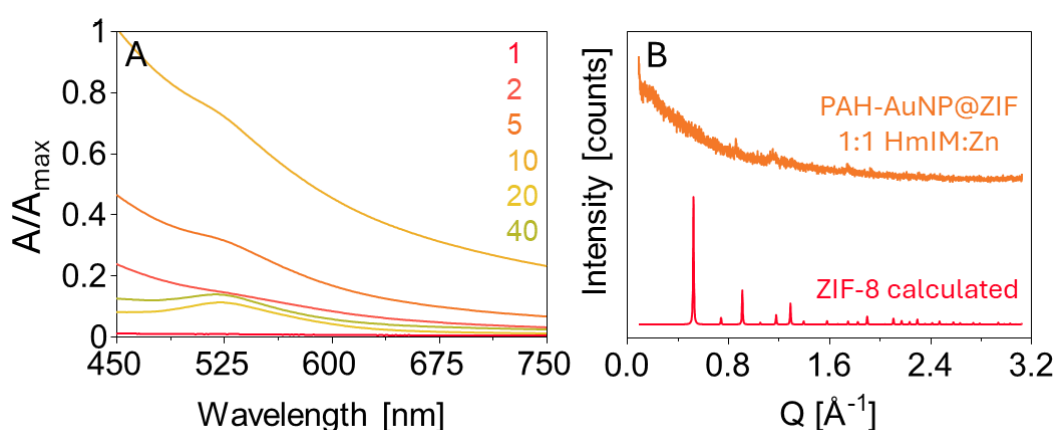


Figure 4-10: Effect of HmIM:Zn ratio on encapsulation efficiency of PAH-AuNP. A) Residual PAH-AuNPs for increasing HmIM:Zn ratios. Normalized spectra. **B)** Amorphous ZIF phase forms at sub-stoichiometric HmIM:Zn ratios at room temperature.

With increasing linker excess from 1 to 10, light scattering in the UV-Vis spectra increases, indicating that some ZIF-8 remains in suspension. A small LSPR bump also appears, suggesting incomplete encapsulation of PAH-AuNPs. At even higher ratios, scattering decreases again. We hypothesize that larger ZIF-8 crystallites form and are more effectively removed by centrifugation. However, the pronounced gold plasmon peaks indicate significant quantities of unencapsulated PAH-AuNPs remain, especially at ratios of 20 and 40. This observation suggests that excessive ligand content may actually hinder encapsulation efficiency. A study by Zhou *et al.* (2019) shows that ZIF-8 crystals exhibit a positive zeta potential ranging from +17.2 mV at pH 4 to +12.2 mV at pH 6¹⁸⁶. This positive surface charge promotes preferential interaction with the HmIM ligand, while electrostatically repelling positively charged species such as PAH-capped AuNPs. At higher HmIM:Zn ratios, the excess HmIM increases the solution pH. This

pH rise lowers the zeta potential of ZIF-8, slightly reducing electrostatic repulsion between ZIF-8 and PAH-AuNPs. However, the excess linker likely continues to dominate coordination with Zn^{2+} , further limiting opportunities for PAH-AuNPs to bind to or become encapsulated within the growing ZIF-8 structure.

4.4 From powder to colloid: Using acids to unlock gold nanoparticles

4.4.1 How linker-to-metal ratio influences ZIF phases

As seen from PXRD (**Figure 4-11**), not all syntheses result in ZIF-8 formation. A study by Carraro *et al.* (2020) has demonstrated that variations in HmIM:Zn ratio, in combination with biomacromolecule content, determine the resulting ZIF phase. At low HmIM content ($\text{HmIM:Zn} < 5.30$), the resulting materials are predominantly amorphous or exhibit instable crystalline phases, such as the less known U13 phase. Increasing the HmIM:Zn ratio to a range between 5.30 – 8.00 and maintaining low biomacromolecule levels yields the U13 phase, while further increasing HmIM:Zn above 10.70 normally favors the formation of ZIF-8 (sodalite topology). Different ZIF phases exhibit distinct properties in terms of porosity, chemical stability, and acid degradation profiles. For instance, ZIF-8 is highly porous and allows for controlled degradation, whereas phases such as diamondoid or ZIF-C are denser and exhibit slower or less tunable acid degradation.^{15,35,188}

Figure 4-11A illustrates the crystalline phases of ZIF containing PAH-AuNPs obtained at various HmIM:Zn ratios. Higher HmIM:Zn ratios consistently yield more crystalline ZIF-8. The presence of AuNPs seemed to have no impact on crystallinity when compared to ZIF synthesis without NPs (**Figure 7-9**). Additionally, as shown in **Figure 4-11B**, the diffractograms become increasingly reproducible at higher ratios. For example, at ratios of 256 and 20, the XRD patterns are always identical, whereas at a ratio of 2, notable variation appears, though a characteristic recurring peak is still observed. At such low ratios, even minor inaccuracies in weighing can lead to sub-stoichiometric conditions, significantly affecting the resulting crystal phase. **Figure 4-11C** visualizes the sensitivity of the system at a 1:1 HmIM:Zn ratio. In the absence of AuNPs, a well-defined crystalline phase forms. However, it is not ZIF-8. ZIF-8 formation is already sensitive to many parameters which is further enhanced at these low ratios. Even the temperature plays a key role. At 0°C some crystallinity is observed, while a completely amorphous material is obtained at room temperature

(Figure 4-11D). This phenomenon is likely related to the reduced reaction kinetics at lower temperatures, allowing time to crystallize slowly.

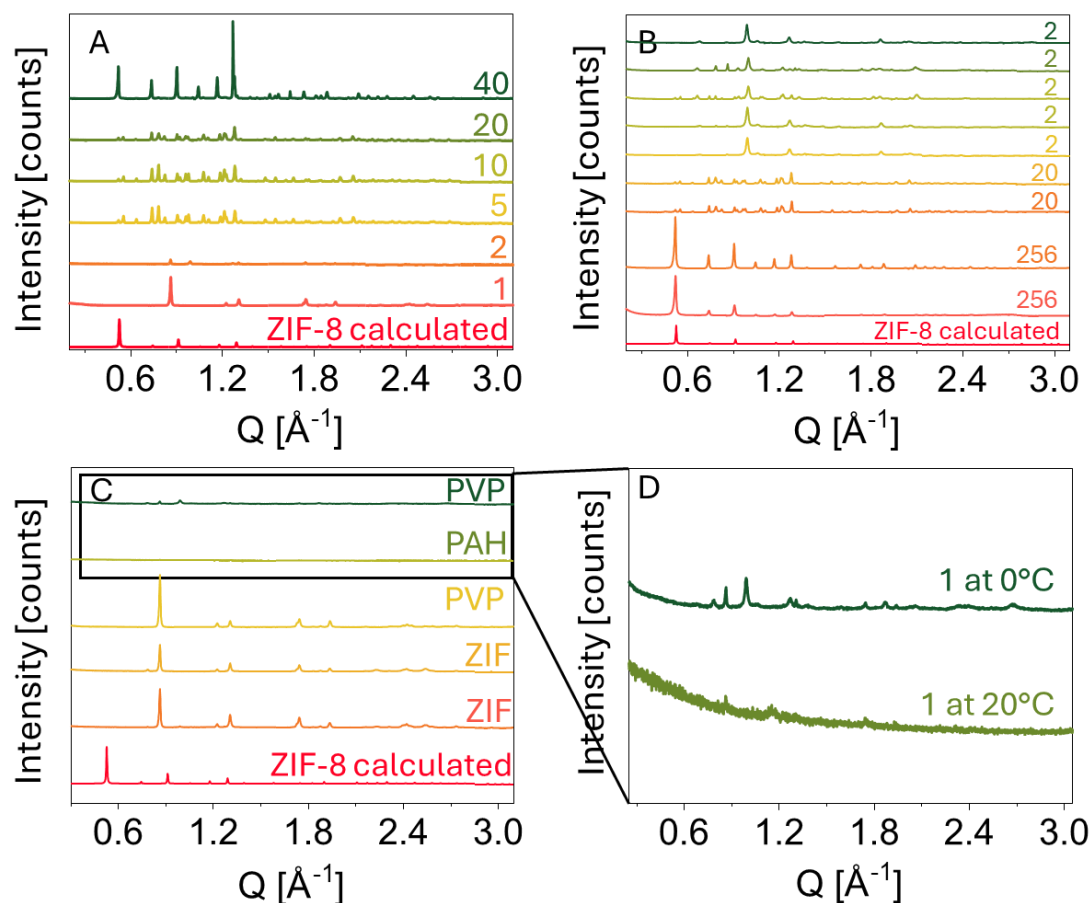


Figure 4-11: PXRD patterns illustrating the influence of synthesis parameters on the formation of ZIF phases. A) Crystalline phases obtained at varying HmIM:Zn ratios for PAH-AuNP@ZIF-8. **B)** Reproducibility of PXRD patterns at different ratios, highlighting variability at low linker content. **C)** Differences in crystallinity between samples synthesized in a 1:1 HmIM:Zn ratio. PVP or PAH indicate that these type capped AuNPs were present. **D)** Temperature-dependent crystallinity at a 1:1 ratio.

The objective of this study is not to achieve a specific ZIF. However, the phase partially determines the material's behavior. PXRD analysis indicates that these non-ZIF-8 phases, exhibit fewer large d-spacings, suggesting reduced pore sizes (**Table 4-1**). As a result, diffusion of acid components is hindered. This limitation explains the increased acid resistance observed in these phases (see section 4.4.2), as more acid is required to degrade ZIF-8. Notably, the phase analysis suggests different phases in similarly synthesized materials again proving the sensitivity of ZIF phases at low HmIM:Zn ratios (**Figure 7-10**). Some materials even show multiple phases. Even though materials are labeled as X@ZIF-8, keep in mind that it might be another ZIF phase.

Table 4-1: Specific surface areas (SSA) and pore volume and size (V_{pore} and d_{pore}) of ZIF phases. Based on the PXRD data, these phases were determined using an app developed by Hafner *et al.* (2022)¹⁸⁹.

ZIF phase	SSA [m ² /g]	V_{pore} [cm ³ /g]	d_{pore} [nm]	HmIM:Zn used
ZIF-8 ^{11,25}	1207	0.6	1.16	> 40
ZIF-L ^{190,191}	67.02	0.2	0.34	4, 2 but 5x higher concentration
ZIF-C ¹⁹²	260.52	0.26	0.96	2
U12 ¹⁹³	50.9	Not well-documented	Not well-documented	2
Amorphous ¹⁹⁴	16	0.002	Not well-documented	1

4.4.2 Breaking down AuNP@ZIF-8 species

ZIF-8 is highly sensitive to mildly acid environments, readily degrading even at near-neutral pH. As shown in **Figure 4-12A**, scattering from ZIF-8 particles in suspension decreases upon dropwise acidification with 0.1 M acetic acid (AA), indicating disassembly of ZIF-8. Complete degradation occurs around pH 6.6, which is within the range of DI water (measured to be 6.2), demonstrating that ZIF-8 can also degrade upon resuspension in DI water. This statement is further supported by the stagnant LSPR signal of AuNP@ZIF-8 particles before and after HCl addition, confirming prior ZIF-8 disintegrated (**Figure 4-12B**).

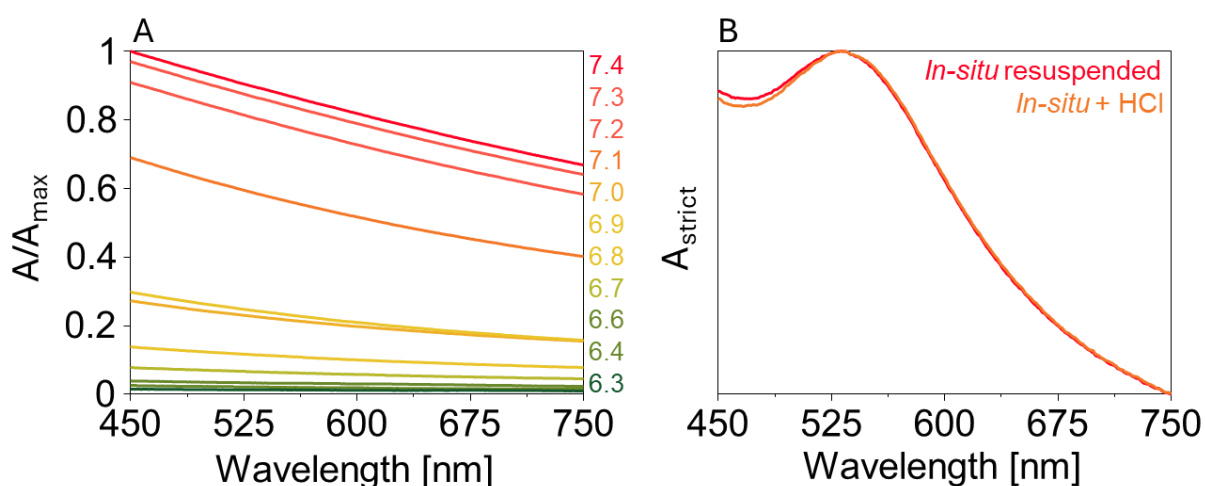


Figure 4-12: Degradation behavior of ZIF-8 in mildly acid and aqueous environments. A) Decrease in scattering intensity of ZIF-8 particles upon acidification with 0.1 M acetic acid. Normalized. **B)** UV-Vis spectra of *in-situ* synthesized AuNP@ZIF-8 after resuspension in DI water. Strictly normalized.

