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Encapsulating Gold Nanoparticles in Zeolitic Imidazolate Framework Crystal for Novel Optical Response

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Abstract

We investigated optical properties of Au nanoparticles (Au NPs) loaded into the crystal of a porous material ZIF-8, abbreviated as Au@ZIF-8, by a diffuse reflectance spectroscopy. Au@ZIF-8 was synthesized by a reaction of ZIF-8 precursor with PVP-encapsulated-Au-
NPs in methanol solution. The concentration of Au NPs in an aqueous solution of the ZIF-8 precursor was controlled from 0.05 mL to 1.0 mL. The crystal structure of ZIF-8 and detailed formation of Au@ZIF-8 are fully characterized by powder X-ray diffraction (PXRD) analysis, Raman spectroscopy, SEM, and TEM images. The upper limit of concentration for Au NPs positioned inside ZIF-8 crystal is approximately 0.05 mL. At higher concentrations, the crystal size of ZIF-8 becomes smaller; and some Au NPs are observed to be located outside the framework. The optical spectra of Au@ZIF-8 exhibit two main absorption bands at ≈520 nm and ≈820 nm. The former of which is attributed to the surface plasmon resonance of Au NPs, while the band at ≈820 nm can be assigned to the longitudinal mode and/or collective plasmonic modes, as long as the particles are closely aggregated. Finite-Difference Time-Domain (FDTD) calculation for extinction cross-section spectrum for a BCC arrangement of Au NPs with the radius of 5 nm and the center-to-center distance of 13 nm was utilized to confirm the observation of new optical response of Au@ZIF-8. The calculation is in rather good agreement with the experimental data showing two main bands at ≈500 nm and ≈800 nm. This work suggests a way to create a magnetic material in optical frequency in case of locating Au NPs periodically in the pores of ZIF-8 or more generally in the metal-organic frameworks (MOFs).

Keywords: Metal-organic frameworks; ZIF-8; Au@ZIF-8; Metallic nanoparticles; Surface plasmon resonance; Collective plasmonic mode
1. Introduction:

Localized surface plasmon resonance is a collective oscillation of the conduction electrons in metallic particles when they are stimulated by light [1]. The collective oscillation originates from the spatial distribution of the polarized charges confined on the surface of nanostructure [2]. The change of the size or the shape of a metallic nanoparticle gives rise to vary the positive and negative charges separation, i.e. polarization. Therefore, it is possible to tune the surface plasmon resonant frequency and intensity in the optical region [3]. In the case of spherical nanoparticles, the optical response exhibits only a single plasmonic mode due to their high-order symmetry. On the other hand, more than one mode, e.g. transverse and longitudinal modes, is observed if the particles have different symmetries [4]. Furthermore, the plasmonic resonance is also sensitive to the dielectric medium surrounding the nanoparticle [3,5]. Those characteristics make metallic nanoparticles very suitable for sensing applications by placing a molecule closely to nanoparticles and then observing the shift of the plasmonic peak as a result of changing the dielectric environment [6].

Recently, periodically arrayed metallic nanoparticles are of great attention in plasmonic research due to not only altering plasmonic resonance but also bringing about electronic and magnetic properties that are distinct from isolated nanoparticles. The emergence of the negative permittivity and permeability can be derived from this structure. So far, the negative permittivity and permeability were observed in microwave frequencies [7,8]. It was possible to tune the refractive indices and permittivities in the optical region [9-11]. H.
Alaeian et al. performed a rigorous coupled-wave analysis (RCWA) calculation for gold nanoparticles arrayed in a cubic superlattice structure and showed a tunable magnetic resonance in the visible region despite no inclusion of magnetic constituents [12]. The magnetism was attributed to the collective plasmonic modes near the resonant frequency.

**Fig. 1:** Schematic illustration for sodalite cage of ZIF-8 (upper figure), and simplified supercell of ZIF-8 framework structure with gold nanoparticles. In ideal case, Au NPs can be regularly arrayed in the pores of ZIF-8 forming a BCC superlattice. The Au NP, Zn$^{2+}$, and 2-methylimidazole are illustrated by gold, blue, and red spheres, respectively. 2-methyl functionalities were removed to clarify the structure of ZIF-8.

