



Organic phase synthesis of noble metal-zinc chalcogenide core-shell nanostructures

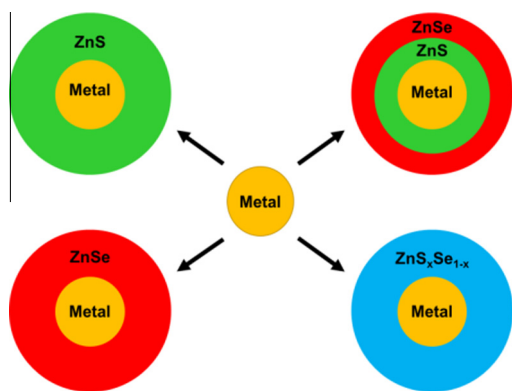


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GRAPHICAL ABSTRACT

We developed a general and robust strategy for the formation of metal (Au, Ag) – zinc chalcogenide core-shell nanostructures with various shell compositions.



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ABSTRACT

Multi-component nanostructures have been attracting tremendous attention due to their ability to form novel materials with unique chemical, optical and physical properties. Development of hybrid nanostructures that are composed of metal-semiconductor components using a simple approach is of interest. Herein, we report a robust and general organic phase synthesis of metal (Au or Ag)-Zinc chalcogenide (ZnS or ZnSe) core-shell nanostructures. This synthetic protocol also enabled the growth of more compositionally complex nanostructures of Au-ZnS_xSe_{1-x} alloys and Au-ZnS-ZnSe core-shell-shell. The optical and structural properties of these hybrid nanostructures are also presented.

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1. Introduction

The ability to control the Surface Plasmon Resonance (SPR) of metal nanoparticles is critical for scientific and technological

advancement in many areas including chemical and biological sensing, catalysis, energy harvesting and conversion, optoelectronics, and medicine [1–3]. In general, the nanoparticles' SPR is influenced by their size, shape, and the dielectric constant of their surrounding environment [4]. A promising strategy for tuning the latter is by growing a second material (metal organic frameworks (MOF), metal or semiconductor) on the metal nanoparticle to form a hybrid nanostructure, such as Pd-MOF [5,6], Au-Ag [7], Au-CdSe

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[8], Au-ZnO [9], Pd-Cu₇S₄ [10], Pt-Cu₂ZnSnS₄ [11], Ag-Ag₂S [12], Ag-Fe₃O₄ [13] and many others [14–20]. Formation of such nanostructures, especially with a core-shell (CS) configuration that maximizes the interface area between the two components, enables to tune the SPR absorption of the metal core over a wide range of wavelengths. As a consequence, exploration of synthetic strategies for growing metal-semiconductor CS hybrid nanostructures is of fundamental interest. Noble metal nanoparticles are among the most studied nanomaterials owing to their chemical stability and the existence of well-established protocols for their size and shape controlled synthesis. Au in particular have attracted much attention due to the fact that its SPR absorption lays in the visible region which makes it a good candidate for a variety of technological applications [21,22]. Several methods have been explored for the synthesis of CS hybrid nanostructures consisting of a Au core and a semiconductor shell [23–26]. However, only few reports on the coating of Au nanoparticles with ZnS or ZnSe shell materials were published. For example, the groups of Wang [27] and Hsu [28] synthesized Au-ZnS CS nanostructures using a hydrothermal approach while Yang et al. synthesized Au-ZnS CS nanostructures in aqueous medium at room temperature [29]. To the best of our knowledge to date there are no reports on the direct growth of ZnX (X = S, Se) shell on Au seeds in organic phase, although an indirect growth of ZnS shell was achieved by cation exchange of Ag ions in Au@Ag₂S hybrid nanostructures [30]. All reported attempts for such direct growth in organic solutions resulted in the formation of a dimer hybrid nanostructure [31,32].

Herein, we report an organic phase synthesis of metal (Au or Ag)-Zinc chalcogenides (ZnS and ZnSe) CS nanostructures. We also show the growth of ZnSe shell on Au-ZnS CS nanocrystals to form core-shell-shell (CSS) nanostructures (i.e. Au-ZnS-ZnSe). Furthermore, tuning the composition of the shell material by formation of Au-ZnS_xSe_{1-x} alloy with different S:Se ratios was achieved which signifies the robustness of our method. The optical and structural properties of the hybrid nanostructures were also studied.

2. Materials and methods

2.1. Materials

Zinc acetate (ZnAc₂, 99.99%), silver nitrate (AgNO₃, 99%), oleic acid (90%), oleylamine (70%), 1,2-dichlorobenzene (99%), didodecylmethylammonium bromide (DDAB, 98%), sodium borohydride (99%), sulfur (S, 99.98%), and 1-dodecanethiol (1-DDT, 99%) were purchased from Sigma Aldrich. Trioctylphosphine (TOP, 97%), Trioctylphosphine oxide (TOPO, 99%), selenium (Se, 99.99%), trioctylamine (TOA, 95%), and gold (III) chloride (AuCl₃, 99.9%) were purchased from Strem. Octadecene (ODE, 99%) was purchased from Alfa Aesar.