The post-degradation stability of various encapsulated AuNP suspensions was further evaluated following acid-induced breakdown of ZIF. While PVP-AuNPs exhibit reasonable stability in the presence of acetic acid alone (**Figure 4-13A**), significant clustering occurs when the encapsulated hybrids are degraded (**Figure 4-13B**). This clustering may be attributed to the carboxyl groups of AA, which could facilitate interparticle interactions. In contrast, degradation using HCl resulted in markedly improved colloidal stability. However, since PVP-AuNP@ZIF-8 shows some cluster formation for both AA and HCl, the focus shifted towards PAH-AuNP@ZIF-8.

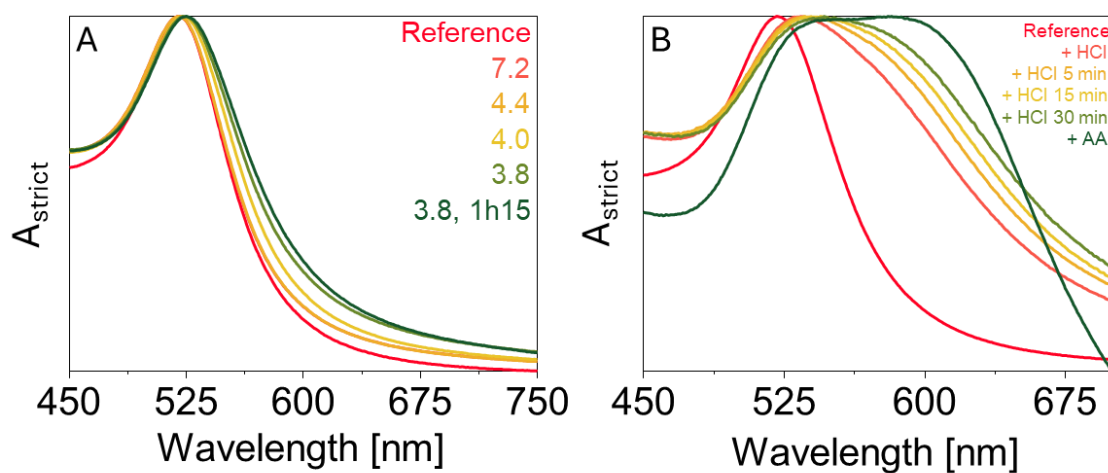


Figure 4-13: Influence of pH on the stability of PVP-AuNPs and PVP-AuNP@ZIF-8. A) UV-Vis spectra of PVP-AuNPs treated with 0.1 M acetic acid. B) Comparison between addition of 1 M AA and 1 M HCl for PVP-AuNP@ZIF-8 degradation. Reference are PVP-AuNPs. All spectra are strictly normalized.

As established earlier, PAH-coated AuNPs exhibit strong stability across a range of chemical environments, including zinc precursors and linker (**Figure 4-4A**), and acid media (**Figure 7-11**). Their stability is preserved upon acid-induced degradation of ZIF-8 and is consistent with previous observations for PAH-AuNPs. Lowering the pH by adding an acid enhances protonation of PAH (an amine-functionalized polymer) and thus increases electrostatic repulsion between the PAH-AuNPs. The colloidal stability of PAH-AuNPs is further improved by using HCl instead of acetic acid (**Figure 4-14A**). In contrast, Cit-AuNPs exhibit aggregation upon addition of an acid (**Figure 4-14B**), likely related to free zinc ions forming bridging complexes with citrate ligands following ZIF-8 decomposition, and decreased electrostatic repulsion due to protonation of the citrate resulting in a neutral ligand. The effect appears more pronounced with acetic acid, promoting more interparticle interactions. In the case of *in-situ* synthesized AuNPs, redispersion yields a characteristic gold plasmon peak. However, it is less

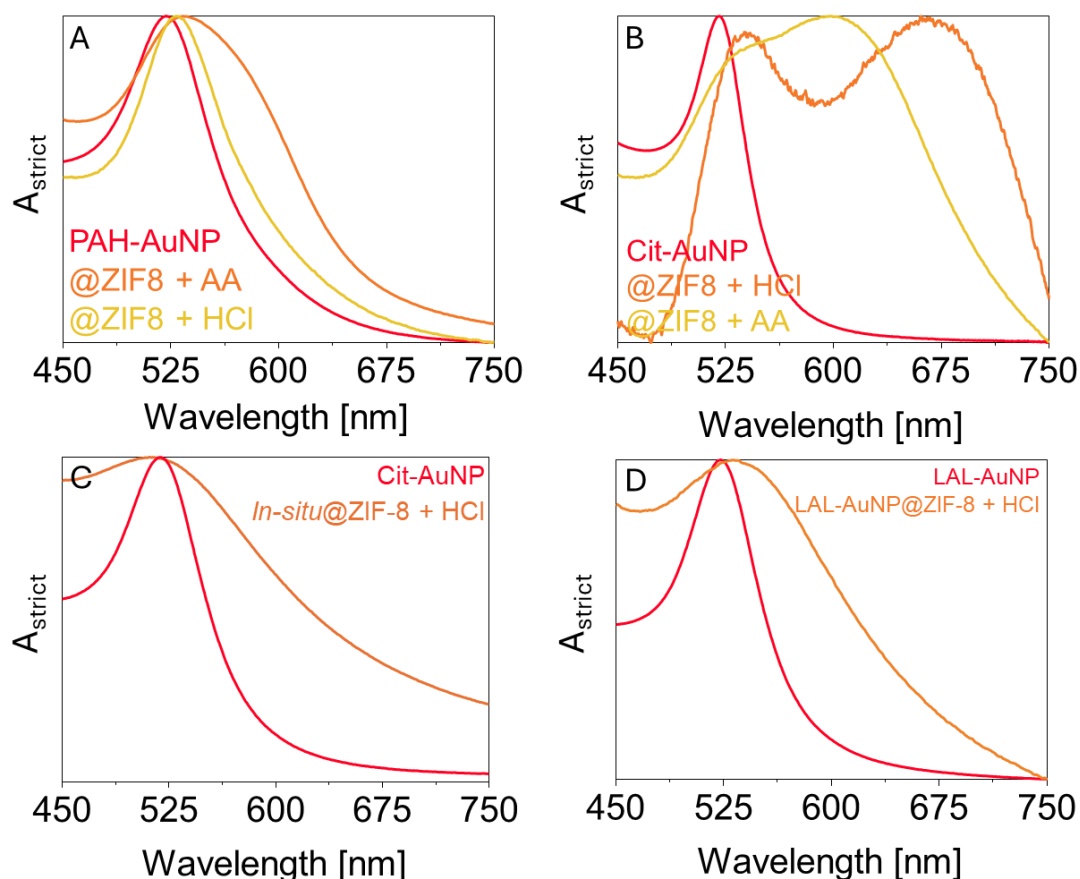


Figure 4-14: Colloidal stability of various AuNP types after ZIF-8 degradation. A) PAH-AuNPs, B) Cit-AuNP, C) *In-situ* synthesized AuNPs, D) LAL-AuNPs. 1 M HCl or 1 M AA was used for acid-induced degradation. All spectra are strictly normalized.

sharp compared to that of Turkevich-synthesized particles. This finding is not unexpected, as HAADF-STEM imaging (**Figure 4-8A** and **Figure 7-12**) reveals that while the AuNPs are monodisperse in size, they exhibit considerable shape anisotropy. This non-uniform morphology enables multipolar plasmon oscillations, resulting in peak broadening. Though we suspect that free HmIM stabilizes the AuNPs upon ZIF-8 degradation, the initial lack of stabilizing agents around the NP can be a source of cluster formation. Similarly, redispersed LAL-AuNPs display comparable behavior.

When comparing the removal efficiency of Cys-AuNP@ZIF-8 with Cys-PAH-AuNP@ZIF-8 (**Figure 4-7B**), the improved removal of Cys-AuNPs stems from the strong interactions of cysteine both with the AuNP surface and ZIF-8 similar to the Cit-AuNPs and PVP-AuNPs. However, attempts to redisperse Cys-AuNP@ZIF-8 following acid degradation were largely unsuccessful. While a weak plasmonic peak is detectable upon HCl addition, the overall NP concentration appears to be low, likely due to aggregation into larger aggregates that settle or show a strong dispersed optical

activity in the UV-Vis region (**Figure 4-15** and **Figure 7-13**). Similarly to Cit-AuNPs, the aggregation is likely to the release of zinc ions upon dissolution of ZIF-8. In that case, zinc ions act as coordination bridges with the carboxyl groups of cysteine (**Figure 4-7A**), promoting nanoparticle clustering. The extent of this aggregation is influenced by the amount of cysteine used during the initial capping process. Higher cysteine concentrations correlate with increased aggregation (**Figure 7-14**).

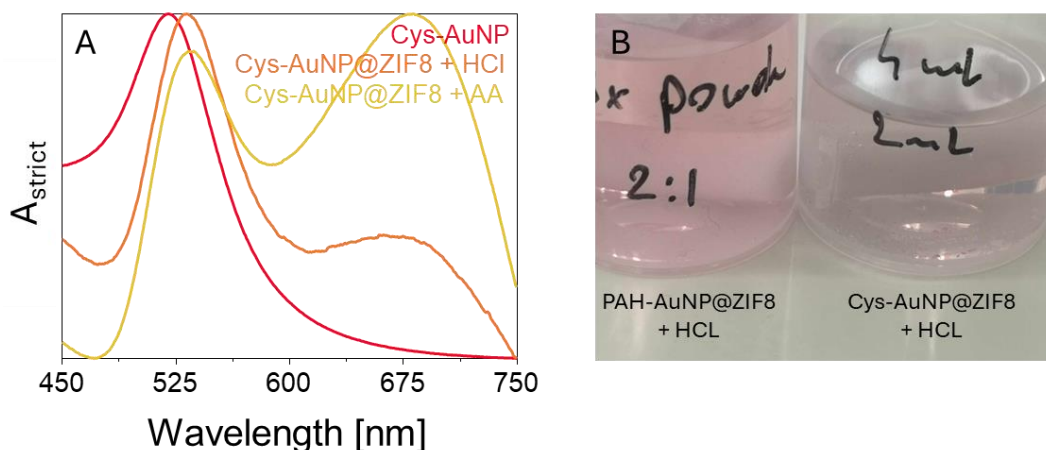


Figure 4-15: Resuspension behavior of Cys-AuNP@ZIF-8 after ZIF-8 degradation. **A)** Strictly normalized UV-Vis spectra showing reduced plasmonic signal following treatment with 1 M HCl or 1 M AA. **B)** Visual comparison of resuspended PAH-AuNPs and Cys-AuNPs after 1M HCl treatment.

HAADF-STEM confirms that Cys-AuNPs demonstrate aggregation after acid-induced resuspension (**Figure 4-16A**). However, the observed size variation of Cys-AuNPs was already present in the original AuNP suspension (**Figure 7-16**). In contrast, HAADF-STEM images reveal that PAH-capped AuNPs retain a uniform size and high

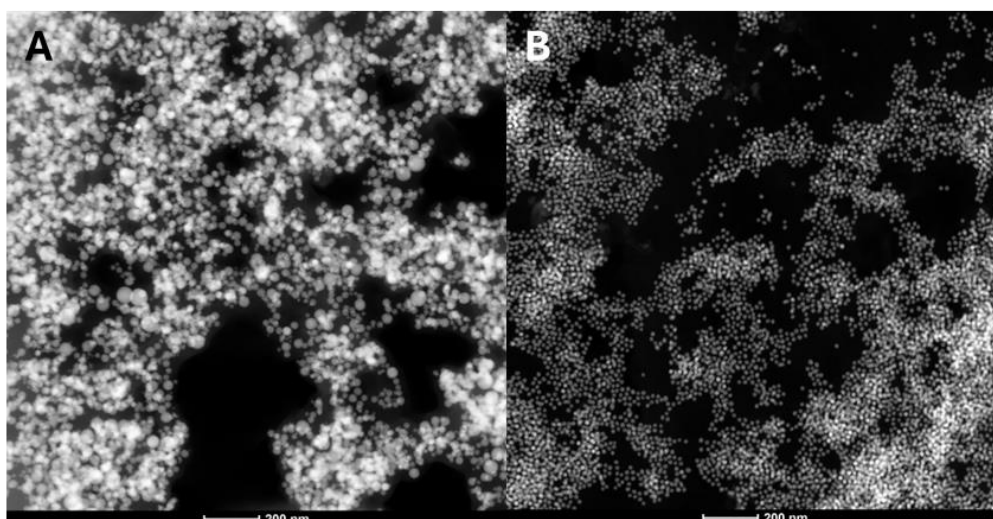


Figure 4-16: HAADF-STEM images of AuNPs after acid-induced ZIF degradation. **A)** Cys-AuNP. Note that these Cys-AuNPs were synthesized using LAL-AuNPs. **B)** PAH-AuNP.

dispersion following acid-induced ZIF-8 degradation, reflecting strong colloidal stability (**Figure 4-16B**). These observations are consistent with UV-Vis data indicating better stability for PAH-AuNPs compared to Cys-AuNPs.