Practically, the array of metallic nanoparticles can be created by using host materials [13] or self-assembly [14]. Among host materials, metal-organic frameworks (MOFs), which
constructed by linkage of metal ions and organic ligands, arise as the most promising candidates because of their versatile structures [15,16]. The framework of MOFs possesses permanent porosity with well-defined pores and large internal surface areas. Zeolitic imidazolate frameworks (ZIFs) are a sub-class of MOFs comprising of organic components that are imidazole linker or imidazole derivatives, and the tetrahedral building units of Zn$^{2+}$, Co$^{2+}$ or Cu$^{2+}$ [17]. ZIFs material not only topologically displays Zeolites network with the designable and tailorable structures that can be enabled to access the post-synthetic modification for targeted applications, but also owns the high surface area and robust framework leading to the fact that ZIFs can be applied for many applications under severe working conditions. Among those post-synthetic modifications, metallic nanoparticles encapsulation into the pores of ZIFs has been the pivotal technique for a wide range of practical applications and that was detailed described in literature, in which NPs had been successfully loaded into the ZIFs structure by various ways such as CO oxidation [18,19], encapsulation of pre-synthesized metal nanoparticles in MOFs [13] or de novo synthesis [20], etc. In those works, ZIF-8 was utilized as the host framework for gold nanoparticles loading with the size of $\approx$10 nm. Many researches identify the effects of the parity of solvent on the location of gold nanoparticles with respect to MOFs [21]. Nevertheless, the purpose of incorporating gold nanoparticles into MOFs is mainly to enhance the catalytic properties [13,21-24]. The optical properties of such composites remain ambiguous in terms of localized surface plasmon and light-matter interaction.
In this work, we have tried to incorporate Au NPs into the crystal of ZIF-8, termed as Au@ZIF-8, and investigated in detail optical properties of the material by optical measurement and Finite-Difference Time-Domain (FDTD) calculation. The framework structure of ZIF-8 and the simplified Au@ZIF-8 are shown in Fig. 1. The 3-dimensional framework of ZIF-8 is constructed by a connection between Zn$^{2+}$ geometrically possessing tetrahedral SBU and 2-methylimidazole forming a SOD structure, as shown in the upper part of Fig. 1. The pores of the host material are arrayed in a BCC structure (bottom figure). In an ideal case, Au NPs should be placed periodically inside every pore of ZIF-8. Nevertheless, it is important to notice that such ideal structure is very difficult to be produced in the practice due to the unsuitable size effect between the window of ZIF-8 and Au NPs. Instead, Au NPs can be encapsulated in the crystal of ZIF-8. Herein, we report a facile method to synthesize gold nanoparticles incorporated into ZIF-8 to form Au@ZIF-8 by systematically adjusting the Au concentrations. The resulting material was subsequently investigated the optical properties by employing a diffuse reflectance spectroscopy. The obtained absorption spectra of Au@ZIF-8 exhibit two reflection bands at $\approx$520 nm, which we assign to the localized surface plasmon resonance of gold nanoparticles in the transverse mode and $\approx$820 nm related to the surface plasmon in the longitudinal mode and/or the collective plasmonic modes. Our finding further supported by FDTD calculation methodology paves the way into the understanding of using NPs for systematically
arrangement inside the pores of MOFs material resulting in the synergistic interaction between the NPs and the host frameworks which is useful for novel optical response.

2. Experimental details:

2.1. Reagents and characterization methods:

All reagents HAuCl₄, Na₃C₅H₆O₇, polyvinylpyrrolidone (PVP), Zn(NO₃)₂·6H₂O, 2-methylimidazole (Hmin) were purchased from Sigma-Aldrich. Powder X-ray diffraction (PXRD) of ZIF-8 and Au@ZIF-8 were collected by using a Bruker D8 Advance diffractometer employed with Cu Kα radiation. ATR-FTIR spectra were recorded by Bruker Vertex 70 in the frequency range of 600 – 4000 cm⁻¹. Raman spectra were measured by Horiba XplorA ONE at Duy Tan University. A diffuse reflectance UV-Vis by JASCO V-600 with absolute reflectance measurement accessory ARN-731 was used to investigate the optical properties in the wavelength of 350 – 1100 nm. The morphology of ZIF-8 and Au@ZIF-8 was investigated by a scanning electron microscope (SEM) using Hitachi S-4800 employed with energy dispersive spectroscopy (EDS) as well as transmission electron microscopes (TEM) using JEOL JEM-1400 and by Hitachi H-8000 model.

