

Plasmonic Semiconductor Nanoparticles in a Metal-Organic Framework Structure and their *In Situ* Cation Exchange

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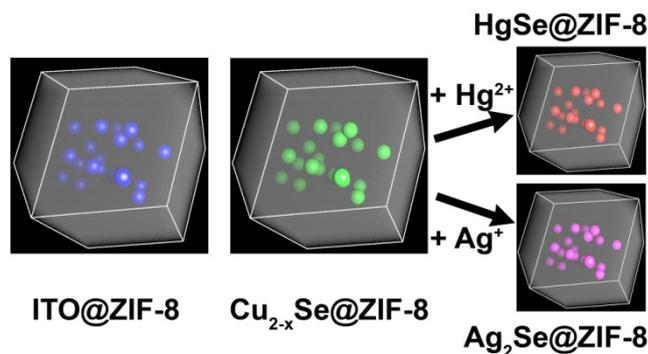
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ABSTRACT:

Composites of nanoparticles (NPs) in metal-organic frameworks (MOFs) combine the versatile properties of nanoparticles with the defined porosity of MOFs. Here, we show the encapsulation of plasmonic semiconductor NPs in ZIF-8 crystals. Both p-type and n-type doped plasmonic semiconductor NPs (consisting of Cu_{2-x}Se and indium tin oxide, respectively) are encapsulated. The plasmonic and structural properties of each system are preserved during the formation of the composites. Furthermore we demonstrate the accessibility of the in ZIF-8 integrated nanoparticles via the successful first time *in situ* cation exchange of MOF embedded Cu_{2-x}Se NPs to HgSe NPs and Ag_2Se NPs. This ion exchange occurs without influencing the composition or structural integrity of the metal-organic framework. This approach hence enables a fixation of plasmonic nanoparticles avoiding strong plasmon-plasmon coupling but still keeping the plasmonic nanoparticles accessible.



Introduction:

The discovery of the origin of the NIR absorption band in copper chalcogenides has sparked intensive research in degenerately self-doped semiconductor nanoparticles that exhibit localized surface plasmon resonances (LSPRs).²⁻⁴ Compared to classical metal nanoparticles (NPs), these materials opened a further path to tune the LSPR. While the tuning for metal NPs is limited to size, shape and material choice during synthesis, the LSPR of self-doped copper chalcogenides can further be tuned by post synthetic oxidation and reduction.³ In addition the cation exchange with different cations enables the shift of the LSPR maximum.⁵ The LSPR in Cu_{2-x}Se is caused by p-type self-doped free charge carriers.³ In contrast to that indium tin oxide (ITO) is n-type doped. These two systems are excellent examples of plasmonic semiconductors with a LSPR in the near infra-red (NIR), that are covering p-type as well as n-type doped semiconductors.

Nanoporous metal-organic framework (MOF) structures have been studied and applied in various applications during the last decade.⁶ Their homogeneous structure with defined cavity and gate size fueled the research efforts in this area. Combining the properties of MOFs with the unique properties of nano sized materials was a logical consequence to achieve highly functional composite materials.^{7,8}

We show here, to the best of our knowledge, the first time ever incorporation of plasmonic semiconductor NPs in a MOF structure. While previous works have shown the incorporation of several plasmonic metal nanoparticles, plasmonic semiconductor NPs have not been successfully built into MOF NPs to date. In this project the formation of composite particles consisting of multiple Cu_{2-x}Se NPs or indium tin oxide (ITO) in one ZIF-8 particle resulting in Cu_{2-x}Se @ZIF-8 or ITO@ZIF-8 composites, respectively, will be shown. The resulting composite particles exhibit a strong absorption band in the NIR originating from the LSPR of the incorporated NPs. Oxidation enables the tuning of the Cu_{2-x}Se LSPR inside the Cu_{2-x}Se @ZIF-8.

We here report for the first time a cation exchange of NPs inside a NP@MOF composite. Specifically we exchange the Cu_{2-x}Se NPs inside a $\text{Cu}_{2-x}\text{Se}@ZIF-8$ composite with Ag^+ and Hg^{2+} ions resulting in $\text{HgSe}@ZIF-8$ and $\text{Ag}_2\text{Se}@ZIF-8$ composite particles, without modifying the ZIF-8 host structure. This further demonstrates the accessibility of the plasmonic NPs, while the fixation within the MOF framework prevents an agglomeration of them.

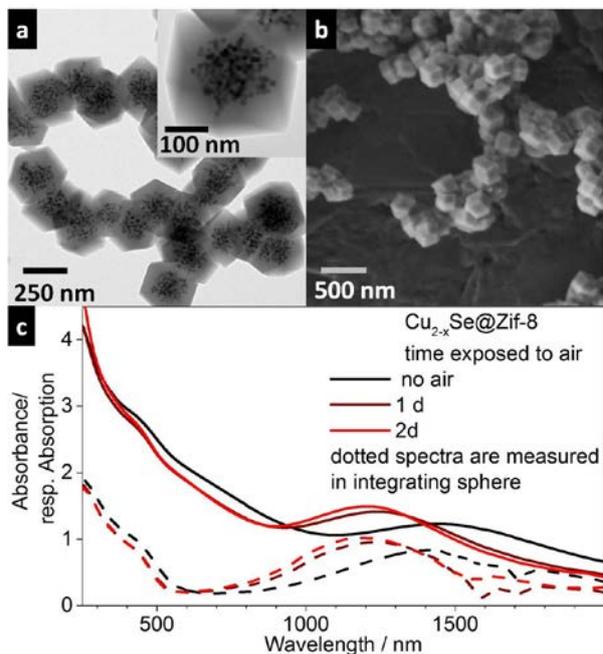


Figure 1: TEM (a) and SEM (b) micrographs of typical $\text{Cu}_{2-x}\text{Se}@ZIF-8$ particles, The inset shows the magnifications of single composite particles. Absorbance spectra (a) of $\text{Cu}_{2-x}\text{Se}@ZIF-8$ composite particles after different time of exposure to air, measured in transmission mode (solid lines) and the absorption spectra in the integrating sphere (dotted lines).