LAL-AuNP@ZIF-8, AuNP@ZIF-8 via *in-situ* formation, and PAH-AuNP@ZIF-8 are most promising, because of their high suspension stability after acid-induced resuspension. After PAH-AuNP@ZIF-8 powder was stored in a sealed glass vial under N₂ atmosphere for 5 months, it showcased successful redispersion (**Figure 4-17**).

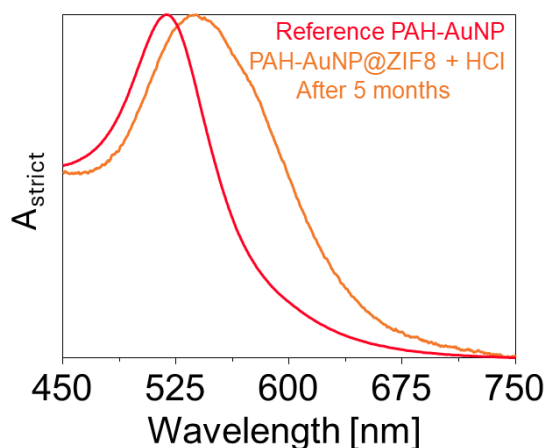


Figure 4-17: Strictly normalized UV-Vis spectra showing the long-term stability (~5 months) of PAH-AuNPs in ZIF-8.

4.5 Making nanoparticles spin-proof: Centrifugation efficiency of non-encapsulated vs. encapsulated AuNPs

To compare the purification efficiency of non-encapsulated (unembedded) AuNPs to that of encapsulated AuNPs, both systems were centrifuged using a microcentrifuge with a sample volume of 2 mL. This approach was necessary, as larger volumes of unembedded AuNPs suspensions result in low yields after a single purification cycle, due to the formation of a densely packed pellet (see section 4.1). It is important to note that all prior syntheses and experiments involving AuNP@ZIF-8 were conducted using larger volumes for centrifugation.

A photometric assay that accurately quantifies gold concentration in the supernatant was used to generate **Figure 4-18**. The results demonstrate that the ZIF-8 encapsulation approach outperforms the conventional method using unembedded AuNPs. Notably, the embedded AuNPs were centrifuged at only 3000 × g, compared to 6000 × g for the unembedded AuNPs. Despite the lower centrifugal force, the

encapsulated samples allowed increased NP retention. In some cases, the supernatant remained slightly turbid (**Figure 7-15**), indicating incomplete settling. Therefore, further increasing the centrifugal force would likely enhance the purification performance of encapsulated NPs.

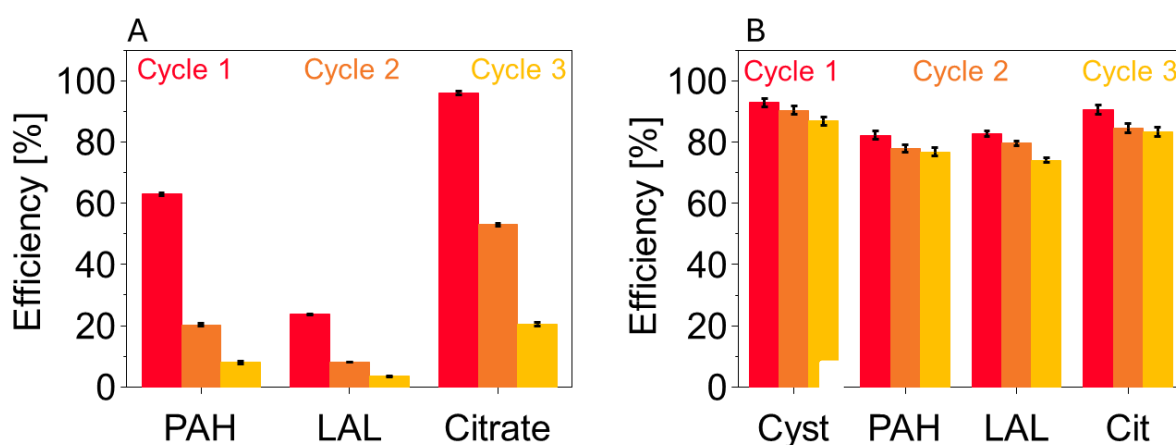


Figure 4-18: Comparison of purification efficiency between unembedded AuNPs and encapsulated AuNPs. **A)** Purification efficiency of unembedded AuNPs, performed at $6000 \times g$ for 15 minutes. **B)** AuNP@ZIF-8 exhibit significantly higher purification efficiency, even when centrifuged at a lower force of $3000 \times g$ for 15 minutes.

The lower efficiency observed for unembedded PAH-coated and LAL-AuNPs, relative to Cit-AuNPs, can be attributed to the fact that the centrifugation conditions ($6000 \times g$ for 15 minutes) were optimized for the latter. PAH-AuNPs, due to their additional polymer coating, and LAL-AuNPs are larger than Turkevich-synthesized AuNPs. This extra mass results in an increased settling force and the formation of denser pellets, which are more difficult to redisperse completely.

However, the redispersion behavior of the AuNPs following acid-induced ZIF-8 degradation is critical for their practical use. Given their previously demonstrated stability, PAH-AuNPs were selected for further analysis, while results for other systems are included in the supplementary information (**Figure 7-17**). For PAH-AuNP@ZIF-8, the redispersion results are consistent with earlier findings. A stable suspension with a well-defined gold plasmon peak is observed after acid degradation of the ZIF, confirming good colloidal stability (**Figure 4-19A**). Comparing these results to the UV-Vis spectra of unembedded AuNPs after purification, we can see that there is minimal to almost no clustering in those cases (**Figure 4-19B**).

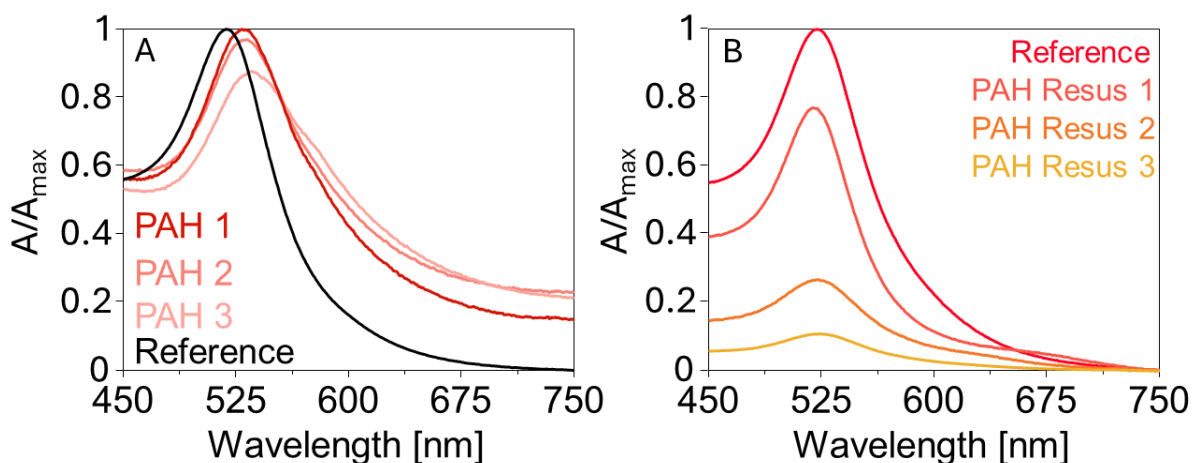


Figure 4-19: Normalized UV-Vis spectra of redispersed PAH-AuNPs for three purification cycles. **A)** PAH-AuNP@ZIF-8, **B)** PAH-AuNPs.

Lastly, the redispersion of *in-situ* AuNP@ZIF-8 will be discussed. After centrifugation of the freshly formed AuNP@ZIF-8 material, an unintended floating pellet was observed (**Figure 4-20A**). The NPs failed to settle and instead formed a low-density layer at the surface in which the NPs are likely stabilized by free HmIM. Because of the high HmIM:Zn ratio of 256, highly crystalline ZIF-8 formed, which is prone to degradation even in mildly acidic media such as DI water. This degradation likely resulted in the observed ill-defined phase. To resolve this, washing was repeated with slightly alkaline water (pH 8.0, adjusted with 0.1 M NaOH), but this only worsened the separation: no settling formed, and the red-colored supernatant persisted

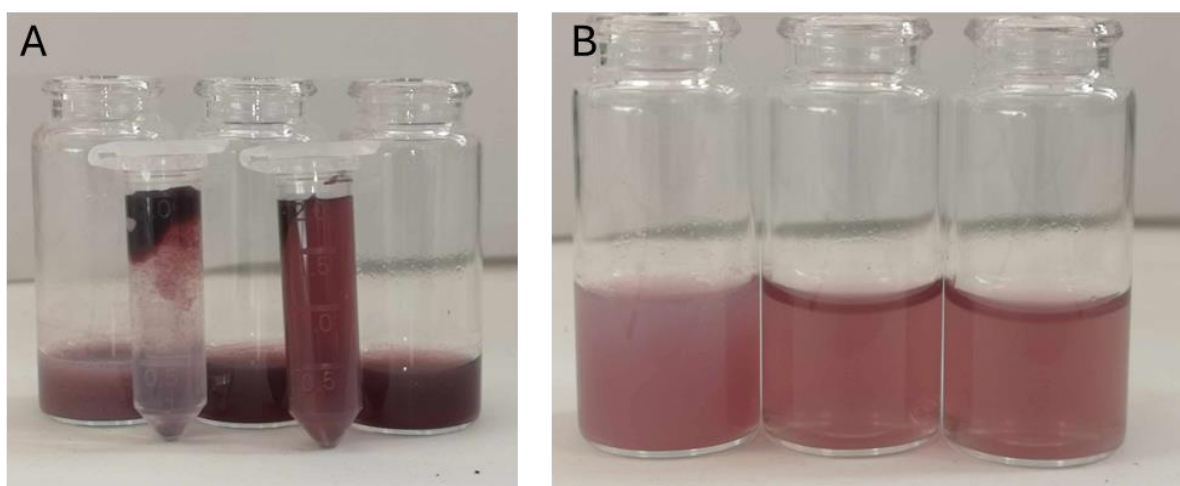


Figure 4-20: Visual comparison of AuNP@ZIF-8 suspensions prepared via the *in-situ* synthesis method under different washing conditions. **A)** Original suspension (left vial), after one wash with DI water (middle vial), and after one wash with slightly alkaline DI water (right vial). The left centrifuge tube shows a floating pellet following DI water washing, while the right tube shows no settling after alkaline washing. **B)** Diluted versions of the same three suspensions displayed in panel A.

(**Figure 4-20A and B**). A small clump of degraded material remained floating. Since this behavior hindered recovery no further efficiency testing was performed on this sample. However, because of the nature of this synthesis method, the final AuNP@ZIF-8 powder is already highly pure and suitable for direct use, eliminating the need for additional post-synthesis purification steps. Nevertheless, gold quantification after reduction showed an overall gold retention of 96% for the *in-situ* synthesized AuNP@ZIF-8 material. While this efficiency is only as much as for purifying 2 mL of a Cit-AuNP suspension once (**Figure 4-1B**), AuNP@ZIF-8 via the *in-situ* protocol has advantages such as easy AuNP handling and long-term storage.

4.6 Conclusion and outlook

This chapter focused on using ZIF-8 to encapsulate, purify, and redisperse AuNPs for improving nanoparticle handling. While the embedment of AuNPs in ZIF-8 is not new in itself, applying this strategy to enable efficient purification and conversion of colloidal suspensions into solid, re-dispersible powders is a novel approach.

Several types of AuNPs were tested, each with different surface chemistries, including citrate, PAH, PVP, cysteine, LAL, and *in-situ* synthesized NPs. Their behavior during ZIF-8 formation, purification, and acid-induced degradation was compared, revealing that surface functionality strongly influences both encapsulation efficiency and final colloidal stability (**Table 4-2**). Among these, PAH-coated, LAL-, and *in-situ* synthesized AuNPs showed the highest stability over all working conditions. Crystallographic analysis showed that the resulting ZIF phase depends heavily on parameters such as the HmIM:Zn ratio, and temperature. These variations affect the porosity and chemical robustness of the material, which in turn impacts redispersion and acid stability.

Encapsulated systems consistently outperformed unembedded AuNPs in terms of purification efficiency. Unlike unembedded nanoparticles, they required no tedious fine-tuning of centrifugation parameters and could be washed with lower RPM's while still retaining high gold content. The resulting materials were easy to handle, could be dried into stable powders, and allowed washing of larger volumes in a single step. Together with scalability and long-term stability of the dry powders, these advantages highlight the success of this encapsulation approach.

Table 4-2: Overview of stability of different AuNP@ZIF-8 types towards ZIF-8 precursors and after acid degradation of ZIF-8.