2.2. Methods

2.2.1. Synthesis of Au and Ag nanoparticles

Thiol capped Au nanoparticles were synthesized by following a previous report [33]. First, 0.093 g DDAB was dissolved in 10 ml toluene to make a 0.1 M DDAB stock solution. 0.034 g of AuCl₃ was dissolved in the DDAB solution with ultra-sonication to form a clear dark orange solution. In this solution 40 μl of 9.4 M NaBH₄ was rapidly injected and the solution color turned to purple within 1–2 min. After 20 min, 0.8 ml 1-DDT was added to the solution and the stirring was continued for 5 min. The synthesized nanoparticles were precipitated by the addition of methanol followed by centrifugation. The collected Au particles were further dispersed

in 10 ml toluene and 0.8 ml of 1-DDT, and the solution was refluxed at 113 °C for 30 min under N₂ atmosphere.

Ag nanoparticles were synthesized following a method that was developed by Polavarapu and Liz-Marzán [34]. In a typical synthesis, 0.051 g AgNO₃ (0.3 mmol) and 3 ml oleylamine were dissolved in 25 ml dichlorobenzene. The reaction mixture was sonicated until AgNO₃ was completely dissolved. The solution color changed from colorless to pale yellow upon sonication. The resulting solution was heated at 165 °C for 48 h and then was slowly cooled down to room temperature. The synthesized Ag nanoparticles were precipitated by the addition of toluene and methanol and collected after centrifugation.

2.2.2. Synthesis of Au-Zinc chalcogenides core-shell nanostructures

For the synthesis of Au-ZnS (Au-ZnSe) CS nanostructures, 30 mg of Au nanoparticles were well-dispersed in a mixture of 5 ml TOA, 27 mg (13.5 mg) zinc acetate, and 170 mg (85 mg) of oleic acid, and the mixture was stirred and degassed under N₂ atmosphere. Then, the solution was heated to 300 °C followed by injection of 0.5 ml of a TOP-S (TOP-Se) solution ([S] = 0.6 mmol/ml, [Se] = 0.3 mmol/ml) and the reaction was continued for 30 min at 300 °C.

For the growth of Au-ZnS_xSe_{1-x} alloy, the above procedure for Au-ZnS CS formation was repeated and was followed by injection of 0.5 ml of TOP-Se solution with different selenium concentrations (0.036 mmol/ml, 0.072 mmol/ml, and 0.29 mmol/ml). The TOP-Se was injected 3 min after the TOP-S injection.

For the synthesis of Au-ZnS-ZnSe CSS nanostructures, 81 mg of zinc acetate and 510 mg of oleic acid were mixed well in 5 ml TOA with 30 mg of Au nanoparticles. The solution was stirred well and heated to 300 °C under N₂ atmosphere and then 0.5 ml of TOP-S ([S] = 0.3 mmol/ml) was injected. The reaction was continued for 30 min followed by injection of 0.5 ml of TOP-Se (0.6 mmol/ml). After 30 more minutes the reaction was stopped.

Au-ZnS CS nanostructures were synthesized by injecting 0.5 ml TOP-S ([S] = 0.6 mmol/ml) in 5 ml TOA solution of 30 mg Ag nanoparticles, 27 mg zinc acetate, and 170 mg oleic acid at 300 °C and the reaction was continued for 30 min.

2.2.3. Structural characterization

Transmission electron microscopy (TEM) was done using an FEI Tecnai 12 TWIN microscope, operated at 120 kV. High resolution TEM (HRTEM), high-angle annular dark field - scanning transmission electron microscopy (HAADF-STEM), and elemental mapping via energy dispersive X-ray spectroscopy (EDS) were performed using a JEOL 2100 microscope operated at 200 kV. The X-ray diffraction (XRD) data was collected by an empyrean powder diffractometer (Panalytical) equipped with position sensitive (PSD) X'Celerator detector using Cu Kα radiation (λ = 1.5418 Å) and operated at 40 kV. Energy-dispersive X-ray spectroscopy (EDS) was done using a JEOL SM-7400F HRSEM equipped with Thermo Scientific NORAN System SIX. UV-Vis absorbance measurements were made using a Cary 5000 UV-Vis-NIR spectrophotometer.

3. Results and discussion

Fig. 1(a and b) show the representative TEM images of the synthesized Au-ZnS nanoparticles with ZnS shell thicknesses of 6 ± 2 nm and 8 ± 2 nm, respectively; control over the shell thickness was achieved by varying the reaction time from 15 min to 30 min, respectively. Growth of a thin ZnS shell (~3.5 nm) was also observed after 5 min (Fig. S1). The clear contrast between the inner part of the particles and their periphery supports the existence of a CS structure. Here it should be noted that we did not obtain any plain particles of ZnS or a growth of ZnS on multiple Au cores.

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