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Enhanced photocatalysis by hybrid hierarchical assembly of plasmonic nanocrystals with high surface areas

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ABSTRACT

This paper reports the synthesis of hierarchical assemblies of Au nanocrystals (and AgI nanocrystals) in the Fe_3O_4–SiO_2–Au–Ag–AgI composite particles through the use of AuI_4^- ions as the critical precursor in a wet chemical approach. Both the reduction of AuI_4^- ions by ascorbic acid and the galvanic replacement reaction between AuI_4^- ions and Ag domains occur simultaneously during the synthetic process to ensure the formation of hierarchical assembly of small Au nanocrystals with high surface areas. In combination with the strong absorption of visible light corresponding to the surface plasmon resonances (SPRs), these composite particles exhibit enhanced photocatalytic performance under visible illumination in comparison to the Au or Ag nanoparticles without the hierarchical morphologies. This study indicates that carefully engineering the morphology and assembly configuration of plasmonic nanocrystals to expose high surface areas can improve their photocatalytic activities toward the utilization of visible light.

1. Introduction

Photocatalysis using excited electrons and holes for the reduction and/or oxidation of chemicals under light irradiation has been widely used for energy and environmental applications such as water splitting, waste treatment and solar fuel generation [1–3]. As the most widely used photocatalysts, semiconductors such as metal oxide (e.g. TiO_2) [4] and II–IV semiconductors (e.g. CdS and CdSe) [5] have been intensively studied. Due to the limited absorption of TiO_2 in visible regime [4] and cytotoxicity of cadmium [6], preparation of nontoxic and efficient visible-light-driven photocatalysts becomes more and more important. Recently, noble nanoparticles such as Ag with strong surface plasmon resonances (SPRs) in the visible range have been demonstrated as novel photocatalysts for degradation of organic pollutants [7–10]. The plasmon-induced photocatalytic activity can be attributed to the energized conduction electrons and the excitation of them to higher energy states which can be utilized for chemical reactions [7]. In addition, the surface plasmon polarizes the reactant molecules in the solution, enhances their adsorption to the metal surface and heats up the local environment for increased mass transfer of the molecules and the reaction rates [11]. As a result, noble metal structures with large surface area can increase the contact area with reactants and effectively generate charge-carriers under illumination of visible light for photocatalysis.

The SPRs in noble metal nanoparticles strongly depend on their size, shape, composition and surrounding environment [12]. It has been reported that the SPR absorption of Au nanoparticles can be greatly tailored by tuning their morphology [13]. Gold nanostructures with hyperbranched architectures have drawn great attention due to their broad-band SPR absorption and high surface areas, which are attractive for applications in catalysis, biosensing and nanoelectronics [14–16]. In the past years, there are limited techniques for making Au nanostructures with hierarchical architectures because of the involved synthetic challenges significantly different from the synthesis of regular colloidal nanoparticles. Up till now, most hyperbranched architectures are created by controlled deposition of the corresponding precursors onto substrates. The resulting structures are confined to the substrate surfaces and the yield is low [17]. In comparison, solution-based syntheses provide a more scalable route for branched nanostructures. One example is the formation of hyperbranched Au nanostructures consisting of aggregated nanoparticle through a fast electroless metal deposition route in aqueous solutions [18]. Chen group developed a multi-generation strategy for growing 3D hyperbranched Au nanostructures with the assistance of pyrrole [19]. For potential application such as catalysis, it is highly desirable to realize a controlled synthesis of rationally designed hyperbranched Au structures with high surface areas.

Herein, we present an effective method based on wet chemical processing to produce Fe_3O_4–SiO_2–Au–Ag–AgI hierarchical

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structures assembled by hyperbranched metallic Au (and AgI) on magnetic Fe_3O_4–SiO_2 colloidal substrates. Our strategy involves two competitive reactions to facilitate the growth of the hierarchical structures: (1) the reduction of AuI_4^- by ascorbic acid and (2) the controlled galvanic replacement of Au over Ag domains that are immobilized on the surfaces of Fe_3O_4–SiO_2 colloids. The resulting structures exhibit large surface areas and strong SPR absorption in the visible regime. The enhanced light absorption facilities the creation and separation of active electron-hole pairs to increase efficiency in driving photocatalytic reactions. In addition, the localized heating effect on the surfaces of the Au nanostructures can also boost the fluid mixing and increases the reaction rate. The hybrid hierarchical structures remain good dispersibility and stability in the aqueous dispersions and can be easily scaled up, making them good candidates as photocatalysts.

2. Materials and methods

2.1. Chemicals

Ethanol (denatured), isopropanol (99.9%), ammonium hydroxide aqueous solution (28%) and sodium hydroxide (Certified, A.C.S. grade) were purchased from Fisher Scientific. 3-Aminopropyl-triethoxysilane (APTS, 99%), potassium iodide (KI), and polyvinylpyrrolidone (PVP) K12 ($M_w \approx 3500$) were obtained from Acros Organics. Poly (acrylic acid) (PAA, $M_w \approx 1800$), tetraethyl orthosilicate (TEOS, 98%), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9+%), sodium citrate tribasic dihydrate (99%), silver nitrate ($AgNO_3$, ≥99.0%), acetonitrile (anhydrous, 99.8%), diethylene glycol (DEG), L-ascorbic acid, and methylene blue (MB) were purchases from Sigma–Aldrich. PVP K15 ($M_w \approx 10{,}000$) was purchased from Fluka. All chemicals were used as received without further purification and treatment.