	Citrate	PAH	PVP	LAL	Cys	<i>In-situ</i>
Zinc nitrate						NA
Linker						NA
Acetic acid						NA
HCl						

Green = stable, yellow = cluster formation, red = aggregation.

Though quite successful, this work opens the door to several follow-up opportunities. To prevent clustering upon redispersion, future approaches could combine acid-induced degradation with immediate photodeposition of AuNPs onto catalytic substrates, such as TiO₂, thereby minimizing aggregation. Increasing gold loading within ZIF-8 may also be achieved by using more concentrated AuNP suspensions during encapsulation. This would reduce the amount of ZIF-8 required for AuNP dosing during catalyst preparation. Another outlook could be the adaptation of this method for larger-scale processing. Although mainly small volumes of AuNP suspensions are used, the ability to handle larger batch sizes consistently would be crucial for broader commercial use in high-value applications such as diagnostics and sensing. More importantly, encapsulation offers potential safety advantages. By stabilizing NPs within ZIF-8, the risks associated with handling and transporting nanoparticle powders, including dusting and inhalation hazards, can be significantly reduced. This makes the strategy attractive not only for AuNPs but also for other materials where safe handling and reproducibility are critical.

With continued refinement, this encapsulation approach could evolve into a versatile platform for improving nanoparticle processing, storage, and safety.

5 Results and Discussion: Flashy dyes

This chapter focuses on a whole different application: fluorescence-based acid vapor sensing. While the end-use differs from previous chapter, the underlying concept remains similar. ZIF-8 is used to encapsulate functional guest molecules and releases them upon exposure to acids. In this case, AuNPs are replaced by fluorescent dyes, enabling a fluorescence signal upon ZIF-8 degradation, as developed within the *Acid Alert* project by Smets *et al.* (2024)³⁹. This approach has promising applications within the field of smart food packaging. Dye encapsulated in ZIF-8 (Dye@ZIF-8) responds to acid vapors released during spoilage by an increase in fluorescence (**Figure 5-1**). This change can be detected using simple, low-cost readout electronics, offering a practical solution to partially replace expiration dates.

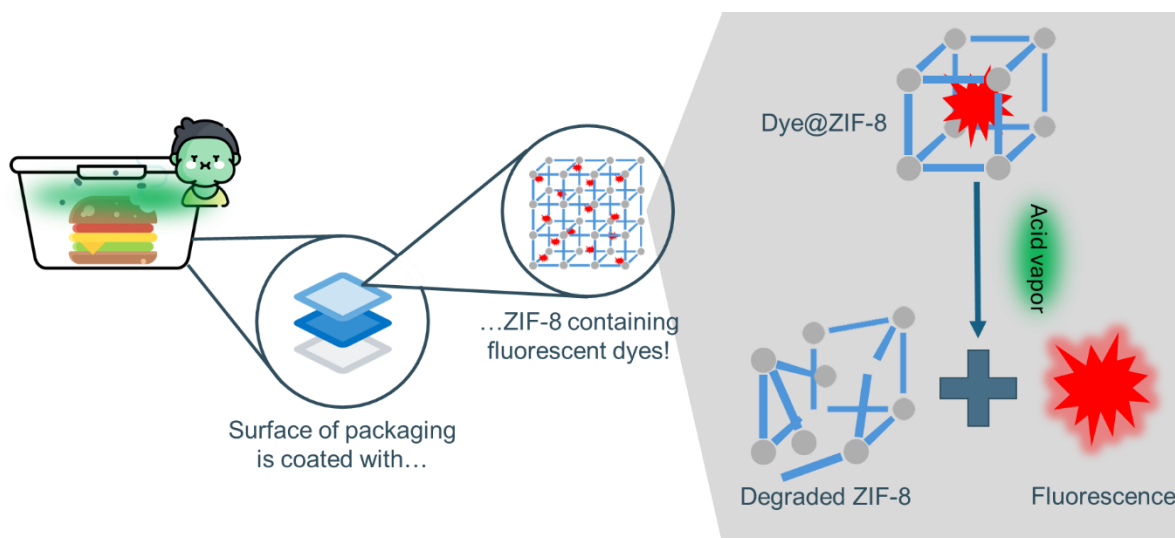


Figure 5-1: Integration of Dye@ZIF-8 compounds in food packaging allows for food quality monitoring.

5.1 Rethinking the dye: Rhodamine 6G instead of rhodamine B... or not?

To study the intrinsic dye behavior, dye solutions (0.5 mM) were prepared with 1 vol% acetic acid in water and analyzed separately (**Figure 5-2**). For both F and C343, protonation by acetic acid results in fluorescence quenching (Smets *et al.* (2024))³⁹. In contrast, RhB shows no quenching under the same conditions, attributed its lower pKa of RhB (pKa ~3.22¹⁹⁵) relative to acetic acid (pKa ~4.79¹⁹⁶). Based on these pKa values, it was hypothesized that stronger acids could protonate the carboxyl group of RhB and change the dyes fluorescence properties. Therefore, RhB was replaced by Rh6G which seems, based on the lack of strong acid groups (**Figure 7-18**), less

sensitive towards strong acids. Since the pKa of RhB is around 6.13, the dye already mostly exists in its cationic form and pH decrease does not alter the structure any further^{176,197}.

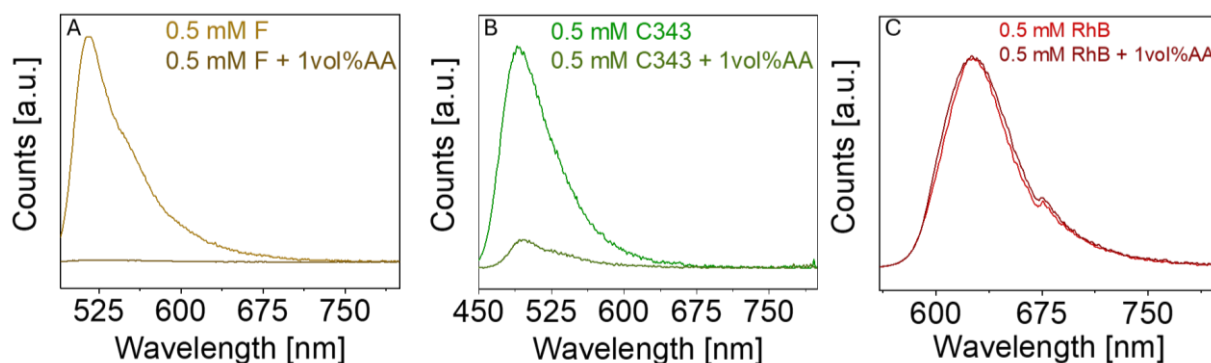


Figure 5-2: Effect of mild acid conditions on the fluorescence of dye solutions. A) Fluorescein, B) Coumarin 343, and C) Rhodamine B solutions (0.5 mM) were mixed with 1 vol% acetic acid.

To evaluate whether Rh6G would offer improved performance over RhB, mRh6G@ZIF-8 was synthesized, and identical acid vapor exposure experiments were conducted. As anticipated based on Rh6G's structure, no fluorescence quenching was observed under acid conditions, even with the stronger formic acid (FA) (pKa ~3.75)¹⁹⁸ (**Figure 5-3**). In this work, the behavior of nano-sized ZIF-8 crystals (nDye@ZIF-8) is also studied in which 'n' refers to the nano-scale size of the ZIF-8 crystals. 'm' refers to larger ZIF-8 crystals.

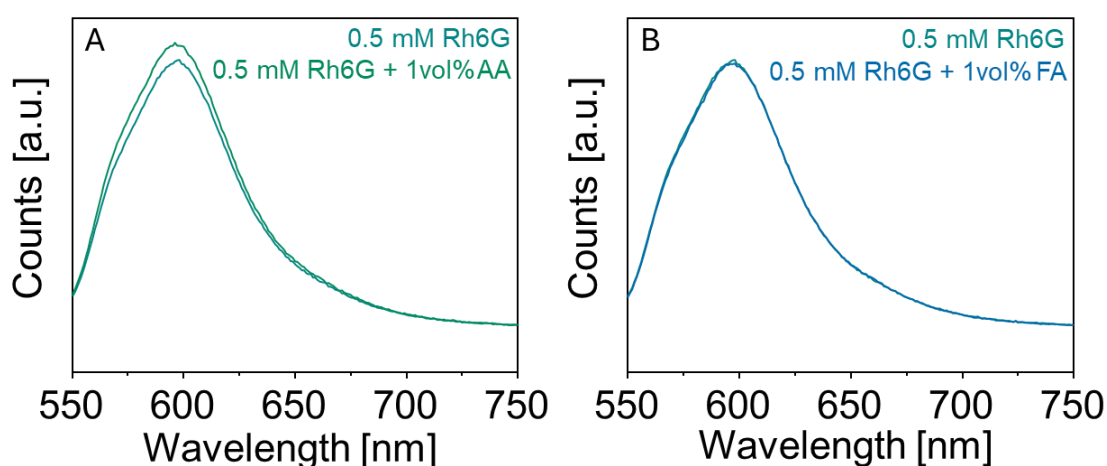


Figure 5-3: Evaluation of Rh6G fluorescence in strong acid solutions. Fluorescence spectra of Rh6G solutions (0.5 mM) before and after the addition of 1 vol% acetic acid (A) or formic acid (B), showing no quenching.

Although mRh6G@ZIF-8 exhibits acid sensitivity, its fluorescence response deviates from the behavior observed in other mDye@ZIF-8 materials (**Figure 5-4A**). In systems like mRhB@ZIF-8, mC343@ZIF-8, and mF@ZIF-8, the response curves

show a sigmoidal shape, indicated by a sharp fluorescence increase between 10 and 41 ppmv, likely corresponding to the release of most of the quenched dye. Further acidification has little effect on signal intensity. While mRh6G@ZIF-8 still exhibits this sigmoidal response, the amplitude is substantially lower. The overall intensity increase is also reduced. HPLC analysis revealed that mRh6G@ZIF-8 contained only 0.07 wt% dye, compared to 11 wt% and 22 wt% for mRhB@ZIF-8 and mC343@ZIF-8, respectively. Despite this low loading, fluorescence enhancement could still be detected, though due to the limited dye incorporation likely contributed to reduced sensitivity and greater signal variability. With less dye present, aggregation-induced quenching is minimal, leaving little quenching to be alleviated.

Due to these inconsistencies for Rh6G, focus shifted to RhB again. Therefore, the effect of stronger acid environments on the fluorescence behavior of RhB was further investigated. As shown in **Figure 5-4B**, RhB exhibits altered fluorescence properties upon exposure to more acid media (*i.e.*, 1 vol% FA, pKa ~3.75), with a noticeable enhancement in fluorescence intensity rather than quenching. Although fluorescence enhancement is not solely determined by ZIF-8 collapse anymore, this deviation can be circumvented by proper calibration.

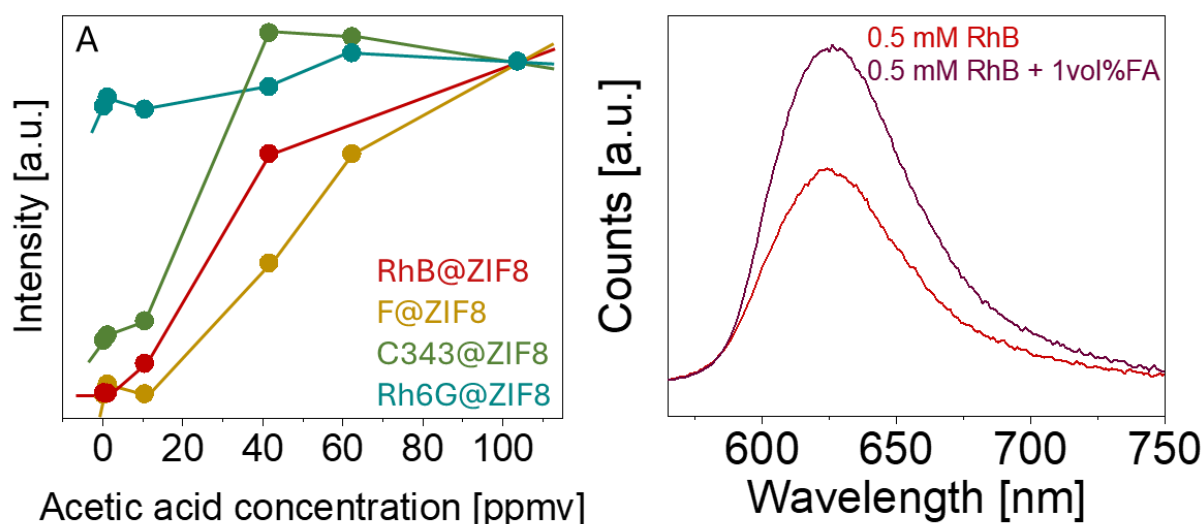


Figure 5-4: Fluorescence of dyes in and outside ZIF-8 under acid conditions. A) Acid response curves of mDye@ZIF-8 after overnight exposure. The lines only serve to guide the eye and have no mathematical or physical significance. B) Fluorescence response of 0.5 mM RhB in 1 vol% formic acid.

