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Synthesis and Characterization of Silver/Titanium dioxide Core-Shell Nanoparticles

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ABSTRACT

Silver nanoparticles (AgNPs) with mean diameter of 150 nm were synthesized by using an aqueous-based reduction method. Ascorbic acid and sodium hydroxide (NaOH) were used as a reducing agent and as a catalyst, respectively. These AgNPs were subsequently coated with a layer of TiO_2 to form Ag/TiO_2 core-shell nanoparticles by using a sol-gel method. The particle sizes and morphology of Ag/TiO_2 core-shell nanoparticles were characterized using scanning electron microscopy (SEM) and transition electron microscopy (TEM). The photocatalytic activity of the Ag/TiO_2 core-shell nanoparticles were evaluated based on the degradation of methylene blue (MB) as the model reaction. The TiO_2 coating has resulted in the enhanced photocatalytic activity of Ag nanoparticles as compared to bare Ag nanoparticles.

Keywords**:** Silver Nanoparticles, Titanium Dioxide, Photocatalyst, Core-Shell Nanoparticles

INTRODUCTION

In recent years, core-shell nanostructures have received great interest and attention due to the synergistic effects of the cores and shell that give rise to new and improved properties that neither individual material possesses. Although silver nanoparticles (AgNPs) have been widely studied for their catalytic activity, AgNPs have not been used widely in industry due to its unsatisfactory catalytic activity (Zheng *et al*. 2012). On the other hand, TiO_2 nanoparticles have been well recognized as promising materials for various photocatalytic applications due to their high photostability and strong oxidizing power of its holes (Gelover *et al*. 2006). Combination of Ag and TiO_2 nanostructures displayed enhanced optical and catalytic properties due to electron transfer reactions between the Ag and photoexcited TiO_2 (Vaidya *et al*. 2012). Alenzi *et al* (2010) have demonstrated that Ag/TiO_2 core-shell thin films can served as a highly efficient photocatalyst for solar hydrogen production from water-splitting. Various synthetic approaches such as water-in-oil emulsion (Ganguli *et al*. 2010), vapor-thermal (Cheng *et al*. 2010) and organic synthesis approaches (Tom *et al*. 2003) have been developed for the preparation of Ag/TiO_2 core-shell nanoparticles, However, these methods are expensive and not environmental friendly due to high reaction temperatures as well as the usage of large amount of organic solvents and surfactants in the synthesis processes. Therefore, a simpler and more cost-effective synthetic approach should be developed for large scale preparation of Ag/TiO_2 core-shell nanoparticles.

In this work, Ag/TiO_2 core-shell nanoparticles were prepared by coating a layer of TiO_2 directly onto preformed AgNPs surfaces using the sol-gel process. The photocatalytic properties of these Ag/TiO_2 core-shell nanoparticles were evaluated based on the photodegradation reaction of methylene blue (MB) under UV irradiation. The decomposition of MB was measured by measurement of the MB concentrations in the solution using a UV-Vis spectrophotometer. MB was selected as the model dye because it is one of the most commonly used dyes in industries and it had been used as a model dye for photodegradation studies (Sangpour *et al*. 2010).

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MATERIALS & METHODS

Materials

All chemicals were of reagent grade purchased from Sigma-Aldrich and Merck, and used without further purification. Ultrapure water (18 MΩ) was obtained from a Water Purification System (ELGA, Model Ultra Genetic).

Synthesis of silver nanoparticles (AgNPs)

AgNPs was synthesized by an aqueous-based reduction method (Chin et al. 2009). In a typical synthesis, 10 mmol silver nitrate (AgNO3) was dissolved in 10 mL of ultrapure water. The pH of the solution was adjusted to ~9 by using NaOH solution and the solution was heated to 50oC. Ascorbic acid was then added drop by drop into the solution until the solution turned brown in color, which indicated the formation of AgNPs.

Synthesis of silver nanoparticles/titanium dioxide (Ag/TiO2) core-shell nanoparticles

A layer of TiO2 was coated onto preformed AgNPs by using the sol-gel process. A measured amount of titanium tetraisopropoxide (TTIP) was added to AgNPs and the mixture was stirred for 24 h at room temperature to allow complete hydrolysis and condensation of TTIP (Su et al. 2004). Ag/TiO2 nanoparticles were isolated by centrifugation, and then washed with ethanol to remove excess TTIP and free TiO2.

Characterization

The surface and structural morphologies of samples were studied by scanning electron microscope (SEM) (JEOL Model JSM 6390LA) and transmission electron microscope (TEM) (JEOL Model JEM-1230).