2.2. Synthesis of Fe_3O_4–SiO_2 core–shell particles decorated with Au nanoparticles

The synthesis followed the processes reported previously [20]. In detail, superparamagnetic Fe_3O_4 nanoparticles were firstly synthesized via a combination of controlled hydrolysis and reduction of $FeCl_3$ in basic diethylene glycol (DEG) [21]. PAA was added to the reaction system to serve as surfactant for stabilizing the resulting Fe_3O_4 nanoparticles. The as-synthesized Fe_3O_4 nanoparticles were then coated with a silica layer through a modified Stöber process, in which 20 mL of ethanol was mixed with 3 mL aqueous dispersion of Fe_3O_4 nanoparticles (~23 mg Fe_3O_4). To this mixture was added 1 mL of ammonium hydroxide aqueous solution (28 wt.%), followed by an injection of 0.1 mL of TEOS to initiate the deposition of silica on the surfaces of the Fe_3O_4 nanoparticles. The resulting Fe_3O_4–SiO_2 core–shell particles were collected through centrifugation after the Stöber reaction proceeded for 20 min. The collected core–shell particles were then washed with ethanol for two times to remove the chemical species adsorbed on the silica layer. In the next step, the clean silica surface was modified with amino groups by incubating the core–shell particles in 20 mL of isopropanol containing 50 μL of APTS at 80 °C for 2 h. The modified particles were collected, washed, and re-dispersed in 3 mL of deionized (DI) water. Finally, mixing 1.5 mL of the modified core–shell particles with 20 mL aqueous dispersion of citrate stabilized Au nanoparticles (described as Au seeds for clarification in the following contents) led to the adsorption of Au seeds on the Fe_3O_4–SiO_2 core–shell particles with the assistance of strong sonication. The Fe_3O_4–SiO_2 core–shell particles decorated with Au seeds were collected by applying an external magnetic field that interact with the superparamagnetic Fe_3O_4 cores, resulting in the easy separation from the free-standing Au seeds. The collected composite particles were then washed, and re-dispersed in 1 mL of DI water. The Fe_3O_4–SiO_2 core–shell particles decorated with the Au seeds was then coated with a second SiO_2 layer through the similar Stöber method. By controlling the reaction time, the Au seeds could be partially embedded in the silica matrix. The particles were then collected, washed, and re-dispersed in 1 mL of water for use. The entire synthesis was performed at room temperature in ambient environment.

2.3. Overgrowth of Ag on the Au seeds

The composite particles formed through step 2.2 had the Au seeds partially exposed to the surrounding environment, which promoted a seed – mediated growth of Ag on the Au seeds. In a typical seeded growth reaction, 4 mL of DI water, 1 mL of acetonitrile, 500 μL of aqueous PVP K12 solution (5% in weight), 1 mL of sodium citrate solution (0.1 M), 400 μL of aqueous ascorbic acid solution (0.1 M), and 300 μL of aqueous $AgNO_3$ solution (0.01 M) were sequentially added to a 20 mL vial under continuous magnetic stirring to form the growth solution. To this growth solution was injected 150 μL of the particles synthesized in step 2.2 to trigger an immediate growth of Ag domains on the Au seeds, accompanied by a significant color change from colorless to light pink, boysenberry, then blue–purple, and finally gray brown. After 10 min of growth reaction, the Fe_3O_4–SiO_2–Au–Ag composite nanoparticles were separated from solution with the assistance of an external magnetic field and washed with water. Finally, the product was dispersed in 5 mL of water. The entire synthesis was performed at room temperature in ambient environment.

2.4. Synthesis of Fe_3O_4–SiO_2–Au–Ag–AgI hierarchical structures

A modified galvanic replacement reaction of the Ag domains was used to generate the hierarchical structures. In a typical reaction, 4 mL of DI water, 400 μL of aqueous PVP K12 solution (5% in weight), 400 μL of aqueous KI solution (0.2 M), and 30 μL of aqueous $HAuCl_4$ solution (0.1 g/mL) were sequentially added to a 20 mL vial under continuous magnetic stirring to form the reactant solution I. In this solution, the I^- ions could coordinate with Au(III) to form AuI_4^- ions. To form the reactant solution II, 400 μL of aqueous ascorbic acid solution (0.1 M) was added to 5 mL aqueous dispersion of the Fe_3O_4–SiO_2–Au–Ag composite nanoparticles synthesized by step 2.3. The reactant solution I was then injected to the reactant solution II drop by drop and the color changed from gray brown, dark gray to gray black. Aliquots were taken at different reaction stages when different amount of reactant solution I was added. The particles were collected with the assistance of an external magnetic field and washed with water. The final product was dispersed in 2 mL DI water for characterization and photocatalysis. The entire synthesis was performed at room temperature in ambient environment.

2.5. Characterization

A JEOL 2010F(s) transmission electron microscope was used to characterize the morphology of the particles. To prepare a TEM sample, a drop of the aqueous particle dispersion was delivered to a carbon-coated copper grid with the use of pipette, followed by drying in a fume hood at room temperature. The TEM images were obtained at 200 kV operation voltages. The energy dispersive X-ray spectra (EDS) were collected with an INCA X-ray microanalysis system equipped on JEOL 2010F(s) transmission electron microscope. A VARIAN CARY-50 spectrophotometer was used to record the absorption spectra of dispersions of the synthesized particles.