5.2 Thin, even, effective: Airbrushing films for acid vapor sensing

The next step toward translating this concept into a device involves replacing advanced fluorescence spectroscopy with a simpler, low-cost setup. By using LEDs as excitation sources and a camera for detection, measurements are straightforward and cost-effective. Ultimately, this approach could be integrated into a compact handheld device, offering a novel and accessible method for detecting trace amounts of acid vapor (Figure 5-5).

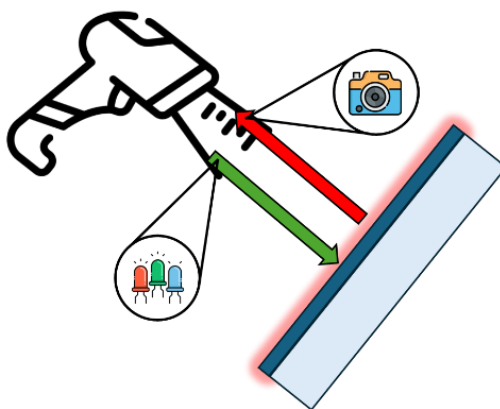


Figure 5-5: Schematic of a handheld device for low-tech acid vapor sensing. LEDs excite the fluorescent dyes and the camera measures the intensity.

While the handheld device is under development, a simplified setup incorporating similar components was used to evaluate the feasibility of this sensing concept. To support future device integration, the fluorescent ZIF-8 powders were converted into films (15 - 50 μm) employing an airbrushing method. This transition improves handling and enables integration onto a wide range of surfaces. An airbrush was used to apply coatings onto the non-polished side of silicon wafers, as smooth surfaces resulted in macroscopically non-uniform deposition.

Figure 5-6A and B show that transitioning to thin films improves sensor sensitivity, as intensity shifts are observable not only between 10 and 41 ppmv, but also at lower concentrations in the 0 - 10 ppmv range. This shift to lower ranges is consistent with the degradation range of 80 nm-sized ZIF-8 films around 2.5 ppmv AA as discussed in section 2.4.3. Large ZIF-8 powder beds likely exhibit slower responsiveness, as acid vapor must penetrate deeper into facilitate full degradation. This results in delayed dye release and a weaker fluorescence signal within a fixed exposure period. In contrast, thin ZIF-8 films provide shorter diffusion paths, likely

enabling faster ZIF-8 degradation and more immediate dye release. These observations are similar for nano and macro-sized ZIF-8 particles. To further study what happens in the lower ppmv-range, additional experiments were conducted.

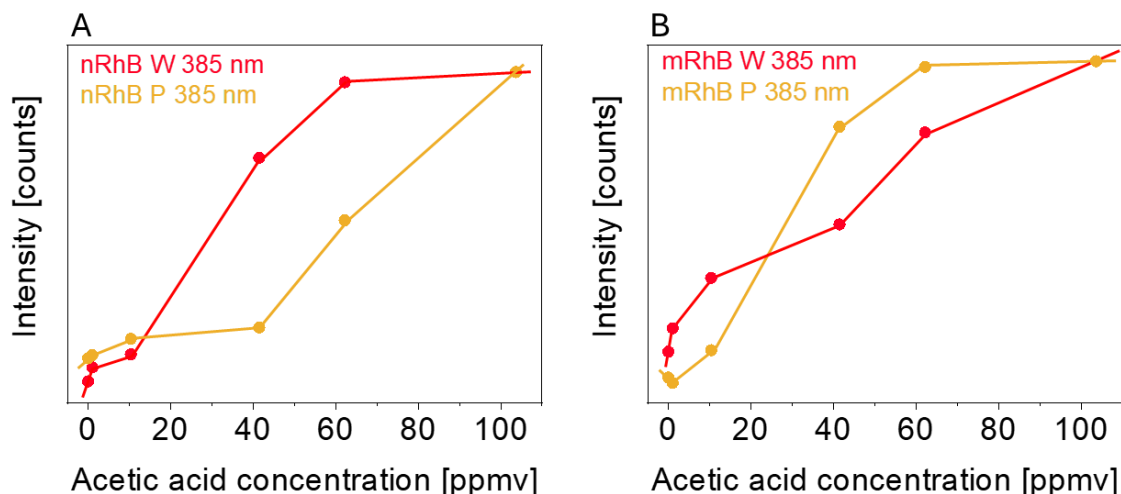


Figure 5-6: Fluorescence response of RhB@ZIF-8 powders measured using a simplified optical setup. **A)** nRhB@ZIF-8 as powder (P) or wafer (W) under 385 nm excitation. **B)** mRhB@ZIF-8 as powder (P) or wafer (W) under 385 nm excitation. The lines only serve to guide the eye.

When comparing macroparticles to nanoparticles in powder form (mRhB P 385 nm and nRhB P 385 nm, **Figure 5-7A**), the overall relative fluorescence increase with rising acetic acid concentration was smaller for the nanoparticles, which can be attributed to its lower dye loading, approximately 5.6 wt%, compared to 11 wt% for mRhB@ZIF-8. In panel **A**, mRhB W 385 nm outperforms all other samples in terms of sensitivity. Also in panel **B**, nRhB W 450 nm shows the largest increase. This suggests that acid vapor diffusion was more efficient in the wafer coatings, possibly due to thinner diffusion layers or improved accessibility of the particles when immobilized on the wafer. However, it remains unclear why the onset of degradation does not strictly align with the 2.5 ppmv threshold observed previously by ellipsometry for 80 nm-sized films. Differences in sample geometry, particle packing, and local microenvironments may contribute to this discrepancy. Finally, across most samples and morphologies, 450 nm excitation consistently produced stronger relative fluorescence increases than 385 nm. Although 450 nm excitation is close to RhB's optimal excitation wavelength, 385 nm excitation was still sufficient to observe degradation trends, albeit with weaker fluorescence signals and less pronounced increases.

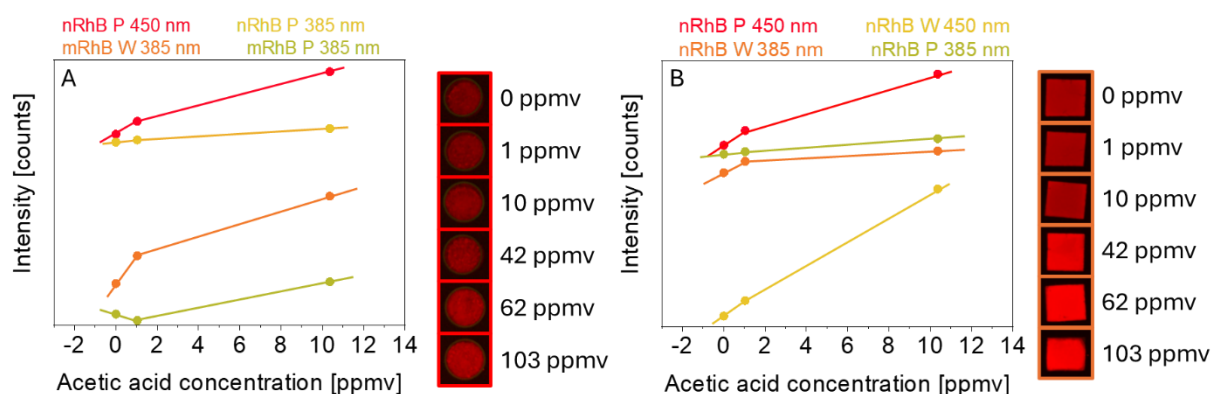


Figure 5-7: Fluorescence response of Dye@ZIF-8 powders and wafers after overnight AA vapor exposure.

A) Comparison between different powders (P). Images as taken by the camera are included for nRhB@ZIF-8 excited at 450 nm. The vials have a diameter of 20 mm. **B)** Comparison between wafers (W) and powders. Images as taken by the camera are included for nRhB@ZIF-8 wafers excited at 385 nm. The wafers have a dimension of 2 x 2 cm². The lines only serve as visual aid and have no mathematical or physical significance.

ImageJ intensity analysis was used to quantify pixel brightness to assess sample homogeneity. A low standard deviation indicates uniform intensity, while a high standard deviation reflects greater variability. Intensity analysis of the powders showed a standard deviation between 2 and 7 counts, while this was only between 0.5 and 1.5 counts for films, indicating that the films are more homogeneous than the powder beds. The effect of number of coatings on the homogeneity of mRhB@ZIF-8 and nRhB@ZIF-8 wafers was further studied with optical microscopy (**Figure 5-8**). For both samples, trends in particle analysis are similar. The number of isolated particles (**A**) decreases as a consequence of an increasing average particle size (**B**) for a higher number of coatings (CX, with X from 1 to 4). These results indicate increased homogeneity for more coatings and directly support the processed images in **Figure 5-8C** and **D**. Note that these particles represent large aggregates and are influenced by the processing software's interpretation, which depends on the brightness settings. The nano-sized material shows better homogeneity on this macroscopic scale. However, optical profilometry indicates formation of large aggregates in nRhB@ZIF-8 at the microscopic scale (**Figure 7-19**) when multiple coatings are applied which is not observed for mRhB@ZIF-8 (**Figure 7-20**). Differences in film uniformity between ZIF-8 nanoparticle and macroparticle coatings likely result from scale-dependent packing, drying dynamics, and the quality of the suspension. Nanoparticles form a relatively stable suspension, allowing effective airbrushing, whereas larger particles tend to settle quickly and often lead to nozzle blockage. As pointed out by Man *et al.* (2008) NP coatings often exhibit nanoscale flaking due to capillary forces and shrinkage stresses

during solvent evaporation, leading to microcracks or delamination¹⁹⁹. Poor mechanical interlocking further contributes to brittle microstructures^{199–201}. However, their good dispersibility promote macroscale homogeneity²⁰². In contrast, macroparticle coatings display nanoscale uniformity, but suffer from uneven particle stratification and sedimentation during drying, resulting in macroscale irregularities^{203,204}.

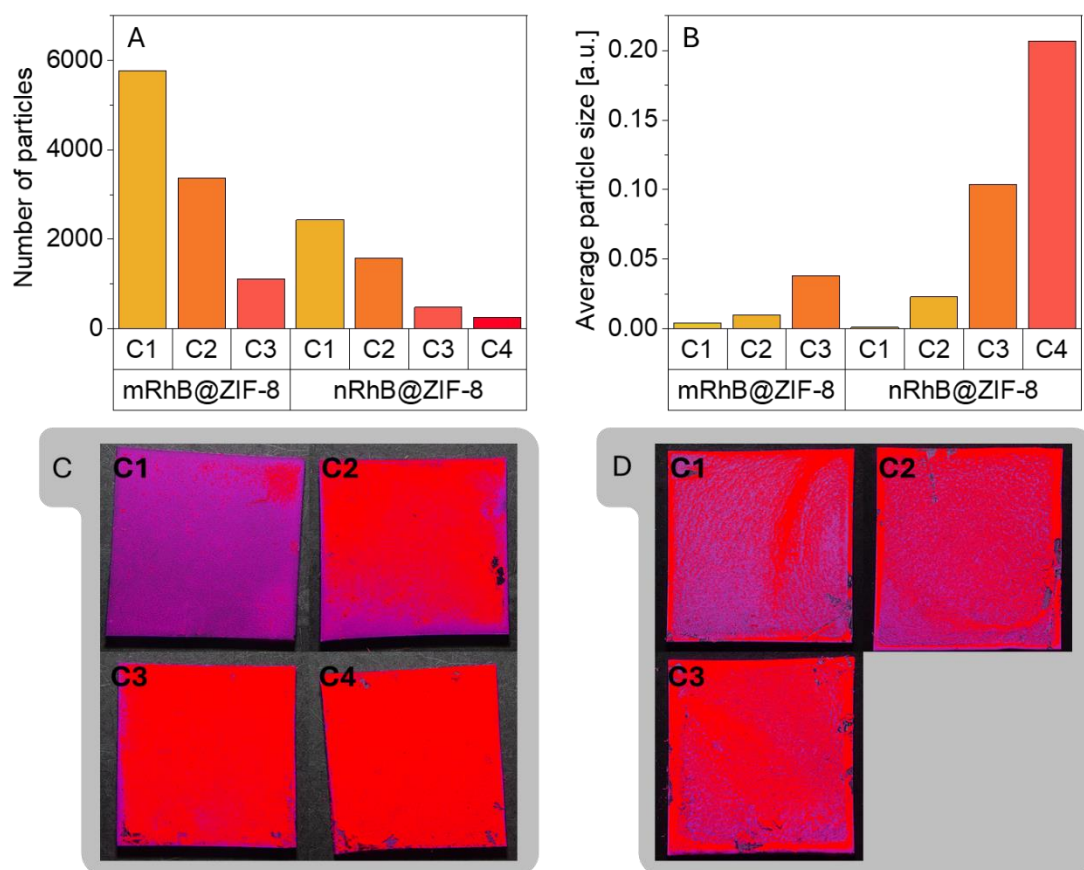


Figure 5-8: Particle analysis demonstrates increased coating homogeneity for more coatings. A) Number of particles, B) average particle size, C) processed images of nRhB@ZIF-8, D) processed images of mRhB@ZIF-8. The wafers have a dimension of 2 x 2 cm².

