Immobilization of Silver-based Bimetallic Nanoparticles on Titania-Support for Photocatalysis

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Abstract. Photocatalysts have potential for many applications including environmental remediation and selective catalytic transformations requiring decreased energy consumption. This study presents a systematic approach for the synthesis, characterization, and evaluation of titania-supported silver-based bimetallic nanoparticles. Titania was selected as a support due to its ability to form electron-hole pairs in the presence of appropriate radiation. This process is expected to be enhanced in the presence of silver-based bimetallic through the visible light absorption of its surface plasmon resonance. This work has been described the synthesis of silver-based bimetallic nanoparticles using colloid chemistry and the subsequent immobilization onto titania to form composite photocatalytic materials. The photocatalysts are characterized by electron microscopy, nitrogen physisorption, and x-ray diffraction. The work will also describe computational modeling of the silver-based particles surface plasmon resonance features. The results will be applied to photocatalytic environmental remediation.

1. Introduction

Photocatalysis is an emerging area for a range of applications including energy and environmental remediation [1-5]. The current application is aimed at composite photocatalysts for the energy efficient environmental remediation of hydrocarbon pollutants. This topic is of great interest to global society. The current effort is the use of surface plasmon resonance of silver-based nanoparticles as a method for converting visible sunlight into energy for activating titanium dioxide. Surface Plasmon resonance (SPR) phenomena have been identified as means for absorbing visible light for silver and gold particles. The absorption wavelength of the material changes with particle morphology, which is generally altered by modifying the particle morphology. Common morphology parameters are particle size, shape, and aspect ratio.

The synergistic combination occurs by having the plasmonic material assist titanium dioxide in generating electron-hole pairs for the decomposition of the targeted pollutants in water. Recent work [4] has shown 10 times rate enhancement for the photocatalytic decomposition of model organic molecules through the synergistic combination of silver (visible light adsorption) and titania (photocatalytic agent for splitting water spurring hydrocarbon decomposition). A further expected enhancement is expected by combining the plasmonic material with a catalytically active material.
Platinum is the leading and applied candidate for many catalytic reactions [6-8] and, thus, it is used a model catalyst material in the present study. The use of bimetallic particles may allow for the control of visible light absorption so that then entire range of visible light can be used for the photocatalytic hydrocarbon decomposition reactions. The demonstration of this control has occurred in previous studies of bimetallic particles. The surface plasmon resonance peak is a strong function of alloying in silver-copper nanoparticles and its position can be controlled. That is, it can be shifted towards absorption in the visible spectrum [9-10]. By modifying the composition and the atomic arrangement we can tune both the breadth and the location of the peak of the SPR spectrum of silver-copper alloy nanoparticles and thereby absorb a larger portion of the sunlight.

Recently, Christopher et al. [4] have shown that plasmonic silver nanocubes, characterized by excellent absorption of visible light through the creation of resonant surface plasmons can utilize concurrently thermal energy and a low-intensity photon flux (on the order of solar intensity) to drive catalytic oxidation reactions at significantly lower temperatures than those associated with conventional thermal processes. They demonstrated for the first time that metallic nanostructures can couple efficiently thermal energy and low-intensity visible photons to drive commercially important catalytic reactions; these results open new avenues towards the design of more energy-efficient catalytic processes with a significant fraction of energy input provided in the form of sunlight; the results suggest that, potentially, the long-term stability of catalysts and product selectivity could be enhanced because the reactions can be operated at low temperatures. Although the Ag nanocubes drastically enhance the absorption of visible light by the creation of resonant surface plasmons, the SPR peak is near the UV region and hence, there is lower utilization of the visible light spectrum of the sunlight.

Advances in nanotechnology now permit avenues to control the size, shape, and aspect ratio of the plasmonic materials. Great developments in this field have occurred in the recent years [11-14]. In particular, a great devotion of effort has focused on key catalytic metals which include platinum and rhodium [15-19]. In the present study, the size control of platinum-silver nanoparticles is demonstrated. The combination of a plasmonic metal (silver) and a catalytic metal (platinum) is proposed a powerful approach for developing the next-level materials for photocatalytic applications.

2. Materials and Methods
The synthesis of all particles follows the same general procedure and is outlined in each of the following sections. The overall process is also described in Figure 1.

![Figure 1. Synthesis of platinum, silver, and platinum-silver nanoparticles.](image)
2.1. Synthesis of Pt Nanoparticles
Platinum nanoparticles, approximately 3 nm in size, were synthesized using previously established mechanisms [17, 20]. Solvents used in this synthesis were reagent grade chemicals from Sigma-Aldrich. Chloroplatinic acid (H₂PtCl₆; Sigma-Aldrich; mass of 62.15 mg) was combined with 20 ml of distilled water. Methanol (180 ml) was added to the fully dissolved acid solution in a round bottom flask. Subsequently, polyvinylpyrrolidone (PVP MW: 40,000 g/mol; Sigma-Aldrich; mass of 133 mg) was added and the solution, refluxed for three hours at 110°C. The solution turned dark brown during this process. Following the synthesis, the solvent was evaporated from the particles at 55°C and the particles were re-dispersed in ethanol. The particles were washed with hexane and re-dispersed in ethanol three times. For each washing, 3 ml of the ethanol – particle solution was combined with 9 ml of hexane and centrifuged (VWR clinical 100 centrifuge) at 3000 rpm for 10 minutes.

