

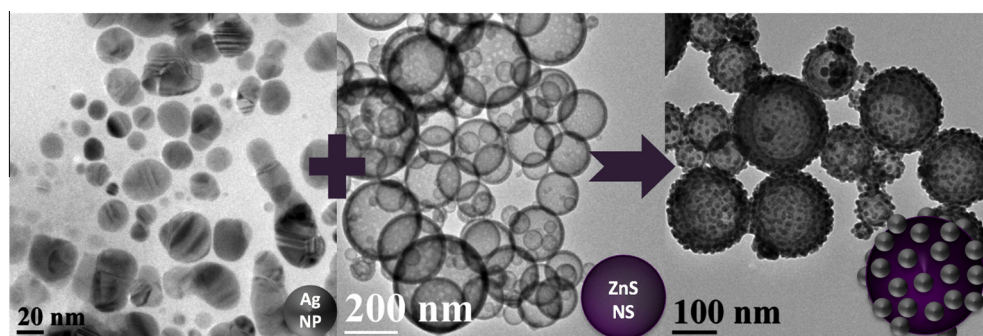
# Core–satellite ZnS–Ag nanoassemblies: Synthesis, structure, and optical properties



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## GRAPHICAL ABSTRACT



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## ABSTRACT

We synthesized hollow core–satellite nanoassemblies comprised of hollow zinc sulfide (ZnS) shells decorated with silver nanoparticles (Ag NPs). This was achieved by solution-phase attachment of Ag NPs to hollow ZnS nanospheres (NSs) prepared by spray pyrolysis. This produces an aqueous dispersion of ZnS–Ag hybrid structures, 50–500 nm in overall diameter. We characterized the nanostructures by scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDX) to elucidate the ZnS (core)–Ag (satellite) morphology and optimize conditions for producing such structures. Optical spectroscopy showed that photoluminescence of ZnS was quenched by Ag while absorbance was enhanced. This work provides a simple and general means of producing hollow core–satellite structures that could be of broad applicability.

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## 1. Introduction

ZnS is a II–VI semiconductor with direct bandgap of 3.67 eV that can be widened up to 3.94 eV [1]. It is used as a photocatalyst, as a phosphor with a strong emission peak at 410 nm, and in anti-reflection coatings due to its high refractive index ( $n \approx 2.35$ ) [2–5]. At the nanoscale, optical and catalytic properties can differ

from bulk properties, due to quantum confinement and high surface area to volume ratio. Recent interest in ZnS nanoparticles (NPs) has been enhanced by their expected low toxicity [6], compared to heavy-metal-containing semiconductors such as CdS, CdSe, PbS, and PbSe. Researchers have doped ZnS NPs with metals including Mn, Ce, In, Cu, Ni, Ag, and Au to tune optical and catalytic properties [7–12]. The metal ions introduce donor states within the wide bandgap of ZnS, inducing optical transitions (absorbance and emission) at longer wavelengths. Several groups have also used carbon nanotubes (CNTs), TiO<sub>2</sub>, and metals as electron traps in ZnS-based photocatalysts [12–14]. These hybrid structures have

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potential for applications ranging from photocatalysis, to drug delivery to fluorescent contrast agents for bioassays and bioimaging [5,15–17].

In this work, we coupled Ag NPs onto the surface of ZnS nanostructures; an approach that is distinct from doping with metal ions, but that can likewise be used to change electrical and optical properties. Ag NPs provides electron trapping sites that can reduce the radiative recombination of excitons generated by light absorbance in the ZnS. The work function of Ag (4.26 eV) places its Fermi level below the conduction band edge of ZnS (bulk electron affinity of 3.46 eV) but far above the valence band edge of ZnS (bulk ionization potential of 7.06 eV). Thus, photogenerated holes stay in the ZnS domain, while photogenerated electrons rapidly transfer from the conduction band of ZnS into Ag. Other metals could be used, but silver is well-suited here because it is readily prepared as stable nanoparticles that can be attached to the ZnS, and it is reasonably chemically stable (noble or inert) without being exceptionally expensive (relative to gold, platinum and other noble metals). The Ag NPs also have a localized surface plasmon resonance near 400 nm which could potentially enhance absorbance by the hybrid nanostructures. Therefore, coupling ZnS with Ag NPs could potentially enhance the photocatalytic activity of ZnS, which has shown promise for pollutant degradation. The Ag NPs are also expected to impart anti-bacterial properties. We employed a two-step approach that combines spray pyrolysis with wet chemistry to synthesize Ag-decorated ZnS nanospheres (NSs). In the first step, we synthesized hollow and porous ZnS NSs using a spray pyrolysis reactor with poly ethylene glycol (PEG) polymer as a sacrificial template. In the next step, Ag NPs were coupled onto the hollow ZnS spheres in solution. Spray pyrolysis is a continuous, scalable, and low cost process to synthesize NPs using droplet-to-particle conversion, and this is the approach we have employed here to create hollow ZnS NSs [18].

## 2. Experimental section

Zinc acetate dihydrate (Fisher Scientific) and thiourea (Fisher Scientific) dissolved in deionized water were used as precursors for spray pyrolysis. Poly (ethylene glycol) methyl ether (MW 5000, Aldrich) was used to template hollow NSs. Hexadecyl trimethyl ammonium bromide (CTAB, FW 364.45, 99% pure, Acros Chemicals) was used to prepare colloidal dispersion of the ZnS NSs in water. Precursors used in the preparation of colloidal Ag NPs included AgNO<sub>3</sub> (ACS reagent, ≥99.0%, Acros Organics) and NaBH<sub>4</sub> (ACS reagent ≥99.0%, Fluka).