5.3 Conclusion and outlook

This chapter demonstrated the feasibility of using ZIF-8's acid sensitivity for vapor sensing by encapsulating fluorescent dyes. RhB was confirmed as the most promising candidate due to its stable fluorescence response under acid conditions and compatibility with the MOF matrix. Although Rh6G was investigated as an alternative, its low encapsulation efficiency, likely led to reduced aggregation-induced quenching. Consequently, a smaller increase in fluorescence upon release. Sensing proved highly

sensitive, with detectable differences at single-digit ppmv levels of acid vapor. This sensitivity arises from the degradation-based approach, where acid-triggered decomposition of ZIF-8 leads to a distinct and irreversible fluorescence increase. In contrast to adsorption-based systems, which depend on reversible and often subtle changes in material properties, this mechanism provides a more robust and easily interpretable signal, particularly advantageous at low analyte concentrations.

Looking forward, fluorescence-based acid vapor sensors hold great promise as portable, user-friendly devices. By transitioning from spectroscopic analysis to LED-camera-based readouts and developing thin films via airbrushing, this chapter laid the foundation for low-tech, scalable sensor designs suitable for a wide range of environments. Such sensors could empower non-specialists to perform on-site monitoring. In the food industry, they offer potential for detecting acid vapors during production and storage, where early spoilage detection is crucial. While individual packaging applications may be impractical and costly, monitoring larger storage areas or processing tanks present a viable and impactful solution. In industrial settings, these sensors could provide early warnings of acid leaks in chemical plants. Their sensitivity and fast fluorescence response make them well-suited for integration into personal protective equipment, offering real-time feedback to workers in corrosive environments. Although current detection is qualitative, future calibration efforts could enable quantitative analysis of acid vapor concentrations in the ppmv range, greatly expanding their utility for safety monitoring and regulatory compliance.

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7 Supplementary

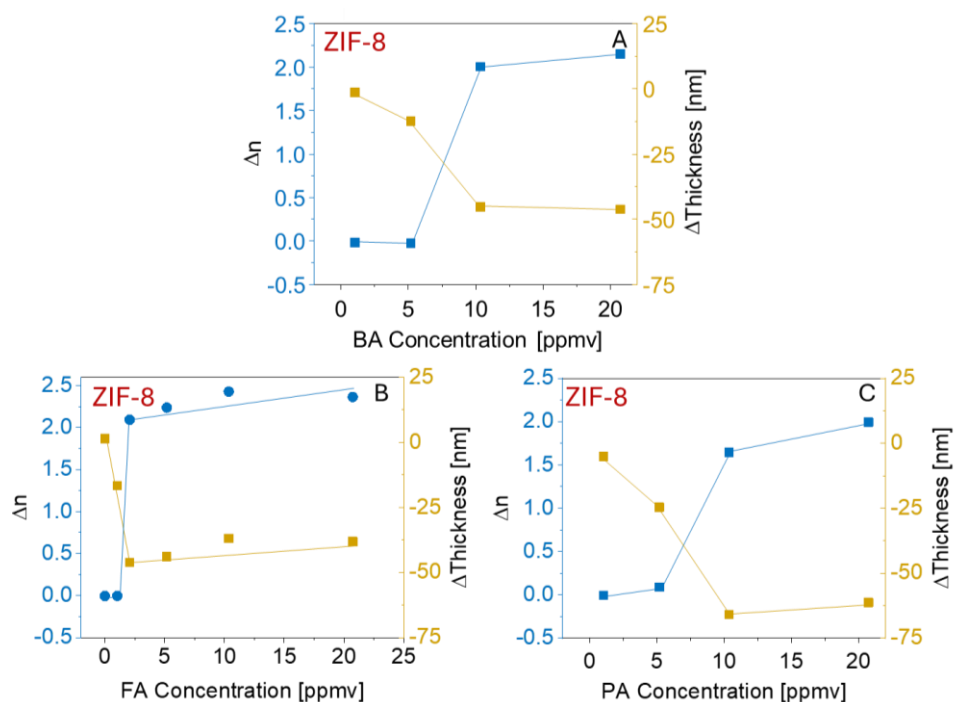


Figure 7-1: Acid vapor-induced degradation of ZIF-8 films. A) Butyric acid, B) formic acid, C) propionic acid.



Figure 7-2: Pictures of plastic Pasteur pipets and a stirring bar, covered with gold nanoparticles after transfer and mixing of gold colloid during purification.

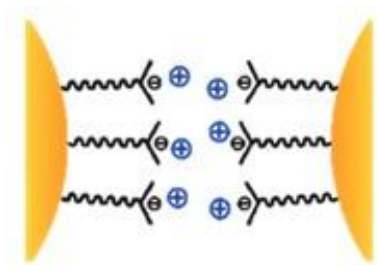


Figure 7-3: Schematic of bridging interaction between gold nanoparticles. The blue dots could be zinc ions, and the black ligands could be citrate for example. From Dawei *et al.* (2011)¹³².

Figure 7-4: To determine the minimum concentration of capping agent required to stabilize AuNP suspensions, varying amounts of PVP and PAH were added to 10 mL of colloidal Cit-AuNPs. For PAH (panels **A** and **B**), concentrations from 0.05 to 60 mg were tested. At low concentrations, flat UV-Vis spectra indicate that all PAH-AuNPs are settling due to aggregation. We hypothesize this happens because smaller amounts of PAH generate less electrostatic repulsion, ultimately leading to neutral NPs. Between 0.5 and 1 mg, peak broadening and a redshift in the LSPR band suggested partial clustering. A minimum of 5 mg PAH was required to fully stabilize 10 mL AuNP suspension.

In contrast, PVP stabilizes the colloid via steric hindrance. Therefore, colloidal stability across a broader range is maintained. Even at 0.01 mg, no aggregation was observed. However, when zinc ions were introduced to simulate ZIF-8 growth conditions, only samples containing 0.5 mg or more remained stable. Thus, 0.5 mg PVP per 10 mL Cit-AuNPs was identified as the minimum concentration required to preserve colloidal stability under these conditions.

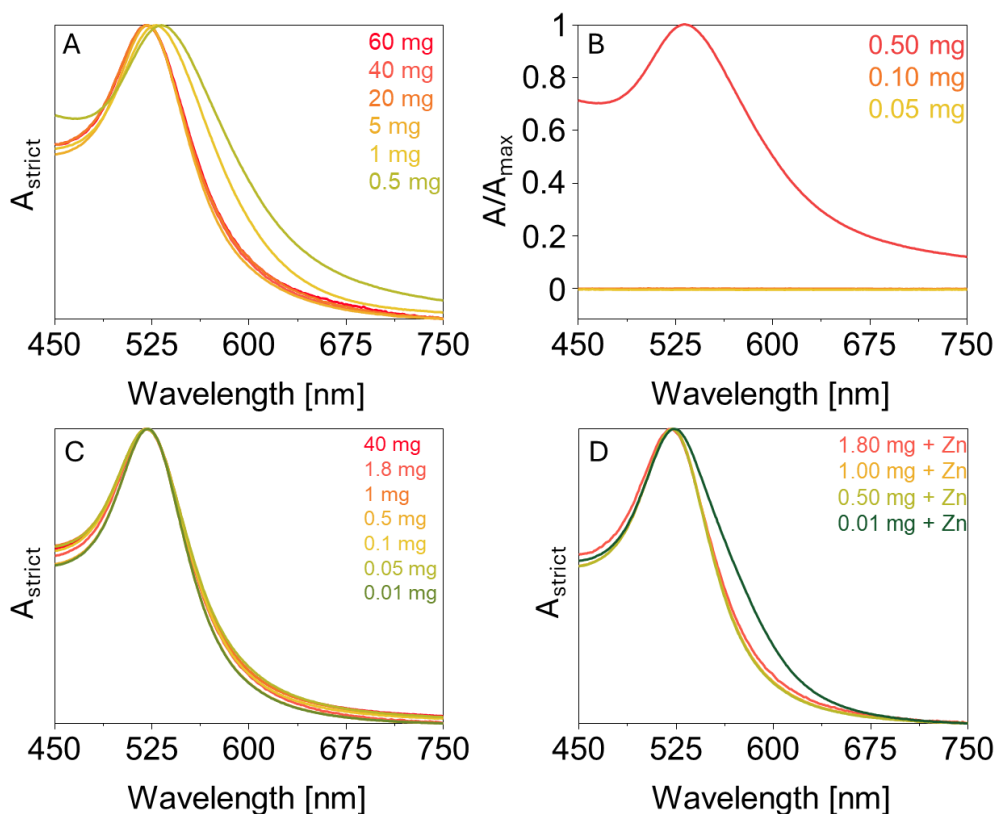


Figure 7-4: UV-Vis spectra of Cit-AuNPs with varying amounts of PAH (A, D) and PVP (B, C). All strictly normalized except figure B.

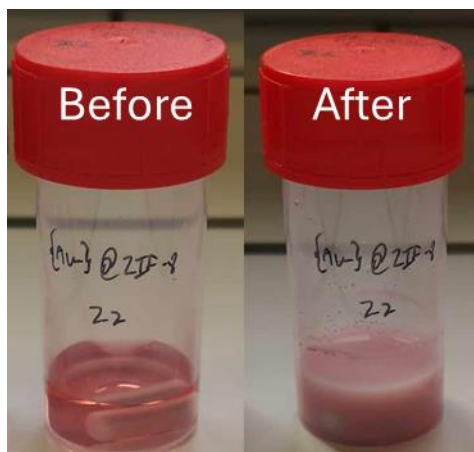


Figure 7-5: Picture of PVP-AuNPs before and after encapsulation by ZIF-8.

Figure 7-6: FTIR spectra of the encapsulated and coated AuNPs in ZIF-8 show great similarity with normal ZIF-8. Characteristic ZIF-8 vibrations are observed between 700 and 1700 cm^{-1} , including C–H out-of-plane bending ($\sim 750 \text{ cm}^{-1}$), Zn–N stretching ($\sim 980\text{--}1000 \text{ cm}^{-1}$), imidazole ring skeletal vibrations ($\sim 1150\text{--}1190 \text{ cm}^{-1}$), C–N stretching ($\sim 1310 \text{ cm}^{-1}$), and C=N and C–N ring stretching ($\sim 1400\text{--}1500 \text{ cm}^{-1}$). Extra peaks in the spectra likely result from the coating agents.

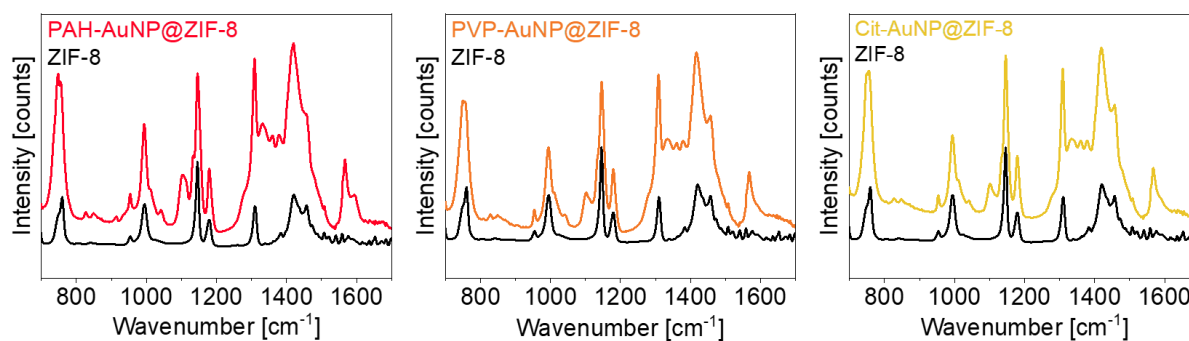


Figure 7-6: FTIR of different types of capped-AuNPs in ZIF-8.

