Synthesis of gold nanorods with small thiolated molecules

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Introduction

Towards the high yield synthesis of small gold nanorods by using bioadditives during growth

Gold nanorods (AuNRs) are one of the most studied anisotropic nanoparticles because of their unique optical properties [1]. Besides, AuNRs have attracted great attention because their distinct sizes can enable applications in sensing, biomedical imaging and photothermal therapy [2, 3].

AuNRs are characterized by the surface plasmon resonance (SPR) which is a collective oscillation of the conduction band electrons of gold upon interaction with light of certain frequency. The plasmon absorption of AuNRs (Figure 1) splits into two bands: the transverse and longitudinal surface plasmon resonances (TSPR and LSPR) in which the position of the latter band depends on the nanorods aspect ratio (AR).

Despite many reports on the broad LSPR band tunability and improvement of shape yield for the seed-mediated method [4, 5], there are few studies on the seedless synthesis of small AuNRs in high yield, their reproducibility and scalability.

Here, we describe novel seeded and seedless protocols of AuNRs by using small thiolated molecules such as glutathione (GSH), oxidized glutathione (GSSG), L-cysteine (L-cys) and L-methionine (L-met) during growth. Our reproducible and scalable protocol produces AuNRs of different dimensions and aspect ratios depending on the concentration and addition time of the bioadditive. Interestingly, the nanorod growth is accelerated in the presence of the bioadditives but only glutathione enables the high yield synthesis of small AuNRs [6].

Experimental Strategy

Effect of concentration and addition time of GSH: small amounts of GSH blue-shift the LSPR band and AuNRs quality improves in the seedless protocol

Figure 1. Schematic of AuNRs seeds synthesis with hydrosulfide as weak reducing agent.

The surfactant is cysteine/methylammonium bromide (CTAB).

Figure 2. Scheme of AuNRs seedless synthesis with hydrosulfide as weak reducing agent.

High yield AuNRs

Surface characterization and AuNRs functionalization with PEG-SH and MUTAB

Figure 3. Representation of some GSH molecules adsorbed on AuNR surface.

Figure 4. CTA is replaced from AuNRs surface with thiolate polyethylene glycol (PEG-SH) and 13 mercaptoundecyltrimethylammonium bromide (MUTAB) in aqueous solution.

Experimental Results

Kinetics of nanorod growth for glutathione and L-cysteine

Figure 10. Variation of AuNRs LSPR band position (A) and its absorbance (B) as a function of time for the seedless method: AuNRs control (red), with 0.2 µg/mL GSH (blue) and L-cys (green) added at 30 min after NaBr4.

The fast nanorod formation with GSH and L-cys produces saturation of the absorbance at an earlier reaction time (Figure 10B). Thus, when small thiolated compounds are incorporated during growth, the stabilization of the growing nanorods occurs in a shorter period of time.

Table 2. Zeta potential (mV) of AuNRs before and after surface modification with 2% PEG-SH and MUTAB

Table 1. LSPR band position, shape yield and dimensions of AuNRs synthesized by the seeded and seedless methods with and without bioadditives.

Table 2. Zeta potential (mV) of AuNRs before and after surface modification with 2% PEG-SH and MUTAB

The absence of the less intense 520 nm peak at higher binding energy is because of the low concentration of bioadditives adsorbed on AuNRs (Figure 11).

The distinct effects of these small thiolated molecules are attributed to their adsorption strength (thiol, disulfide and thioether).

Conclusions

• Small amounts of bioadditives added during growth produce AuNRs with tunable LSPR band depending on the bioadditive concentration and addition time.

• In this novel seedless synthesis, the nanorod growth is accelerated by more than two times in the presence of GSH and L-cysteine.

• Our reproducible and scalable seedless protocol enables the synthesis of AuNRs with smaller sizes and the nanorod morphology is preserved.

• Only GSH and GSSG produce AuNRs in high yield and the colloidal stability of nanorods containing glutathione is enhanced after functionalization with MUTAB.

• Future studies may explore the incorporation of other additives in nanorod concentrations to improve the quality of other anisotropic shapes for diverse applications.

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REFERENCES
Selecting Attachment of Covalent Organic Frameworks to 2D Nanomaterials

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Abstract

Chemical sensing using 2-D nanomaterials has been an area of intense investigation exhibiting high sensitivity, however it has been limited as a field due to the lack of selectivity among analytes. Covalent organic frameworks are large porous and repeated organic frameworks which have been shown to act as selectivity agents due to functionalization and porosity. This research focuses on the association of COFs with 2-D nanomaterials using bottom-up and top-down design methodologies and investigated under solvothermal and microwave assisted synthesis. Several known COF species have been examined in order to understand the fundamental surface interactions between 2-D nanomaterials and COFs.

Chemical Sensing

Chemical Sensing is a relevant and challenging field. While changes in optical and electrical measurements are used to determine values in concentration, selectivity is not inherent and therefore an essential area of investigation.