2.2. Synthesis of Au nanoparticles and Au@ZIF-8:

Gold nanoparticles (Au NPs) were synthesized by hydrothermal method. Briefly, tetrachloroauric acid (HAuCl₄) was dissolved in 150 mL de-ionized (DI) water (0.01%) and then boiled in a reflux condenser with a magnetic stirrer. After boiling, an aqueous solution
of trisodium citrate (Na$_3$C$_6$H$_5$O$_7$; 0.1%, 4.5 mL) was wisely dropped to the HAuCl$_4$ solution while keeping magnetic stirrer. After the color of HAuCl$_4$ solution turned from yellow to red (about 20 min), the heater was off and let to cool down to room temperature. Here, we utilized polyvinylpyrrolidone (PVP) to avoid aggregation of Au NPs. In addition, PVP-encapsulated-Au-NPs (PVP-Au-NPs) was used as seeds to grow ZIF-8 framework. In order to achieve such kind of material, a solution of PVP (0.5 g, Mw = 55,000) in DI water was added dropwise to the solution of Au NPs with magnetic stirring, and then the mixture was further stirred at room temperature in 24 hours. PVP-Au-NPs solution was then centrifuged at 16000 RCF in 30 min and washed 3 times with MeOH. We concentrated 100 mL of as-synthesized PVP-Au-NPs solution to 1.5 mL.

Au@ZIF-8 was synthesized from PVP-Au-NPs in methanol (MeOH), as described in detail in literature [13]. We synthesized PVP-Au-NPs as aforementioned procedure and then added Zn(NO$_3$)$_2$·6H$_2$O and 2-methylimidazole (Hmin) as precursors to grow ZIF-8 framework. The Zn$^{2+}$:Hmin ratio is fixed to be of 1:1. In short, a desired volume of centrifuged PVP-Au-NPs was added into aqueous solution of Zn(NO$_3$)$_2$·6H$_2$O (50 mL, 25 mM), and then dropped to aqueous solution of Hmin (50 mL, 25 mM). The reaction mixture allowed to be stirred continuously for 24 h to observe a red precipitation which was then centrifuged at 8,000 RPM to obtain the product. The resulting product was dried at ambient condition. In this study, the centrifuged PVP-Au-NPs solution was systematically added at volumes, V, of 0.025 mL, 0.05 mL, 0.1 mL, 0.2 mL, 0.5 mL and 1.0 mL.
Moreover, the concentration of Au NPs is defined as the volume of PVP-Au-NPs in the aqueous solution of ZIF-8 precursors (Zn^{2+} and Hmin).

3. Results and discussions:

In order to demonstrate the success of loading Au NPs into ZIF-8 material, the synthesized Au@ZIF-8 at various Au NPs concentrations from 0.025 mL to 1.0 mL was firstly measured by PXRD which is shown in Fig. 2. The characteristic peaks of the pristine ZIF-8 structure are entirely found at 7.3°, 10.3°, 12.6°, 14.6°, 16.3°, and 17.9° corresponding to (011), (002), (112), (022), (013), and (222) planes [17]. These peaks are quite sharp and their intensity ratios are well consistent with the calculated PXRD pattern generated from the single crystal of ZIF-8. The PXRD patterns also confirm that ZIF-8 is well crystallized once growing on PVP-Au-NPs as seeds.
Fig. 2: Powder X-ray diffraction (PXRD) patterns for Au@ZIF-8 synthesized at various Au NPs concentrations displaying the well crystallinity of resulting materials. Assigned peaks related to bulk Au are marked as dotted lines corresponding to its diffracted planes.