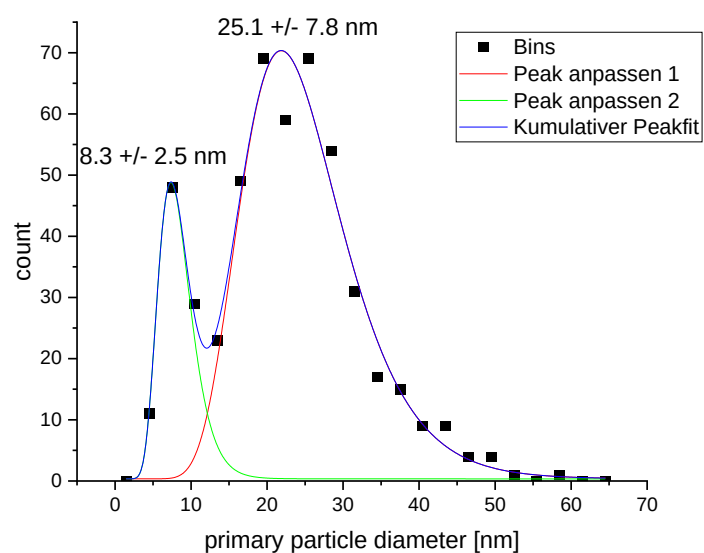


Figure 7-7: Specifications of LAL-AuNPs. Provided by the group of Dr. Sven Reichenberger (Duisburg-Essen)

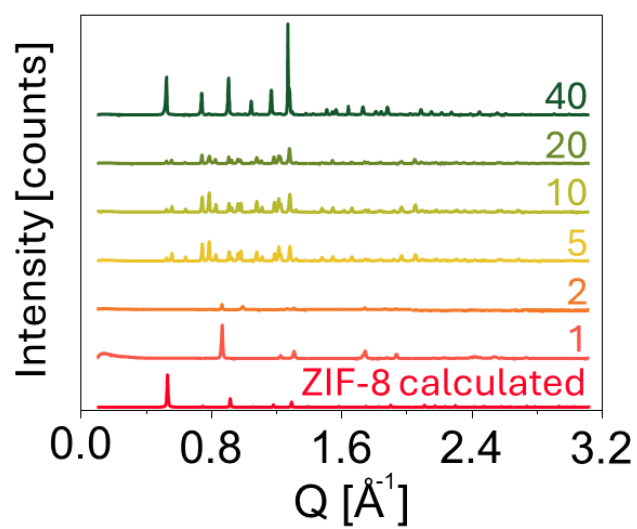


Figure 7-8: PXRD of ZIF-8 without AuNPs for varying HmIM:Zn ratios

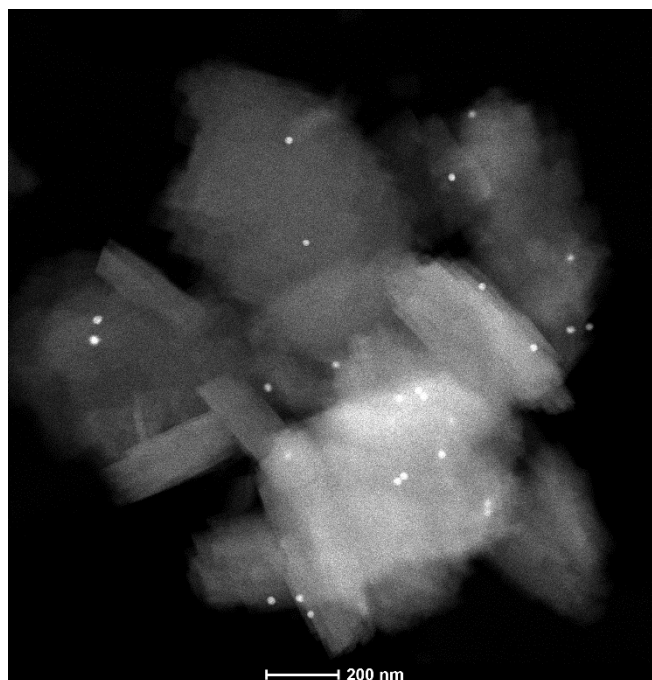


Figure 7-9: LAL-AuNP@ZIF-8 (HmIM:Zn ratio = 256). HAADF-STEM suggests encapsulation of AuNPs (bright spots) in ZIF-8 (grey areas) since NPs are not completely on the edge of the ZIF-8 crystals.

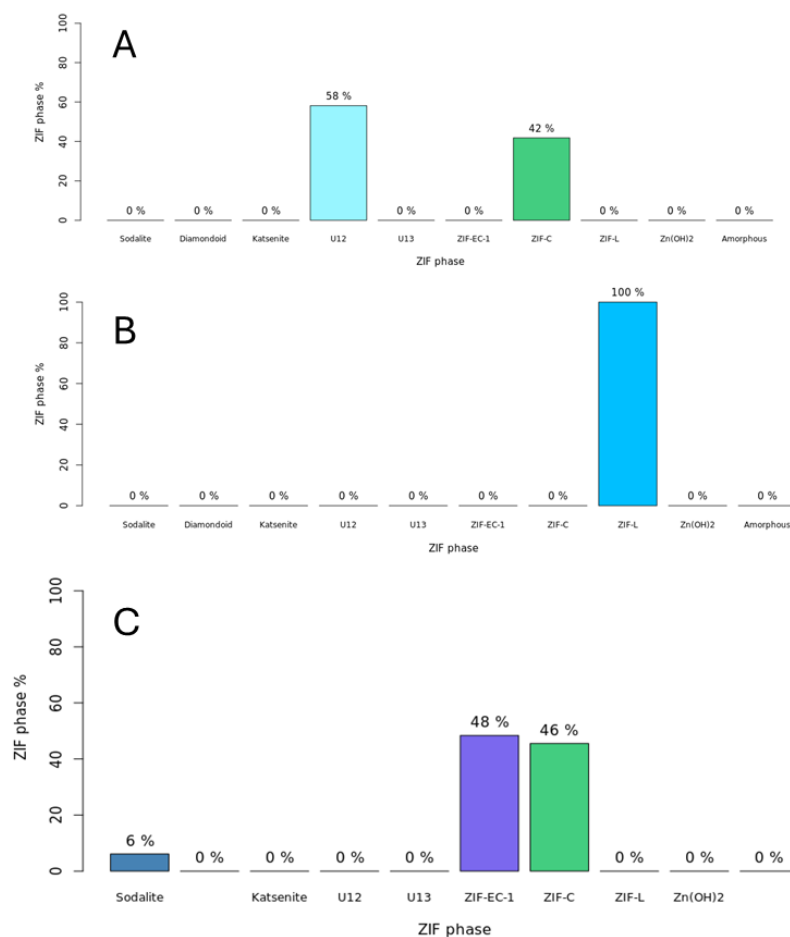


Figure 7-10: Phase analysis of Cys-AuNP@ZIF-8 PXRD. Determined using an app developed by Hafner *et al.* (2022)¹⁸⁹. All synthesized with a 2:1 HmIM:Zn ratio.

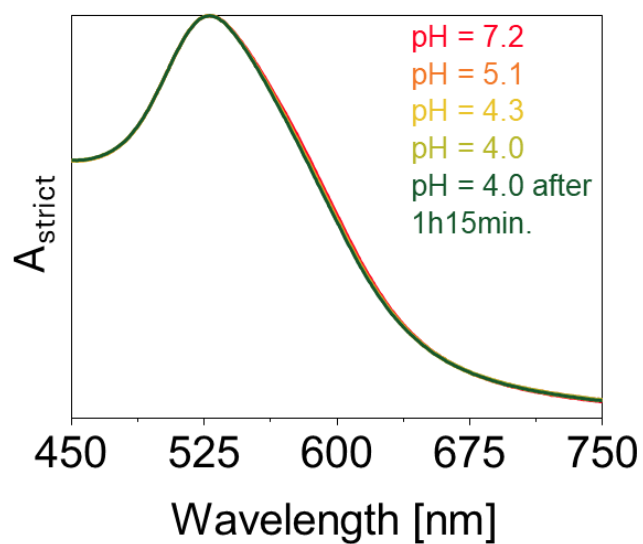


Figure 7-11: Exceptional stability of PAH-AuNPs towards acetic acid. Strictly normalized spectra.

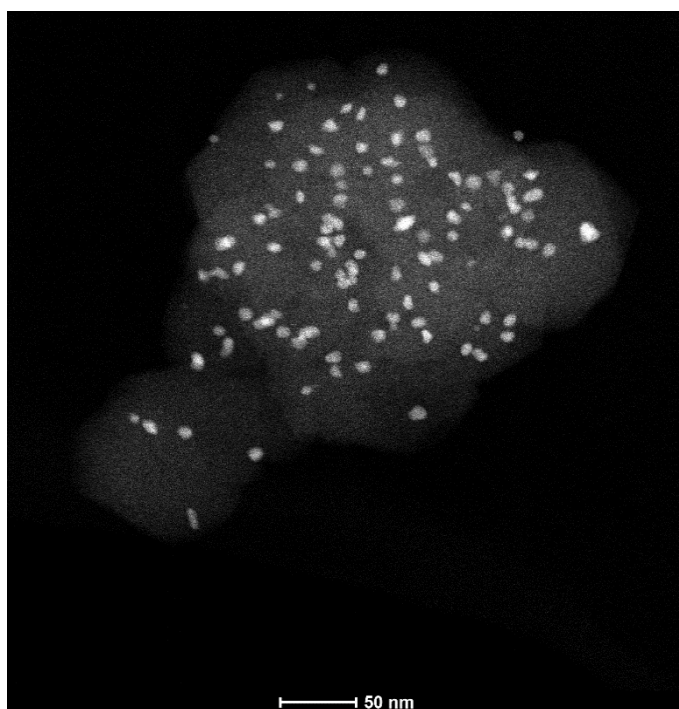


Figure 7-12: HAADF-STEM of AuNP@ZIF-8 formed using *in-situ* synthesis.



Figure 7-13: Cys-AuNP@ZIF-8 resuspended with 1 M HCl. Large visible clumps are formed, minimizing the amount of dispersed Cys-AuNPs in suspension.

Figure 7-14: Cysteine influences PAH-AuNP clustering after acid-induced ZIF-8 degradation. Various amounts of 40 mM L-cysteine were added to PAH-AuNPs and stirred overnight before encapsulation and washing. Although the interaction between cysteine and PAH is likely weak, residual cysteine remains present after washing. Upon framework degradation and redispersion, samples with higher cysteine content (A) exhibit increased clustering, whereas unmodified PAH-AuNPs (C) show no visible aggregation.

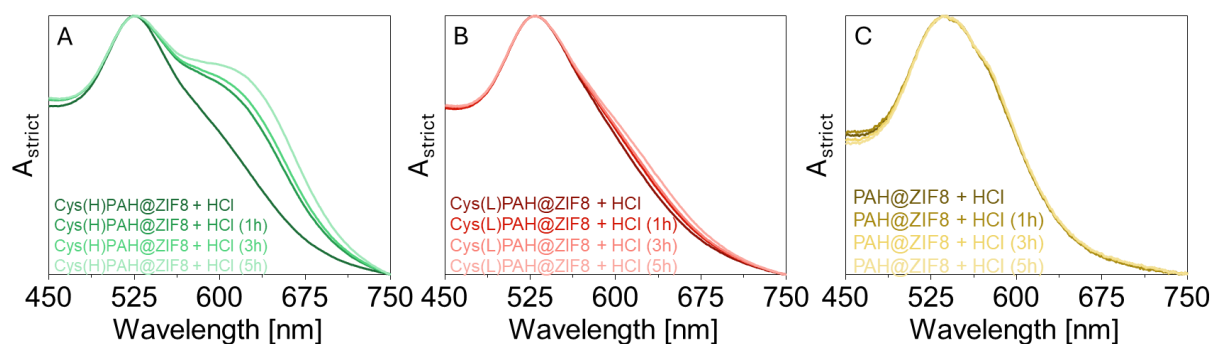


Figure 7-14: Effect of cysteine on clustering during acid-induced resuspension. A) 500 μ L 40 mM cysteine in 10 mL PAH-AuNPs, B) 100 μ L 40 mM cysteine in 10 mL PAH-AuNPs, C) PAH-AuNPs. All strictly normalized spectra.

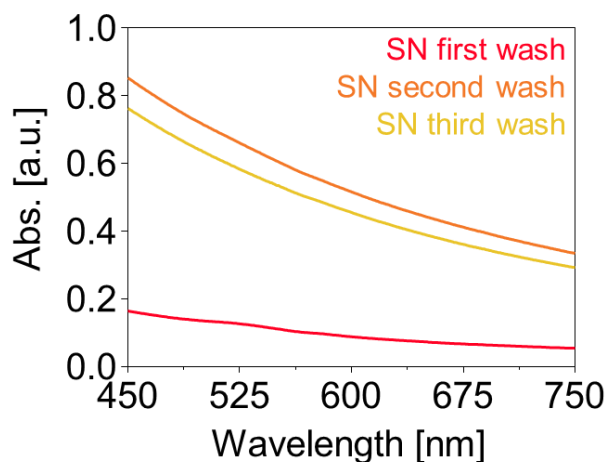


Figure 7-15: UV-Vis spectra of supernatant of PAH-AuNP@ZIF-8. Scattering due to the presence of ZIF-8 crystals. The small bump in the UV-Vis spectra labeled 'first wash' indicates unremoved PAH-AuNPs.

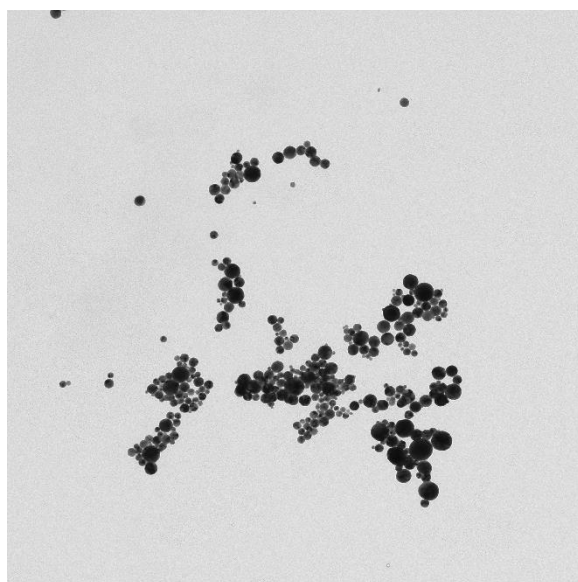


Figure 7-16: TEM of LAL-AuNPs from the group of Dr. Reichenberger. Size is labelled between 20 and 30 nm (also see **Figure 7-7**). Variations in size can clearly be observed.