Transmission electron microscopy reveals the formation of $281 \text{ nm} \pm 23 \text{ nm}$ sized $\text{Cu}_{2-x}\text{Se}@ZIF-8$ composite crystals, with multiple smaller, higher contrast Cu_{2-x}Se NPs embedded (Figure 1a). Combined with the associated scanning electron microscopy (SEM) micrograph (Figure 1b), it can be seen that the majority of the ZIF-8-based composite particles exhibit a rhombic dodecahedron shape. We observed that with the described synthesis parameters a quantitative integration of the Cu_{2-x}Se NPs into the ZIF-8 crystals can be achieved. The successful integration of the NPs was further shown by energy-dispersive X-ray spectroscopy (EDX) and X-ray powder diffraction (XRD) measurements, that can be found in the full manuscript (see link below). The $\text{Cu}_{2-x}\text{Se}@ZIF-8$ composite particles strongly scatter due to their size, but also exhibit an absorbance maximum at 1450 nm in normal transmission mode (see Figure 1c). Measuring only the absorption of the same sample results in a spectrum that corresponds to the one of typical Cu_{2-x}Se NPs. This further shows that while being fixated in the MOF framework no agglomeration of the NPs occurred, as this would have caused a strong bathochromic shift and broadening of the resonance band.

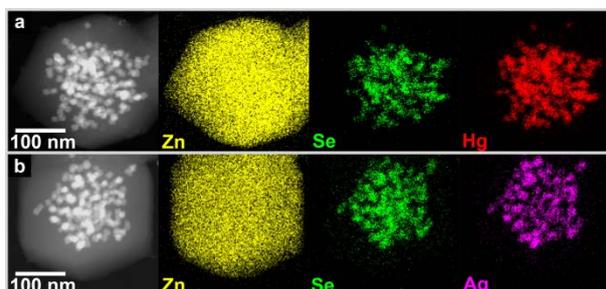


Figure 2: HAADF-STEM micrograph and EDX mappings of Zn, Se, Hg or Ag for the $\text{HgSe}@ZIF-8$ (a) and the $\text{Ag}_2\text{Se}@ZIF-8$ (b) composite particles obtained by ion exchange.

Furthermore, we analyzed the behavior of the $\text{Cu}_{2-x}\text{Se}@ZIF-8$ composite particles when exposed to Ag^+ and Hg^{2+} ions in the solvent methanol. The addition of both ions leads to the complete disappearance of the LSPR, as it was previously observed for plain non-embedded and therefore freely accessible Cu_{2-x}Se NPs.^{5,9} Analyzing the particles with TEM, shows that the composite particles have an average size of $257 \text{ nm} \pm 28 \text{ nm}$ (Hg^{2+}) and $255 \pm 22 \text{ nm}$ (Ag^+) respectively. Despite the minimal etching at the ZIF-8 edges, the embedded NPs are still fully encapsulated after around 2 h treatment with Ag^+ or Hg^{2+} ions. The elemental mapping in Figure 2 shows that the Cu_{2-x}Se NPs underwent complete ion exchange and were transformed into Ag_2Se or HgSe NPs, respectively. However, no evidence could be found that the added ions exchanged the Zn^{2+} ions in the ZIF-8 framework.

Conclusion:

In this work we present the successful integration of two plasmonic semiconductor systems into the nanoporous MOF type ZIF-8. We call them Cu_{2-x}Se@ZIF-8 and ITO@ZIF-8 composite particles. Both, the p-type doped Cu_{2-x}Se NPs and the n-type doped ITO NPs, preserve their LSPR while being incorporated into the respective ZIF-8 composite structure. The Cu_{2-x}Se@ZIF-8 composite further showed that the LSPR can still be tuned by oxidation, comparable to the pristine Cu_{2-x}Se NPs while the LSPR of ITO@ZIF-8 particles was found to be stable under ambient conditions. Therefore, both systems are potentially interesting for sensory application in which the ZIF network is size discriminating the access to the LSPR particles and can be either used for optical sensing of redox active substances (Cu_{2-x}Se) or for simply sensing changes in the dielectric surrounding (ITO).

Furthermore, we showed that, while being physically protected from the environment and from agglomeration, the NPs are still accessible as can be seen from ion exchange reactions. Via this straight forward strategy we successfully synthesized HgSe@ZIF-8 and Ag₂Se@ZIF-8 composite particles starting from the Cu_{2-x}Se@ZIF-8 composites through an *in situ* cation exchange that is not destroying the ZIF-8 framework. Thus, ion exchange shows a possible approach for functionalized ZIF-8 composite particles that might not be accessible via direct synthesis.

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