Tailored Synthesis of PS@Ag@TiO$_2$ Core-shell Nanocomposite for Photocatalytic Dye Degradation

Shanti Surong, Anindita Chakraborty and Himadri Acharya*
Centre for Soft Matters, Department of Chemistry, Assam University, Silchar-788011, Assam, India

Abstract
Here, we describe a simple chemical method to synthesize multi component PS@Ag@TiO$_2$ nanocomposites. The three-step synthetic approach comprises of synthesis of polystyrene (PS) particles, deposition of silver (Ag) nanostructure and coating of titanium dioxide (TiO$_2$) nanoshells. As synthesized materials is characterised by microscopic and spectroscopic techniques. The size of the PS particles is obtained as approx. 200nm in diameter. Ag nanoparticles deposited PS particles are indicated by the surface plasmon band resonance in UV-vis study. To study the potential application, the photocatalytic activity of the PS@Ag@TiO$_2$ nanocomposites is investigated in Methylene Blue (MB) dye degradation. Nanocomposite provides high photocatalytic degradation with a maximum efficiency of over 90% only in 30min.

Keywords: Polystyrene; Core-shell; Nanocomposite; Photocatalyst; Dye-degradation

Introduction
Nanocrystalline titanium oxide (TiO$_2$) has drawn intensive interests owing to its improved physical and chemical properties and promising technological applications in photocatalysis, photovoltaics, displays, sensors and biolabel applications [1-4]. Anatase TiO$_2$ has been widely investigated because of its easy synthesis and notable role in photocatalysis and photoelectron transfer [5,6]. However, the technological uses of TiO$_2$ nanostructures has been recognised as one of the crucial issues due to its wide band gap (3.2eV) that require ultraviolet (UV) irradiation for photocatalytic activation and limits its application under visible light [7,8]. Thus, researchers has attempted to develop TiO$_2$ nanoparticle photocatalyst with enhanced photocatalytic activity over the past several years. A number of attempts has been made to develop TiO$_2$ photocatalyst with visible light activity [9-12]. Thus, the development of TiO$_2$ photocatalyst with visible light activity has attracted much attention over the past several years. Considerable efforts has been made by doping, surface modification, defects and deposition of noble metals. It was found that engineered TiO$_2$ has high quantum yield and suppress the fast recombination of photogenerated electron-hole pairs [13-15].

The combination of semiconductor nanostructures with suitable metals e.g., Ag/TiO$_2$, Au/TiO$_2$ or Pt/TiO$_2$ hybrids have shown excellent synergized photophysical properties [16-19]. The noble metal component promotes the interfacial charge-transfer processes by trapping the photo-induced charge carriers and exhibits enhanced photocatalytic performance. However, multicomponent systems with well defined morphology and composition is a key for the tailored function of the nanocomposite materials [20]. A facile, cost effective fabrication of integrated multicomponent system along with controlled properties are use for practical applications.

The fabrication of polystyrene-inorganic nanoparticle (core-shell) nanocomposite systems has been enormously studied due to their great advantages in electronics, catalysis,
phononics, drug delivery and sensors etc [21,22]. Polystyrene (PS) particles are widely used as a core substrate in nanocomposite preparation because of their favorable properties, facile surface functionalization and size tunability. Moreover, the PS particles can stabilise the nanostructures and prevent from agglomeration. Core-shell nanoparticles based on PS particles with noble metal nanoparticles has common been accepted as effective nanocomposite materials and could be synthesized by various synthetic strategy including chemical reduction, polyol process, electroless plating etc [23-25]. Similarly, TiO$_2$ nanostructure coated PS particles were synthesized by sol-gel method and layer-by-layer assembly [26,27]. The sol-gel method of nanostructure coating is widely used because of its simple synthesis and high efficiency. However, there is no earlier report on the synthesis of Ag@TiO$_2$ shell on PS particles.

In this study, for the first timer we have synthesized a multicomponent composite is fabricated by step-wise growth of Ag and TiO$_2$ nanostructure on PS particles. PS particles with uniform size and smooth surfaces were first synthesized, and then Ag nanostructure was coated on the surface of the PS nanoparticles. Finally, TiO$_2$ nano shell was grown by sol-gel reaction, namely PS@Ag@TiO$_2$ core-shell nanocomposite. The morphology of the nanocomposite was evaluated and applied in photocatalytic dye degradation.

**Material and Methods**

**Chemicals and reagents**

Styrene [(C$_6$H$_5$)$_2$] 99%), azodoisobutylnytrile (AIBN) and silver nitrate (AgNO$_3$) were purchased from Sigma-aldrich Co. Titanium bis acetylacetonate di isopropoxide (TDAA) (75% solution in 2ml of propanol was purchased from Merck specialities Pvt. Ltd. Sodium borohydride (NaBH$_4$), polyvinylpyrrolidone (PVP) and sodium hydroxide (NaOH) were purchased Fisher Scientific Chemical Co. All the chemicals and solvent were ACS reagent grade. All chemicals were used as received without further purification. Deionized water was used in all the experimental processes.