Figure 7-17: For LAL-AuNPs instead of a defined peak, a broad and poorly resolved signal was observed, indicative of substantial aggregation rather than cluster formation. The underlying cause of this discrepancy is unclear but may be attributed to batch variability. The new received batch of LAL-AuNPs was not complemented with proper characterization and also presented challenges during synthesis. Specifically, it consisted of a heterogeneous mixture of particle sizes (**Figure 7-16**), necessitating a separation step prior to encapsulation, a step that was not required with the original, well-characterized batch. This inconsistency likely contributed to the inferior redispersion performance observed in this experiment.

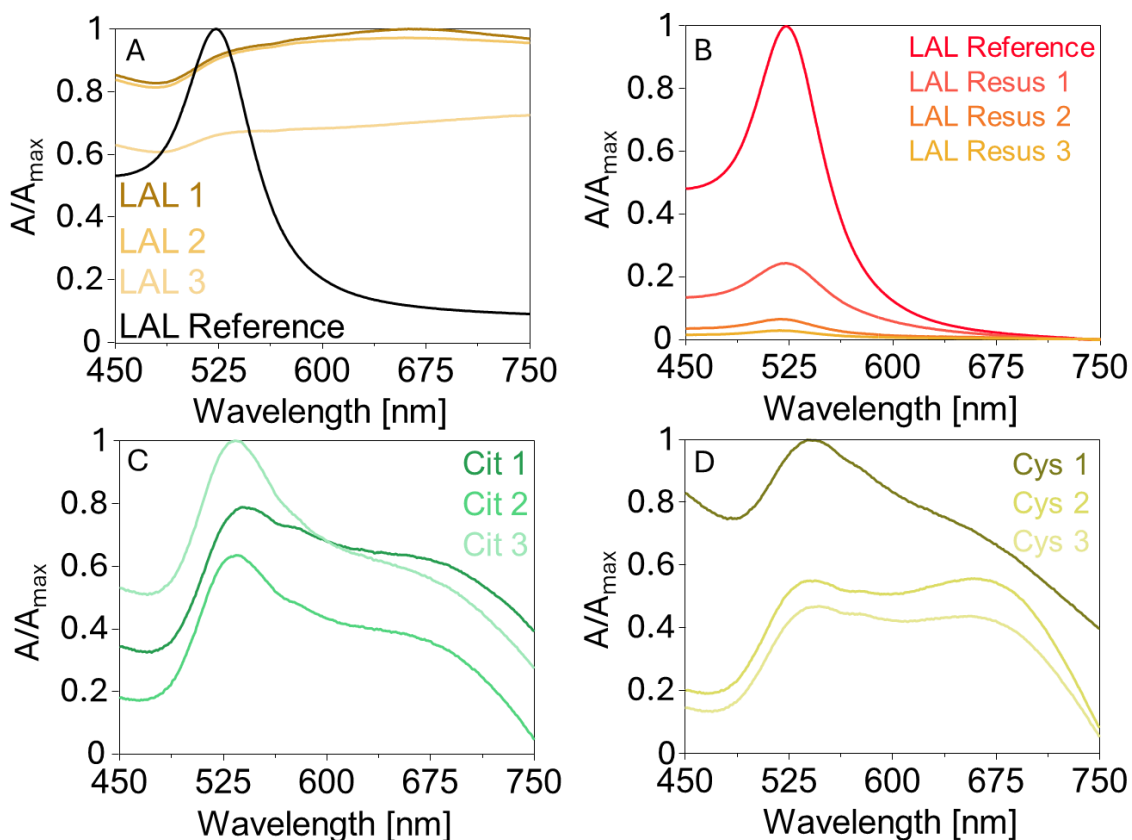


Figure 7-17: Normalized UV-Vis spectra of redispersed AuNP@ZIF-8 species. A) LAL-AuNP@ZIF-8, **B)** unembedded LAL-AuNPs, **C)** Cit-AuNP@ZIF-8, **D)** Cys-AuNP@ZIF-8. The numbers 1, 2, and 3 refer to the purification cycle.

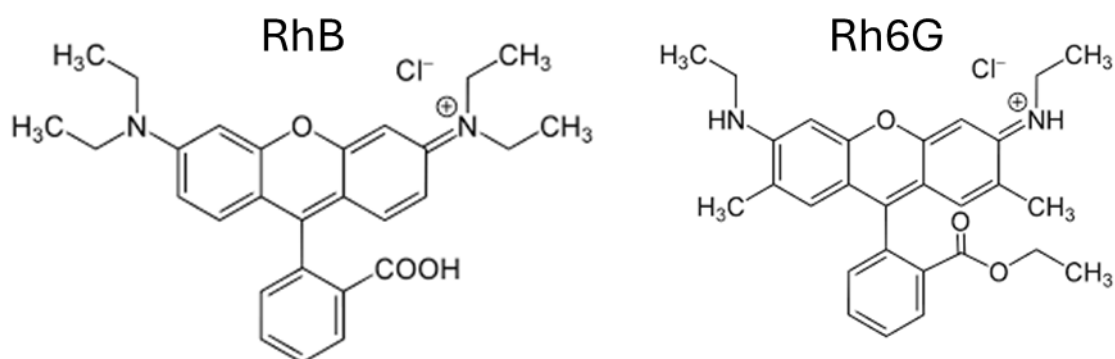


Figure 7-18: Skeletal structures of A) Rhodamine B and B) Rhodamine 6G.

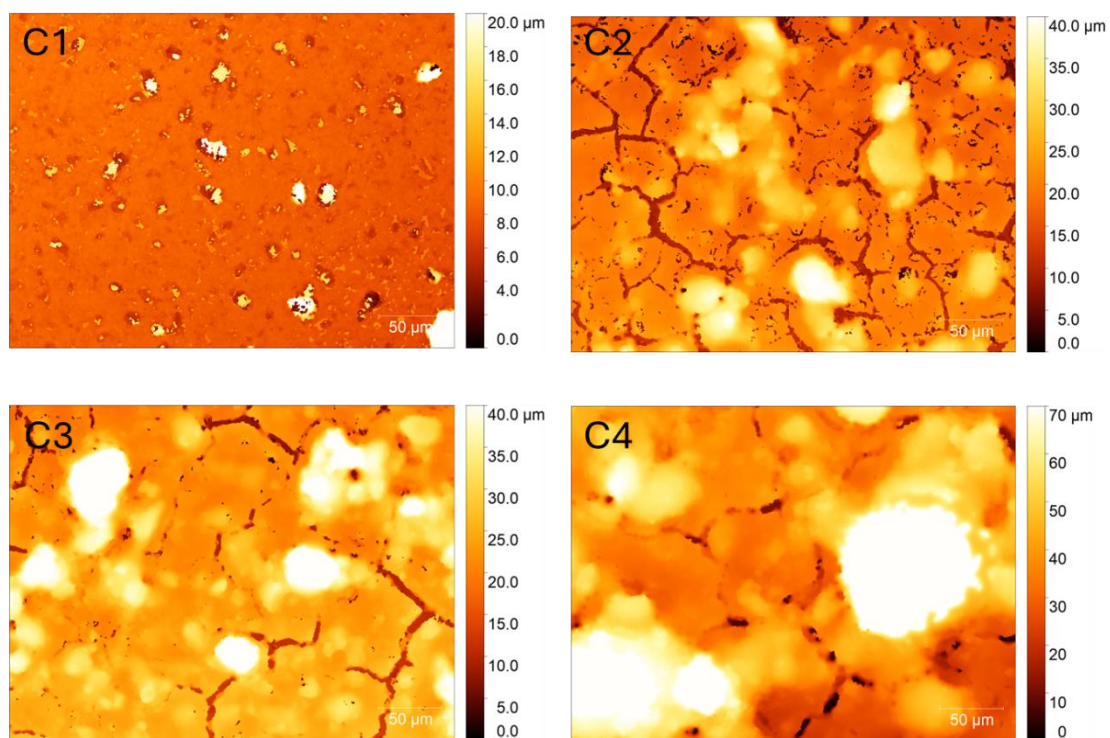


Figure 7-19: Optical profilometry of nRhB@ZIF-8. CX represents the number of coatings with X from 1 to 4.

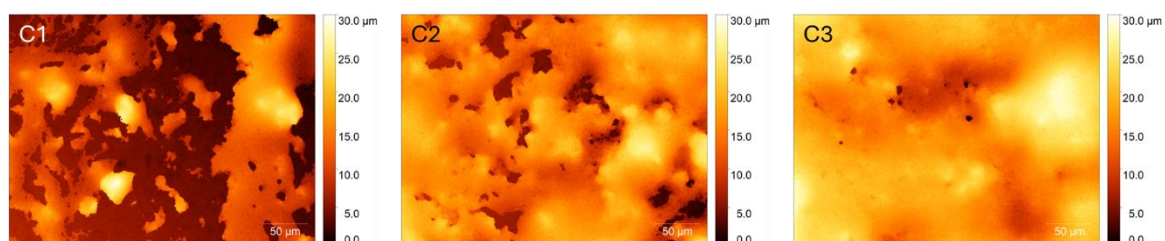


Figure 7-20: Optical profilometry of mRhB@ZIF-8. CX represents the number of coatings with X from 1 to 3.

Gebruik van Generatieve Artificiële Intelligentie (GenAI) - In te vullen formulier

Naam student: Manu Donders

Studentennummer: R0799165

Geef met "X" aan of het gaat om een cursusopdracht, een BIG-project of een masterproef:

X Dit formulier heeft betrekking op mijn masterproef.

Titel masterproef: Trapping gold, flashy dyes: Taking advantage of zeolitic imidazolate framework-8's weakness

Promotor: Rob Ameloot, Sammy Verbruggen

O Dit formulier heeft betrekking op een BIG-project.

Titel BIG-project: ...

Promotor: ...

O Dit formulier heeft betrekking op een cursusopdracht.

Cursusnaam: ...

Cursusnummer: ...

Geef met "X" aan:

o Ik heb geen GenAI tool gebruikt.

X Ik heb wel een Gen AI tool gebruikt. Geef in dat geval aan welke (bv. ChatGPT/GPT-4/...): ChatGPT 4o

Geef met "X" aan (mogelijk meerdere keren) op welke manier je de Gen AI tool hebt gebruikt:

- X Als taalassistent voor het herwerken of verbeteren van zelf geschreven teksten zonder nieuwe inhoud toe te voegen.** (Dit gebruik is gelijk aan spelling- en grammaticacheckers en hoeft je niet expliciet te vermelden.)
- X Als zoekmachine om eerste informatie te krijgen over een onderwerp of voor een eerste aanzet om op zoek te gaan naar literatuur.** (Deze toepassing is gelijkaardig aan het gebruik van een gewone zoekmachine bij de uitwerking van een persoonlijk werkstuk. Als student ben je verantwoordelijk voor het controleren en verifiëren van de afwezigheid of correctheid van referenties. Ga dus vervolgens zelf op zoek naar wetenschappelijke referenties en voer zelf een analyse van de brondocumenten. Interpreteer, analyseer en verwerk de verkregen informatie; kopieer ze niet zomaar. Indien je vervolgens eigenhandig een tekst opstelt, hoeft je het gebruik niet te vermelden.)
- ☐ **Om tekstblokken te genereren.** (Wanneer je tekstblokken van GenAI output letterlijk overneemt, dan vermeld je de GenAI bronnen en citeer je, m.a.w. je meldt duidelijk dat het item via GenAI is aangemaakt d.m.v. citatie/referentie.)
- ☐ **Om grafieken of figuren te genereren.** (Wanneer je grafieken/figuren van GenAI output letterlijk overneemt, dan vermeld je de GenAI bronnen en citeer je, m.a.w. je meldt duidelijk dat het item via GenAI is aangemaakt d.m.v. citatie/referentie.)
- ☐ **Om code te laten genereren als deelaspect binnen een grotere opdracht.** (Let op, dit mag enkel als de docent hier EXPLICIET toestemming voor heeft gegeven.)
- ☐ **Anders** (Neem contact op met de docent van de cursus of de promotor van de thesis of het BIG-project. Leg uit hoe je voldoet aan artikel 84 van het examenreglement. Leg uit wat het nut of de toegevoegde waarde van het gebruik van GenAI.)

Bijkomende richtlijnen en opmerkingen

De faculteit volgt het beleid van KU Leuven om GenAI verantwoord in te zetten. Daarbij is transparantie over het gebruik van GenAI door de student essentieel, waarvoor dit formulier hulp biedt. Onverantwoord en niet-transparant gebruik van GenAI kan beschouwd worden als een onregelmatigheid en gesanctioneerd worden. Studenten die overwegen om GenAI te gebruiken, moeten zich verder informeren via de universitaire website met bijkomende richtlijnen (Hoe GenAI correct te citeren en naar te refereren? Wat is (niet) toegelaten? Tips en aandachtspunten voor een verantwoord gebruik):

<https://www.kuleuven.be/onderwijs/student/onderwijstools/artificiele-intelligentie>