Being accompanied to the original peaks of ZIF-8, new peaks appear at 38.3°, 44.6°, 64.9°, 77.8°, and 82.2° with respect to the planes (111), (200), (220), (311), and (222) of bulk gold as long as the concentration of Au NPs is higher than 0.1 mL. Their intensities increase with increasing concentration of Au NPs. We found the new peaks are quite broad
that implies a spherical shape of Au NPs [25]. Indeed, the particle size of Au NPs is about 10 nm which is estimated from the full width at half maximum (FWHM) for the peak at 38.3° by Scherrer equation.

![Fig. 3: Raman spectra of ZIF-8 and Au@ZIF-8 (V = 0.01 mL) with laser excitation of 785 nm. Peaks are indicated by dotted lines. Inset: A schematic illustration for a cluster of Zn-Hmin.](image)

To further examine, we carried out Raman study using the Raman spectrometer with 785 nm excitation laser source for ZIF-8 and Au@ZIF-8 at Au NPs concentration of 0.1 mL. As depicted in Fig. 3, the observed peaks are in good agreement with previous reports [26]. In particular, two extra peaks at 1116 and 1484 cm\(^{-1}\) found in the Raman spectrum of ZIF-8 were absent in the one of Au@ZIF-8. We believe that the origin of these bands can be due to a split of main bands at 1143 and 1508 cm\(^{-1}\). The peak at 278 cm\(^{-1}\) can be assigned to Zn-N vibration and the bands at 683, 1143, 1456, and 1508 cm\(^{-1}\) are attributed to imidazole
ring puckering, C5-N stretching, methyl bending, and C4=C5 stretching, respectively. Other peaks are related to stretching and bending on imidazole ring [27]. With incorporating Au NPs, we observed only the disappearance of peaks at 1116 and 1484 cm\(^{-1}\) and no significant change in main peaks on spectra. The Raman spectra reveal that there is almost no change in the vibration modes of ZIF-8 and Au@ZIF-8 structure.

**Fig. 4:** SEM images and EDS of Au@ZIF-8 at V = 0.05 mL (left) and 0.1 mL (right).

The success of Au NPs loading was further proven by SEM-EDS which also provides the information of the morphology study for Au@ZIF-8 (Fig. 4) at Au NPs concentrations of 0.05 and 0.1 mL. The SEM image of Au@ZIF-8 clearly shows that the crystal size of ZIF-8 is about 400 – 500 nm and 300 – 400 nm when using Au NPs concentrations of 0.05 mL
and 0.1 mL, respectively. The appearance of Au NPs can be indicated in EDS along with Zn, C, N being the main chemical compositions of ZIF-8 (Fig. 4).

In order to investigate the Au NPs loaded inside the pores or encapsulated in the crystals, we subsequently performed TEM analysis for various samples with $V = 0.05$ mL, $0.2$ mL and $1.0$ mL of Au NPs concentration (Fig. 5). Particularly, ZIF-8 crystals and Au NPs can be clearly indicated in the figure, in which ZIF-8 exhibits the size of 300 nm as $V = 0.05$ mL and appeared to be a truncated shape which is perfectly consistent with the sodalite topology owning the symmetry of $I-43m$ space group [28]. The crystal size of Au@ZIF-8 decreases when increasing the concentration of Au NPs precursor along with slightly distorting of the crystal shape, yet still good crystalline. At $V = 0.05$ mL, all Au NPs are distributed inside the crystal of ZIF-8 but they are not so well regularly arrayed. The size of Au particle is about tens of nanometer, which is larger than the pore size of ZIF-8 ($\approx 11.6$ Å). Hence, Au NPs are trapped in the crystal of ZIF-8 rather than in their pores. With increasing the concentration of Au NPs ($V$), Au NPs are found to be located not only inside ZIF-8 but also on the surface of the crystals (Au NPs partially located outside ZIF-8 at higher concentrations). Based on the TEM images, we speculate that an upper limit amount of Au NPs loaded inside ZIF-8 is at $V = 0.05$ mL. A denser concentration of Au NPs requires more precursors to form the framework, thus the crystal size of ZIF-8 decreases.