**Instruments**

The morphology of the synthesized core-shell materials was investigated using transmission electron microscope (TEM. JEOL JEM-2100) operated at 200kV. The sample was prepared by drop casting the from ethanolic dispersion on to the carbon coated copper grid (200 mesh size) and dried overnight in vacuum. ZEISS-SIGMA Scanning Electron Microscope (SEM) was used and operated at 2.5kV. Samples for SEM was prepared on silicon wafer. By drop casting method and oven-dried overnight. The optical properties of core-shell nanocomposite were carried out by UV-visible spectrophotometry. The absorption spectra were recorded using JASCO V-670 spectrophotometer and 1 nm data interval in the range of 250-800nm.

**Synthesis of Polystyrene (PS) particle**

The PS particle was synthesized by dispersion polymerization of Styrene with AIBN initiator. First of all, the polymerization inhibitor is removed from the styrene by adding 5ml of styrene and 5ml of 10% NaOH solution in a reagent bottle and shakes vigorously to mix the two layers. The lower aqueous layer was removed by using separated funnel. Repeat the same washing process and then dried the styrene by adding granular CaCl$_2$. For the dispersion polymerization of styrene, 0.3g of PVP stabilizer was dissolved in 20ml of isopropanol in a round bottom flask and heated to 70 °C. A solution of AIBN (25mg) pre-dissolved in 3g of dried styrene was added to the reaction flask under vigorous mechanical stirring and proceed the reaction for 24 hours before cooling to the ambient temperature. The PS particles were transferred from isopropanol to deionize water by repeated centrifugation and redispersion process and keep it for further used.

**Preparation of nitro functionalized PS particle**

The nitro-functionalized PS particle was synthesized via nitration of as prepared PS particle (1g) with nitric acid and sulfuric acid mixture (1:2 v/v mixture) under slow stirring at 60 °C for 1h. Then the mixture was cooled to ambient temperature and washed repeatedly with 1(M) NaOH, water and ethanol till free from acid and dried in vacuum at 75 °C for overnight. Finally, the nitro functionalized PS particle are redispersed in distilled water (10wt%).

**Preparation of silver nano particle coated polystyrene**

25ml distilled water containing 0.5ml (10 wt.) of the as-prepared PS particles was stirred for 30 mins with a magnetic stirrer at room temperature. Then, 10ml of freshly prepared 0.5mmol of AgNO$_3$ (30mg) was added to the above solution and stirred for 30 mins. Finally, 5ml of 3mmol of NaBH$_4$, aqueous solution was added drop wise into the solution mixture under ice cold condition and continued stirring for 20 hours. The white solution turned to brownish colour. The precipitate was collected by centrifugation at 5000rpm for 25 mins and washed 3 times with deionized water. The product was dried in vacuum at 60 °C for 2 hours.

**Preparation of PS@TiO$_2$**

The mixture of 10ml of isopropanol and 1ml of the as-prepared PS particles (10 wt . %) was stirred for 30 mins at room temperature. A few drops of ammonium were added to the mixture maintaining pH value between 9-10. Afterward, 0.2ml of TDAA (Titanium (IV) bis acetylacetonate diisopropoxide) pre-dissolved in 3ml of isopropanol was added to the above mixture part by part for three time. Then the mixtures were continuously stirred for about 20 hours at room temperature. Finally, it was centrifuged at 5000rpm for 25 mins, and then the precipitates were washed with deionized water for about three time and dried in vacuum at about 50 °C.

**Preparation TiO$_2$@Ag@PS**

In a 25ml RB flask 20ml of isopropanol was taken and 0.03g of as prepared PS @Ag@TiO$_2$ emulsion was added to it. Then few drops of NH$_4$HCO$_3$ was added to the mixture and it was heated at 9-10. Afterward, 0.2ml of TDAA (Titanium (IV) bis acetylacetonate diisopropoxide) pre-dissolved in 3ml of isopropanol was added to the above mixture part by part for three time. Then the mixtures were continuously stirred for about 20 hours at room temperature. Finally, it was centrifuged at 5000rpm for 25 mins, then the precipitate was
washed with deionised water for about three times and dried in vacuum at about 50 °C.

**Photocatalytic degradation of methylene blue**

The photocatalytic activity of the nanocomposites was evaluated by performing the degradation of methylene blue (MB) as a representative dye. In a typical method, 1 ml of (10wt.%) PS@TiO$_2$ and PS@Ag@TiO$_2$ nanocomposites were taken in 50 ml 5ppm MB solution aqueous solution and stirred at room temperature under dark condition for 30 min to reach adsorption-desorption equilibrium. Then, 0.30 ml of H$_2$O$_2$ (30%) was added to it and a small aliquot was withdrawn from the mixture at each given time interval and quantitatively analyzed using UV-vis spectrometer. After the concentration of the solution was determined by the absorption peak of the particles, the analyzed aliquot was quickly poured back into the reactor. The photocatalytic degradation ratio is recognized as $I_t/I_o$ where $I_o$ is the absorbance at equilibrium concentration and $I_t$ is the absorbance of solution at time t. A 300 W tungsten bulb was used as light source for photocatalytic degradation. The system was cooled by a fan to maintain the room temperature.