RESULTS & DISCUSSION

Figure 1 shows the SEM micrograph of AgNPs synthesized in this study. The particle sizes distribution of AgNPs were around 150-200 nm in diameter.

Figure 2 shows a TEM micrograph of Ag/TiO_2 nanoparticles prepared by the sol-gel process. An amorphous TiO_2 layer of around 10 nm in thickness was observed to encompass AgNPs to form Ag/TiO_2 core-shell nanoparticles. The hydrolysis and subsequent condensation of TTIP had resulted in the formation of TiO_2 layers on the surfaces of AgNPs.

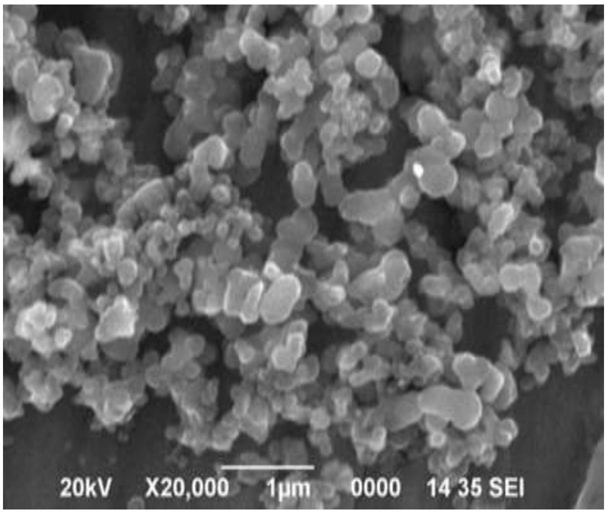

Figure 1. SEM micrograph of AgNPs

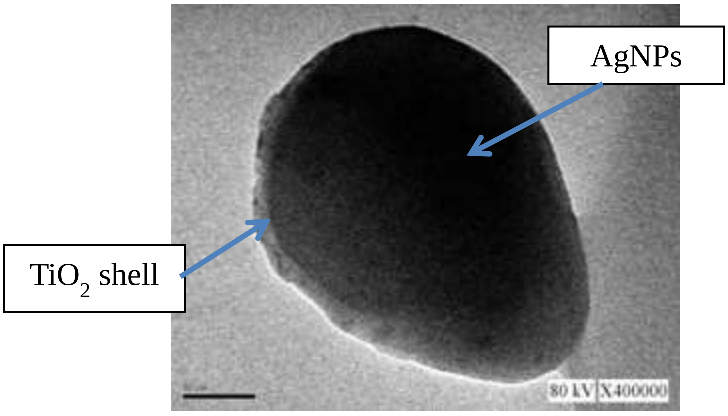

Figure 2. TEM micrograph of Ag/TiO_2 core-shell nanoparticles

The photocatalytic degradation of methylene blue (MB) was used as a model reaction in order to evaluate the photocatalytic activity of Ag/TiO_2 core-shell nanoparticles. The decomposition of MB was monitored by measuring the degradation of MB, which was indicated by the decolorization of MB at 680 nm. Prior to the catalytic decomposition experiments of MB dye, Ag/TiO_2 nanoparticles were being heat treated at 450 °C in air for 3 h in order to convert the TiO_2 layers from its amorphous phase to the photocatalytically active crystalline phase.

Figure 3 shows the absorption peaks of MB dye decomposed by uncoated AgNPs under UV irradiation up to 24 h. As observed in Figure 3, UV light has the ability to photodegrade MB. However, the rate at which this degradation took place was very low as indicated by the insignificant decrease of MB concentration after 24 h of UV irradiation. This was because uncoated AgNPs alone have relatively weak photocatalytic property, thus could not degrade MB dye efficiently.