### 2.1. Preparation of colloidal Ag nanoparticles

The colloidal Ag NPs were prepared by chemical reduction of AgNO<sub>3</sub> with NaBH<sub>4</sub> following an established approach [19]. We dissolved 27.17 mg AgNO<sub>3</sub> in 160 mL milli-Q water to produce a 1 mM AgNO<sub>3</sub> solution. We also dissolved 12.10 mg NaBH<sub>4</sub> in 160 mL milli-Q water in an Erlenmeyer flask inside an ice bath, to produce a 2 mM solution. 10 mL of AgNO<sub>3</sub> solution was added at a rate of ~1 mL/s into 30 mL of the NaBH<sub>4</sub> solution, in an ice bath with constant stirring. Upon addition of AgNO<sub>3</sub>, the solution turned yellow, indicating formation of colloidal Ag NPs.

### 2.2. Synthesis of ZnS nanospheres

We recently presented a comprehensive study of the synthesis of ZnS NSs with different morphologies by spray pyrolysis, and followed the same procedures using the same apparatus here [18]. Fig. S1 shows a schematic of the spray pyrolysis reactor system. Hollow ZnS NSs were synthesized from zinc acetate dihydrate and

thiourea. In a typical experiment, we dissolved 0.878 g zinc acetate, 0.609 g thiourea, and 0.5 g PEG in a total of 160 mL of Milli-Q water. The precursors were sprayed by a pressure-driven atomizer (Collision type, BGI, Waltham, MA, three-jet model) using industrial grade nitrogen (99.8%) as the carrier gas. Solvent evaporation and particle formation took place in a reactor constructed from one-inch diameter (2.2 cm inner diameter) Inconel tubing with a heated length of 76 cm and a furnace setpoint temperature of 700 °C. The gas flow rate through the atomizer was about 7 L/min.

### 2.3. Preparation of core-satellite ZnS-Ag nano-assemblies

An aqueous solution of 0.97 mM CTAB was prepared by adding 57 mg of CTAB into 160 mL milli-Q water and sonicating for 1 h. Then, 20 mg of hollow ZnS spheres were added to the CTAB solution and it was sonicated for an additional hour. Aliquots of 5, 15, 25, or 35 mL of this ZnS dispersion were slowly added to 35 mL of the Ag NP dispersion. The mass concentration of Ag in its dispersion is about 27 mg L<sup>-1</sup>, while the mass concentration of ZnS in its dispersion is about 125 mg L<sup>-1</sup>. Thus, the Ag:ZnS mass ratios in the final mixtures were about 1.5, 0.50, 0.30, and 0.22. The mixture of ZnS and Ag NPs was stirred at room temperature for 8 h in an Erlenmeyer flask before further characterization.

The size and shape of the NPs were characterized by high-resolution transmission electron microscopy (HRTEM, JEOL model 2010). Selected-area electron diffraction (SAED) was also performed in the TEM. Grids were prepared for imaging by dropping the dispersion onto a carbon-coated TEM grid and allowing it to dry in air. UV-vis spectra were measured using a Shimadzu UV-3101PC UV-VIS-NIR scanning spectrophotometer. Photoluminescence emission (PL) spectra were measured using a Shimadzu RF-5301PC spectrofluorometer. The surface morphology and surface composition were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using an AURIGA Cross Beam Workstation (FIB-SEM) from Carl Zeiss SMT with an Oxford Instruments X-Max 20 mm<sup>2</sup> EDS detector. Back-scattered electron imaging was done using a Hitachi SU-70 scanning electron microscope. Electrical conductivity measurements were made using a four-point probe with a Keithley 2400 sourcemeter. Wide-angle powder X-ray diffraction (XRD, Rigaku Ultima IV X-ray diffractometer with Cu Kα source) was used to characterize the crystalline phases present.

## 3. Results and discussion

### 3.1. SEM and TEM analysis of size and morphology

Fig. 1a shows the typical size and morphology of the Ag NPs produced by aqueous reduction of AgNO<sub>3</sub> with NaBH<sub>4</sub>. Additional characterization of these NPs is provided in supporting information, Fig. S2. The Ag NPs are somewhat polydisperse and irregular, as is typical of this aqueous synthesis method. Fig. 1b shows a TEM image of hollow ZnS NSs showing polydispersity in size and uniformity of shape of the hollow particles. The maximum diameter of the ZnS spheres is near 250 nm. This ZnS NP size distribution is a direct reflection of the droplet size distribution produced by the atomizer used in spray pyrolysis. Supporting information Figs. S3 and S4 provide further characterization of the hollow ZnS NSs.

The Ag NPs are stabilized by adsorption of borohydride (BH<sub>4</sub><sup>-</sup>) on their surface, which provides a negative surface charge. The electrostatic repulsion between negatively charged NPs stabilizes their colloidal dispersion. Similarly, the cationic CTAB (C<sub>19</sub>H<sub>42</sub>N<sup>+</sup> or CTA<sup>+</sup> dissociated from the Br<sup>-</sup> counterion) adsorbed on the surface of the ZnS NPs provides a positive charge, with the hydrophilic cationic head group exposed to the solvent. Mixing the two

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