2-D Nanomaterials

• Typical sensing with TMDs occurs via monitoring changes in electrical properties in response to surface adsorption of analytes
• Analyte will either be an electron donor (NH3) or an electron acceptor (NO2)
• Depending on the type of dopant and nature of the material (p type or n type), an increase or decrease in resistance will occur:
  • For p-type materials:
    • Electron Donors \(\rightarrow\) Resistance ↑
    • Electron Acceptors \(\rightarrow\) Resistance ↓
  • For n-type materials:
    • Electron Donors \(\rightarrow\) Resistance ↓
    • Electron Acceptors \(\rightarrow\) Resistance ↑

COF Thin Films

Top-down synthesis of thin films of COF-5 were attempted under both solvothermal and microwave conditions. Microwave conditions produced interesting results where selective nucleation occurs on MoCVD grown MoSe2 crystals, leading to a microwave induced effect due to selective excitation of the TMD crystals.

Devices

Devices are manufactured in-house, leveraging our expertise in materials synthesis. Resistance based measurements are carried out using custom made transducers. Our novel conversion of amorphous MoS2 via laser-induced crystallization into 2H-MoS2 and further transformation into MoO3 and MoO3. Refractive index changes are exhibited in our materials in our proprietary optical sensing devices.

Sensors with 2D organic and inorganic materials

Marriage of the sensitivity of the inorganic 2-D TMD surface with the selectivity of the organic COF surface. Differing material combinations will be employed in order to maximize performance.

Conclusions

We have demonstrated the ability to selectively attach imine-based and boronate ester COF selectively to TMD surfaces. These advances open the doors to future work in synthesis and development of novel Organic-Inorganic based 2D sensors.
Functionalization of Nanoparticles with Temperature and pH activated Smart Polymers for Controllable Self-Assembling Systems

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Smart Polymers

Smart polymers are high-performance polymers that can alter according to the environment they are in and they can respond to temperature, pH, light or other external stimuli. The surface modification of gold nanoparticles (AuNPs) with smart polymers has a diverse range of applications in self-assembled drug delivery, and sensing.

Smart Polymer Synthesis and Characterization

Thermosensitive Co-polymer Synthesis: Low critical solution temperature (LCST) thermosensitive co-polymers (pNIPAAm-co-pAAm) were synthesized using a disulfide initiator. Initiator allows for attachment to the gold nanoparticles (AuNPs) surface. By changing the ratio between two monomers, co-polymers with different LCST was successfully synthesized.

NMR: 1H-NMR measurements were used to confirm the co polymer structures.

LCST Determination: Using thermal UV-Vis measurements, the transition temperature (Tc) of synthesized co-polymers was determined.

DLS measurements: DLS data of co-polymer (Pj) showed the reversible temperature induced conformational change of the synthesized co-polymers.

pH-sensitive Co-polymer Synthesis: Stimuli responsive co-polymers (pNIPAAm-co-pAAm-co-pAAC and pNIPAAm-co-pAAm-co-p4VP) having a disulfide linkage were successfully synthesized through an Atom Transfer Radical Polymerization.

Co-polymer Capped ‘Smart AuNPs’

The co-polymers were attached to the AuNPs by reducing the disulfide linkage using TCEP. The reduced co-polymer in thiol form is then added to the AuNPs and incubated overnight. After purification, thermosensitive and pH-sensitive assembly is accomplished by changing the temperature above and below the polymer Tc. When T < Tc, polymer is hydrophobic. When T > Tc, polymer is hydrophilic and with the time AuNPs reversibly assemble.

Zeta Potential of the ‘Smart AuNPs’

Zeta Potential: Under basic to acidic conditions (3.1 < pH < 8.9), thermosensitive co-polymer (Pj) was shown to have a potential of +2 mV and PAAc/AuNPs system was shown to have a potential of +4.1 mV. Under similar conditions pAAC had a zeta potential of -0.7 mV and p4VP had a zeta potential of +11.1 mV. Also pAAC/AuNPs had a zeta potential of -15.9 mV and p4VP/AuNPs had a zeta potential of +14.9 mV.

Summary

The resulting thermo-responsive co-polymers have a transition temperatures (Tc) ranging from 43 °C to 52 °C. The thermo-responsive behaviour of the co-polymers allowed for the reversible self-assembly of the nanoparticles once they were grafted on to the AuNPs. The resulting pH sensitive co-polymers are sensitive to changes in both temperature and pH. The zeta potential analysis shows co-polymer with AAC is negatively charged and co-polymer with 4VP is positively charged with the magnitude of the charges dependent on each polymers pKa profile. Based on the self-polymer study, charge and the magnitudes of charge of co-polymer functionalized systems can be tuned by changing solution pH. This open new way for studying the electrostatic assembly of nanoparticles in charged systems.