2.2. Synthesis of Ag Nanoparticles
The above procedure for Pt nanoparticles was repeated using the equivalent Ag precursor molar concentration as to that of Pt. The precursor was AgNO₃ (Sigma-Aldrich). Following reduction, the solution turned an orange-yellow type color due to the surface plasmon resonance phenomena of Ag nanoparticles.

2.3. Synthesis of Ag-Pt Bimetallic Nanoparticles
The above procedure for Pt nanoparticles was repeated using the equivalent total metal concentration. The molar ratio of Pt: Ag was 1: 1 in precursor solution. The precursor was AgNO₃ (Sigma-Aldrich). The solution turned dark brown during the reduction process.

2.4. Synthesis of Ag-Pt Mixture Nanoparticles
Monometallic Pt (section 1) and Ag (section 2) nanoparticles were physically mixed as colloidal solutions after washing. The molar ratio of Pt: Ag was 1 : 1 in the resulting mixture.

2.5. Immobilization of Nanoparticles onto Titania Supports
The particles for each above synthesis were immobilized onto titania (Alfa-Aesar). The particles were supported by mild sonication for 3 hours at a metal: titanium dioxide mass ratio of 0.3%: 99.7%. Following sonication, the composite materials were dried with mild heating on a hot plate (T ~ 60 °C) and then in a drying oven (T ~ 90 °C).

2.6. Characterizations
Particle images were obtained using a FEI Morgagni 268D microscope. In addition to imaging, particle size distributions were obtained by measuring the size of 100 particles for each sample using the imageJ freeware, which was downloaded from the NIST site. Nitrogen physisorption was performed on a Quantachrome Autosorb I. The surface area determined using the standard BET analysis.

3. Results and Discussions
The particle imaging results are shown in Figures 2, 3, and 4, respectively, for platinum, silver, and platinum-silver bimetallic particles. In each case, the left sub-figure shows the particles with a scale bar of 500 nm and the right sub-figure shows the particles with a 200 nm scale bar.
Figure 2. TEM images of platinum nanoparticles (Scale bar (A) is 500 nm and (B) is 200 nm).

Figure 3. TEM of silver nanoparticles (Scale bar (A) is 500 nm and (B) is 200 nm).

Figure 4. TEM of silver-platinum bimetallic Nanoparticles (Scale bar (A) is 500 nm and (B) is 200 nm).
The statistics of the particle sizes are compiled in Figure 5. The platinum particles (Figure 2) possessed a range of sizes between ~1.5 and 4 nm with an average near 3 nm. The size distributions are consistent with previous work on this synthesis system for platinum [15, 17]. As with the previous work, washing is very important to cleaning the metal surface from surfactant. The three cycles of ethanol-hexane washing removed more than 95% of excess carbon [15]. Following the synthesis, the platinum particles gave a black color, which indicates that it does not absorb visible light (expected for platinum). The size distributions of these particles (and all particles in this work) yield, using a common model in metal particle catalysis [8], a surface-to-bulk ratios or dispersions of 25 to 33%. That is, between a quarter and a third of the particles are available for catalysis because they are located at the surface of the particles.

![Figure 5. Size distribution statistics obtained from counting 100 synthesized nanoparticles. SD is the standard deviation.](image)

With slight modification, the synthesis approach was adapted to silver. Following the synthesis, the silver particles in solution yield an orange color, which would be consistent with a SPR peak near 590 nm. The silver particles (Figure 3) were slightly larger than the monometallic platinum particles. The bulk portion of the particles was of similar size. The size distribution was skewed to a large particle size because a small minority of particles existed near a particle size of about 10 nm. Interestingly, the bimetallic platinum-silver particles (Figure 4) were more similar in size to platinum than to silver. This relationship implies that the platinum particles may act as nucleation sites for the subsequent growth of silver on its exterior. Advanced characterization studies are currently being performed to better assess the location of silver and platinum in the particles. The particles also yielded a black color, which indicates the platinum dominates silver's optical properties. A physical mixture of monometallic platinum and silver particles is also included. As expected, the results are in very good agreement with the parent compounds.

The four sets of particles described were immobilized on titania for further characterization. The surface area analyses for the particles supported on titania are presented in Figure 6. For comparison, the same particles supported a commercial silica (Cab-O-Sil) is presented. The results showed that the addition of the particles to supports, in general, caused a slight increase in the total surface. The effect is observed with great change when silver is added to the support. These particles are being
investigated for photocatalytic conversion of model pollutants and the results are presented in a separate paper at this conference.

![BET Surface Area, m2/g](image)

**Figure 6.** Specific Surface areas of silver, platinum, bimetallic silver-platinum, mixtures of silver and platinum particles supported on titania. A comparison to silica supports is included for comparison.

### 4. Conclusions
Photocatalysis powered by light through surface plasmon resonance (SPR) is a growing approach for the best use of the world’s resources whether it is through energy or environmental applications. The properties of the light-absorbing metals can be enhanced by the synthesis of composite materials in which a semi-conductor is in intimate contact with the (SPR). The current work directly addresses this important issue by the advanced synthesis of SPR metals (silver and silver-platinum) and immobilization on titania. The silver, platinum, and silver-platinum particles were synthesized with good control of the particle size. After effective washing of the surfactant, the particles were successfully immobilized onto a photoactive titania for use in a range of catalytic and photocatalytic applications. The materials developed in this work are active for photocatalysis applications and this topic is the focus of a separate paper [21].

### Acknowledgements
The authors gratefully acknowledge King Abdulaziz University (KAU, Saudi Arabia) for funding this work through the cooperation agreement with University of South Florida, USA (KAU-USF).

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