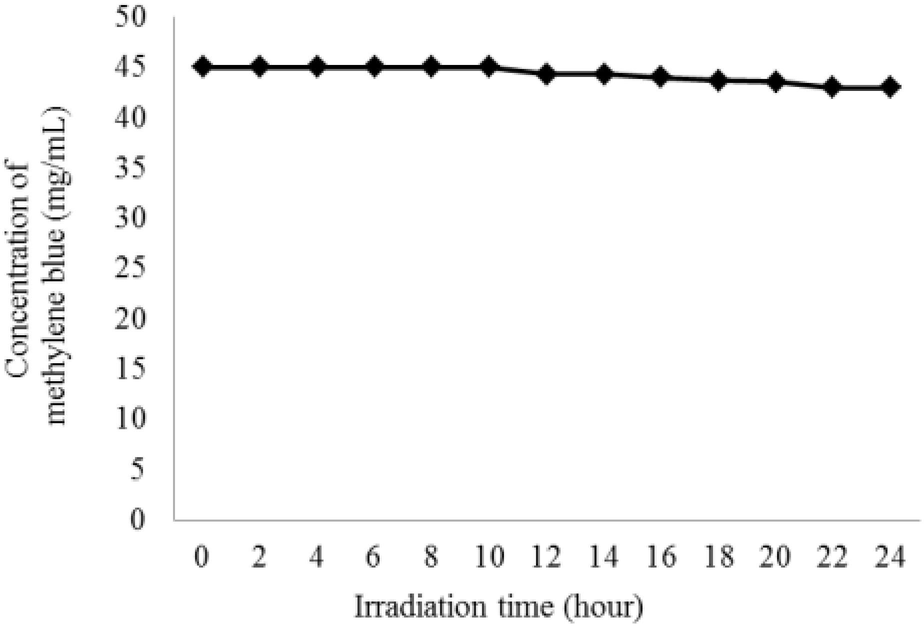

Figure 3. Concentration of MB degraded by bare Ag nanoparticles over 24 h of UV irradiation

Figure 4 shows the concentration of MB dye photocatalytically decomposed by Ag/TiO_2 core-shell nanoparticles under UV irradiation at various reaction durations. As observed, the concentration of MN decreased quickly as the reaction proceed to 1 h. Nearly 50% of MB dye have been decomposed by Ag/TiO_2 core-shell nanoparticles after 1 h as evidenced by the decrease of MB concentration from about 45.30 to 22.35 mg/ml. After 24 h, nearly all of the MB dye has been decomposed by Ag/TiO_2 core-shell nanoparticles. This indicated that MB dye was being decomposed at a much faster rate by Ag/TiO_2 core-shell nanoparticles as compared to that of uncoated AgNPs. The observed substantial improvement in photocatalytic decomposition rates was due to the presence of a TiO_2 layer on the surfaces of AgNPs. These findings clearly showed that TiO_2 shells on the surface of AgNPs cores were responsible for the rapid photocatalytic decomposition of MB dye under UV irradiation.

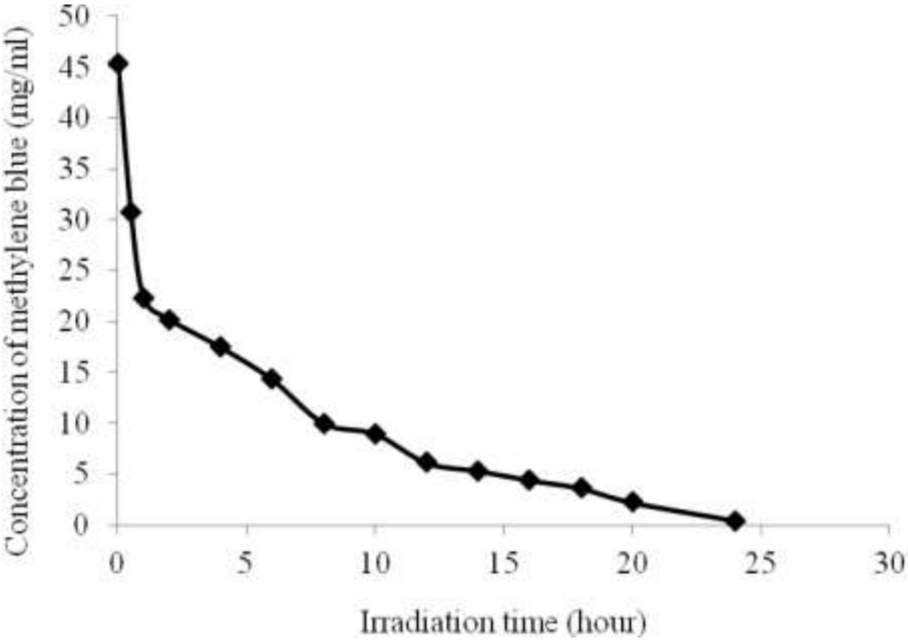

Figure 4. Concentration of MB degraded by Ag/TiO_2 core-shell nanoparticles over 24 h of UV irradiation

CONCLUSION

A thin layer of TiO_2 shell was successfully coated directly onto surfaces of AgNPs by a simple sol-gel process. Coating of TiO_2 shell onto AgNPs has been shown to dramatically enhance the photocatalytic properties of AgNPs due to the presence of photocatalytically active TiO_2 layer on their particles surfaces. Almost all of the MB was degraded by the Ag/TiO_2 core-shell nanoparticles within 24 h. Due to the simplicity of the synthetic approach and improved photocatalytic properties, Ag/TiO_2 core-shell nanoparticles are promising materials for various photocatalytic applications.

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