References

Oriented attachment of CdSe/CdS nanoparticles

Oriented attachment is a useful crystal growth process in synthetic nanomaterials. However, it is limited by its irreversibility which causes defects at the attachment interface between two nanoparticles, such as dislocations, to be locked into place. To address this limitation, we sought to develop methods for facilitating dislocation removal in imperfectly attached nanoparticles. The introduction of chloride ligands to CdX (X=S, Se, Te) semiconductor nanoparticles has been shown to increase grain growth in nanocrystal thin films as well as lower the zinc-blend-wurtzite phase transition temperature upon annealing. In this work, dislocation removal in imperfectly attached CdSe/CdS core-shell nanocrystals with and without chloride surface ligands was studied using in-situ high-resolution transmission electron microscopy.

Chloride surface ligands were introduced to an aliquot of the parent nanoparticle solution via heating to <270°C for 1 hour in the presence of Cetyltrimethyl ammonium chloride (CTAC).

X-ray photoelectron spectroscopy (XPS) confirmed the presence of chlorine in the treated sample. No chlorine was observed in the untreated sample.

Post-CTAC treatment, the particles were observed to maintain their hexagonal prism shape and wurtzite crystal structure.

The wurtzite CdSe/CdS nanocrystals used had a hexagonal prism shape and were terminated predominantly with {1100} facets. Following treatment with (NH4)2S, oriented attachment was observed primarily on {1100} facets. In the case of imperfect attachment, \( b = \frac{a}{3} < \frac{1}{10} \) edge dislocations were observed.

In both cases, the observed removal mechanism was dislocation climb, with the edge dislocation moving out of its slip plane to traverse the shortest distance to the surface.

Successful dislocation removal was predominantly observed in the chloride-terminated sample. When full dislocation removal was observed in both chloride terminated and non-chloride terminated attachment cases, the chloride terminated samples showed faster removal times.

Future Work: Chloride treatment post-SILAR

We are interested to observe whether treating assembled arrays on CdSe/CdS nanoparticles with CTAC or another chloride-based ligand results in better attachment interfaces across the array as a whole, resulting in larger grain sizes with lower angle tilt boundaries.

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Stabilities of adsorption structures of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine on Au(111) surface

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Monolayers of 2,4,6-tris-(4-Bromophenyl)-1,3,5-triazine (TBPT) on Au(111) surfaces show several molecular arrangements, partially similar to the case of 1,3,5-tris(4-bromophenyl)benzene (TBPB) [1]. In the TBPB molecular array formation through solvent evaporation, a phase different from that observed at the solid-liquid interface [2] was found. This phase, in which Br-N interaction is apparently dominant, has low reactivity to dimerize [3]. In order to obtain well-extended covalent bonded molecular network, it is important to understand the origin of structural stabilities of molecular arrangement phases. In the present study, we focus on this low-reactivity phase and investigate molecule-substrate and intermolecular interactions using density functional theory (DFT) calculations.

Model construction for DFT calculations

First we focus on phase A. In the present study both gas-phase (pairwise) and adsorption were investigated.

-$\Delta E_{\text{molecular}} = E_{\text{TBPT, isolated}} - \left[ E_{\text{TBPT}} + E_{\text{Au}} \right]\$

<table>
<thead>
<tr>
<th>$\Delta E / eV$</th>
<th>Model</th>
<th>Threshold 1</th>
<th>Threshold 2</th>
<th>On-top</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-rotated</td>
<td>-2.97</td>
<td>-2.94</td>
<td>-2.93</td>
<td></td>
</tr>
<tr>
<td>Rotated</td>
<td>-3.08</td>
<td>-2.99</td>
<td>-3.17</td>
<td></td>
</tr>
</tbody>
</table>

Stabilization energies were about 3 eV for all cases. Especially the molecule-substrate interaction becomes strong when Br atoms occupy on-top sites.

Conclusion

- We experimentally observed and computationally investigated TBPT/Au(111) adsorption system.
- It is found that one molecular arrangement in which intermolecular Br-N interaction seems dominant (phase A) has high stability (low reactivity to form dimers).
- Therefore in this study we focused on the phase A to understand the origin of the stability.
- DFT calculations revealed the phase A has molecule-substrate interaction energy of 3 eV, while intermolecular stabilization energy is low. These results suggest that Br-Au interaction plays an important role to stabilize the phase A, consistent with the experimental findings.

References


Introduction

Monolayers of 2,4,6-tris-(4-bromophenyl)-1,3,5-triazine (TBPT) on Au(111) surfaces show several molecular arrangements, partially similar to the case of 1,3,5-tris(4-bromophenyl)benzene (TBPB) [1]. In the TBPB molecular array formation through solvent evaporation, a phase different from that observed at the solid-liquid interface [2] was found. This phase, in which Br-N interaction is apparently dominant, has low reactivity to dimerize [3]. In order to obtain well-extended covalent bonded molecular network, it is important to understand the origin of structural stabilities of molecular arrangement phases. In the present study, we focus on this low-reactivity phase and investigate molecule-substrate and intermolecular interactions using density functional theory (DFT) calculations.