**Result and Discussion**

The synthetic approach towards PS@Ag@TiO$_2$ core-shell nanocomposite is schematically illustrated in Figure 1. The PS particles are synthesized, and surface modified by nitro functionalization for Ag nanoparticle coating. Then sol-gel nanocoating of TiO$_2$ shell on PS@Ag obtained from TDAA precursor. The amorphous core-shell nanostructure is spin coated to obtain thin film for photocatalytic reaction.

![Figure 1: Schematic representation of fabrication of multicomponent PS@Ag@TiO2 core shell nanocomposite.](image)

![Figure 2: TEM images of (a) PS particle (b,c) PS@Ag@TiO2 nanocomposite (b) HRTEM image showing the Ag and TiO$_2$ nanostructure (e) SAED image.](image)
The structural morphology of PS, PS@Ag and PS@Ag@TiO$_2$ is evaluated by TEM analysis. Figure 2a shows the TEM image of bare PS particle. It can be seen that the PS particles are uniform, with a smooth surface and a diameter of ca. 200nm. Figure 2b shows the TEM image of PS@Ag@TiO$_2$ core-shell nanostructures. The surface of PS particle becomes rough and few Ag nanoparticles of below 4nm in size deposited on the PS particles. A thin layer of nanostructured Ag and overcoated TiO$_2$ layers can be clearly observed at the edge of the particle in Figure 2c. The TiO$_2$ shell deposited and completely covered the PS@Ag structure. A magnified image of an individual core-shell nanocomposite obtained by HRTEM is shown in Figure 2d reveals a typical core-shell structure with a lattice fringes of crystalline Ag nanostructure (is 0.23nm) corresponding to the fcc (111) facets. The TiO$_2$ shell of approx. 10nm deposited on the Ag nanostructure corresponding to anatase TiO$_2$. The SAED pattern in Figure 2e exhibits the typical diffraction rings indexed as (111), (200), (220), (311) and (222) planes.

Figure 3a shows the optical micrograph of PS@Ag@TiO$_2$ nanocomposites spin coated on the glass substrate. The particles are monodispersed and separated from each other. Figure 3b shows the SEM image of the core-shell particles. The coating of TiO$_2$ can also be observed from the SEM image.

**Figure 3:** a. Optical micrograph of spin coated PS particles b. Sem image of PS@Ag@TiO$_2$ core shell nanocomposite.

The characteristic absorption spectrum measured for bare polystyrene particle in Figure 4a is featureless. As a control experiment, TiO$_2$ coated polystyrene particle in Figure 4b shows a weak UV-Vis band at around 270nm, which is characteristic band of TiO$_2$ nanostructure. TiO$_2$ particles coalesce into a network-like nanostructure on the surfaces of polystyrene particle and exhibit a weak band, instead of distinct peak. Figure 4c reveals a broad absorbance with an absorbance maximum at 403nm for Ag coated PS particle. This broad band is attributed to the localized surface plasmon resonance (SPR) of metallic Ag nanoparticles. The surface plasmon peak of Ag nanoparticles are red-shifted to 412nm when TiO$_2$ deposited on the PS@Ag nanostructure surface. The increased interaction between Ag NPs with high k TiO$_2$ is attributed to the red-shift of SPR of Ag NPs in the UV-vis spectra of PS@Ag@TiO$_2$ core-shell structure. TiO$_2$ with high band gap (~3.3eV) readily excite pairs of electrons and holes upon UV irradiation in the range of the SPR peak of Ag NPs and in turn can enhance the electric near field at the vicinity of the Ag NPs, leading to the red-shift of SPR peak [25].

**Figure 4:** UV-Vis spectra of a. Polystyrene particles b. PS@TiO$_2$ particles c. nano structural Ag deposited PS particles d. PS@Ag@TiO$_2$ core shell nanocomposite.
The photo-catalytic properties of PS@TiO$_2$ and PS@Ag@TiO$_2$ core shell nanocomposites respectively were evaluated by the degradation of methylene blue in hydrogen peroxide. Figure 4a & 4b shows the UV-vis absorption profile of MB dye upon photocatalytic reaction with PS@TiO$_2$ and PS@Ag@TiO$_2$ respectively. PS@Ag@TiO$_2$ core-shell nanocomposite catalyst shows over 90% degradation only in 30 min of reaction time compared to 48% for PS@TiO$_2$. The photocatalytic efficiency of PS@Ag@TiO$_2$ nanocomposite catalyst enhances on Ag deposition is due to slow down in electron hole recombination process.

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