PVP encapsulating around Au NPs plays an essential role in growing ZIF-8 crystal. The growth of ZIF-8 from PVP-Au-NPs can be a successive adsorption of the ZIF-8 precursors
(Zn$^{2+}$ and Hmin) until they are covered by the newly-grown ZIF-8 [13]. Indeed, the mechanism can be explained as follow. The polar groups in PVP (pyrrolidone rings) firstly attach Zn$^{2+}$ acting as the SBUs in ZIF structural network through C=O bonding and apolar groups (methylene and methane groups) subsequently connect with Hmin through hydrophobic interaction. ZIF-8 structure is constructed eventually by the combination of Zn$^{2+}$ and Hmin.
Fig. 5: TEM images of Au@ZIF-8 proving that the Au NPs was encapsulated into ZIF-8 structure at V = 0.05 mL and surrounded on the surface of the crystals of ZIF-8 when increasing the concentration of Au NPs to V = 0.2 mL or 1.0 mL.

After structural characterization of ZIF-8 and Au@ZIF-8, we then sought to explore the optical properties of our synthesized Au@ZIF-8 samples. The optical spectra for Au@ZIF-
8 at V = 0.05 mL, 0.1 mL, and 1.0 mL are illustrated in Fig. 6 which are completely different from the spectrum of pristine ZIF-8 whose absorption edge appears at \( \approx 240 \) nm [29]. Two absorption bands are observed at \( \approx 520 \) nm and \( \approx 820 \) nm. The intensity of the band at \( \approx 820 \) nm is relatively broad and increases with increasing Au NPs concentration.

We used a Lorentz model as described in Eq. 1 to fit the absorption spectra:

\[
\varepsilon(\omega) = \varepsilon_\infty - \sum_{j=1}^{n} \frac{G_j \omega_j^2}{\omega^2 - \omega_j^2 + i \Gamma_j \omega}
\]  

Here, \( \varepsilon(\omega) \) is the complex dielectric function; \( \varepsilon_\infty \) is the permittivity at the infinite frequency; \( \omega_j \) is the resonant frequencies; \( G_j \) is the oscillator strengths; \( \Gamma_j \) is the damping coefficients. As seen in Fig. 6, the optical spectra can be reproduced with three Lorentz oscillators, wherein the main bands are confirmed at \( \approx 520 \) nm and \( \approx 820 \) nm.

To interpret the origin of two observed bands, the absorption spectrum for the aqueous Au NPs in methanol solution is included. The absorption band at \( \approx 520 \) nm is the typical surface plasmon resonant frequency of Au NPs. Thus, we assign the band at \( \approx 520 \) nm in the spectra of Au@ZIF-8 to the surface plasmon resonance. For the band at \( \approx 820 \) nm, there might be two reasons to explain its appearance as follows: (i) two plasmon resonant modes in different light polarizations; (ii) collective plasmonic modes due to lattice effect. In case (i), if we consider a dense aggregation of gold nanoparticles in a narrow area to form likely nanorods yet a finite separation between them, light polarizations in the directions perpendicular and parallel to the nanorods give rise to two absorption bands at \( \approx 520 \) nm.
(transverse mode) and ≈820 nm (longitudinal mode), respectively [30]. In case (ii), light-matter interaction composing of densely packed plasmonic nanoparticles causes a collective plasmonic mode that could bear a magnetic resonance [31,32].

**Fig. 6:** Absorption spectra of Au@ZIF-8 measured by diffuse reflectance at V = 0.05 mL (blue diamond), 0.1 mL (green diamond) and 1.0 mL (black diamond). Drude-Lorentz fittings were presented by the solid line. Absorption bands are marked as asterisks at ≈520 nm and ≈820 nm. Absorption spectrum of Au NPs is shown in solid red curve for comparison. Absorbance (y-axis) is shown in linear scale.
According to our RCWA for Au NPs arrayed in a superlattice [33], multiple bands appeared in reflection spectra when the particle size is larger than 10 nm and the distance of center-to-center particle is 2 nm. The origin of these bands may be attributed to in-plane dipole-dipole interaction and electric quadrupole or collective plasmonic modes induced by anisotropic light polarizations [34]. Multiple bands can be broadened and thus overlapped at room temperature.

