<u>Electronic Supporting Informations</u> Dual role of micelles as templates and reducing agent for the fabrication of catalytically active hollow silver nanospheres

Manickam Sasidharan,* Chendrayan Senthil, Vandana Kumari and Asim Bhaumik*

Experimental Section:-

Material Synthesis:

The polymer PS(20.1K)-b-PVP(14.2K)-PEO(26.0K) was obtained from polymer source Inc. The numbers in the parentheses indicate the average molecular weight of the corresponding blocks; for instance, 20.1K refers to 20100. The desired amount of PS-PVP-PEO was dissolved in dimethylformamide having 10 wt % water by stirring. The solution was dialyzed against water to obtain the micelles of PS-PVP-PEO. Finally, the micelle solution was diluted to obtain 1 g/L of micelle concentration. Then the pH of the micelle solution was adjusted to pH 4 using dilute HCl and used for synthesis of silver nanoparticles. In a typical synthesis of silver nanospheres, the PS-PVP-PEO micelle solution (20 mL) and AgNO₃ (PVP/Ag = 7) was stirred at room temperature for 12 h under inert atmosphere. Then the solution was further treated hydrothermally at 120 °C for 12 h in a Teflon lined autoclaves; after the thermal treatment, the products were recovered by centrifugation and washed several times with ethanol and distilled water. The samples were dried under room temperature. The dried samples were subjected to solvent extraction to remove triblock copolymers present in the composite materials by refluxing in DMF at 100 °C and finally, the samples were washed thoroughly with ethanol and dried in a vacuum oven.

The void volume and shell thickness of hollow nanospheres were tuned by using polymer with increased PS block length and wall thickness by using higher concentration of Ag^+ ions. In the present method, *core* part serves as template for hollow void and therefore, void volume was tuned by using polymer different PS block length; PS(45k) - PVP (16k) – PEO(8.5k) and synthesis was carried out as described above. Whereas, the shell thickness was increased by using higher concentration of silver precursors (PVP/Ag = 15) with PS(20.1K)-b-PVP(14.2K)-PEO(26.0K) under similar experimental conditions.

Catalytic experiments

In a typical reaction of Baeyer-Villiger oxidation, 5 mmol of cyclhexanone was mixed with 5 mmol of *tert*-butylhydroperoxide in a round bottom flask followed by addition of 10 wt% of catalysts in dry acetonitrile solvents. The flask was fitted with a water condenser and the mixture was vigorously stirred using magnetic stirrer at 85 °C while circulating cold water through the condenser. The progress of the reaction was made by analyzing the products with a capillary gas chromatograph (Shimadzu 14A, OV-1 columns with flame ionization detectors).



Figure S1. Color change observed during the formation of silver nanoparticles.



Figure S2. TG/DTA analyses of Ag/polymer composite nanoparticles.



Figure S3. UV-Visible spectra of Ag nanoparticles at different reaction time: (A) Reaction time is 2 h; (B) Reaction time is 8 h; (C) Reaction mixture after hydrothermal treatment at 120 °C.



Fig. S4; Hollow nanospheres with void volume of 21 ± 1 nm (A) and hollow nanospheres with shell thickness 11 ± 0.5 nm (B).



Figure S5. Silver hollow nanospheres at low magnification.



Figure S6. Powder XRD pattern of silver hollow nanospheres



Fig. S7: Solid silver nano particles of size 8 ± 1 nm used for comparison of catalytic activities



Fig. S8: Hollow silver micro particles used for comparison of catalytic activities



Fig. S9: XRD pattern of hollow silver nanospheres after 5 successive reuses