In order to confirm electric quadrupole and collective plasmonic modes for verifying our speculation, we performed an FDTD calculation, using a commercially available electromagnetic simulation software, Microwave Studio by CST [35], for a BCC lattice consisting of 9 Au NPs, in which the particle size is varied with a constraint separation of 3 nm between them. In this simulation, a template for optical periodic structures was used which allows to analyze all the optical characteristics of the design. The excitation source is a plane wave incident from the top with an electric field amplitude of 1 V/m and with a linear polarization. The smallest mesh size was chosen with 1 nm. It is noted that further reducing the smallest mesh size could enhance the accuracy at the short wavelength region, however the computational resource in terms of memory and time will increase dramatically. Finally, a broadband far-field was defined to calculate the extinction cross-section in the wavelength of interest of the design. The calculated extinction cross-section spectrum for the radius of 5 nm and their center-to-center distance of 13 nm is shown in Fig. 7. There exist two main bands at ≈500 nm and ≈800 nm. The first of which
corresponds to the surface plasmon resonance of individual Au NPs. The second one is due to the lattice effect caused by collective plasmonic modes which are hybridized states formed by the interaction of the central plasmonic particle with the surrounding ones. Calculated scattering E-fields presented in Fig. 7(b) also indicate the presence of the collective plasmonic mode at 800 nm in the BCC array with Au NPs which cannot observe in the single Au NP. Therefore, these FDTD calculation results can verify multiple bands observed in the optical spectra in Fig. 6.

Previously, S. Mühlig et. al. synthesized a self-assembled non-touching Au NPs and calculated extinction cross-section spectra [36]. They unraveled that a magnetic dipole appears at ≈800 nm in the y-direction as long as the particle size of 40 nm and the x-polarized light propagating along the z-direction. From our current experimental results, it suggests a way to fabricate an artificial magnetism in the optical region by incorporating Au NPs into a metal-organic framework.
Fig. 7: (a) FDTD calculated extinction cross-section for a BCC array of Au NPs. (b) Scattering E-Fields in comparison between a single Au NP and a BCC array of Au NPs. The radius of Au NPs is 5 nm and the center-to-center separation between them is 13 nm. The calculated spectrum exhibits two bands at ≈500 nm and ≈800 nm. Extinction cross section (y-axis) is shown in linear scale.

4. Conclusion and outlook:

We synthesized Au NPs incorporated into ZIF-8 at various Au NPs concentrations, and investigated their optical properties. Powder X-ray diffraction analyses confirmed that ZIF-8 and Au@ZIF-8 were prepared with high crystallinity. Au NPs with the size of ≈10 nm was proven to be encapsulated into ZIF-8 structure at the concentration of V = 0.05 mL, as
proven by TEM analysis, meanwhile at higher concentration of Au NPs used in the synthetic procedure, Au NPs was partially located on the boundary of ZIF-8. Optical-responsive property of Au@ZIF-8 was investigated showing two absorption bands at \( \approx 520 \) nm assigned to the localized surface plasmon resonance of Au NPs in the transverse mode, and \( \approx 820 \) nm originated to the surface plasmon resonance in the longitudinal mode and/or collective plasmonic modes when Au NPs are gathered near together. Our observation was verified by the FDTD calculation for extinction cross-section. We believe that our finding provides the chance to design better synthetic conditions for encapsulating NPs into the pores of porous materials, especially for the highly ordered MOFs framework with suitable nanoparticle size which will support to enhance the plasmonic phenomenon useful for creating novel optical response such as magnetic resonance in the optical region. From our perspective, one can propose and utilize MOFs as platform to create a so-called MOF-based metamaterials which could be applied for a perfect lens.

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**References:**


Graphical abstract:

Novel optical response of gold nanoparticles encapsulated in ZIF-8 crystal (Au@ZIF-8) was investigated. Optical absorption spectra show two absorption bands at 520 nm and 720 nm that are completely different from gold nanoparticles and ZIF-8 individually. FDTD-based theoretical study was carried to verify optical response of Au@ZIF-8.