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ARTICLE TYPE

Dual role of micelles as templates and reducing agent for the fabrication of catalytically active hollow silver nanospheres

Manickam Sasidharan,^{a*} Chendrayan Senthil,^a Vandana Kumari^b and Asim Bhaumik^{b*}

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We report a simple and efficient protocol for fabrication of colloidal hollow silver nanospheres of size less than 30 nm using ABC triblock copolymer poly(styrene-*b*-vinyl-2-pyridine-*b*-ethylene oxide) in the absence of any reducing agents. The colloidal silver hollow nanoparticles serve as an efficient heterogeneous catalysts for Baeyer-Villiger oxidation of ketones to the corresponding lactones in the presence of anhydrous *tert*-butylhydroxide under liquid-phase conditions.

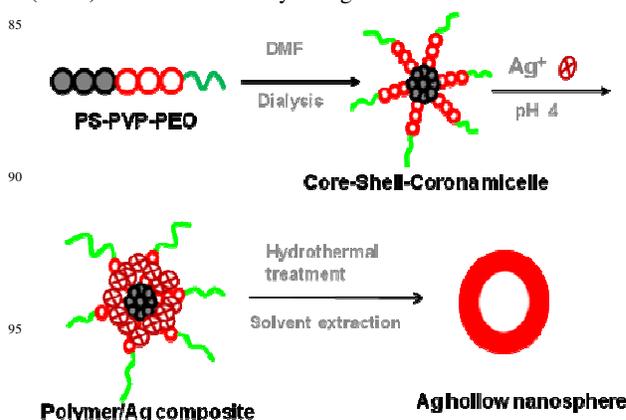
Inorganic nanostructures with hollow interiors have been extensively studied for tailoring the properties involving applications like drug delivery, catalysis, surface enhanced Raman scattering (SERS), and sensors.¹ Noble metal nanoparticles, in particular, silver has an interesting properties that could be tuned or enhanced through the nanoscale control of morphology. The synthesis of silver nanoparticles with well-controlled morphology and a narrow size distribution is important for uncovering their properties and achieving their practical applications. Hollow nanostructures of metals are intriguing in research because they exhibit surface plasmonic properties and catalytic activities superior from their solid counterparts.² For example, silver is the most popular catalyst for oxidation of ethylene to ethylene oxide and methanol to formaldehyde or reduction of nitroarenes.³ Metal hollow nanoparticles have high surface area to volume ratio vis-à-vis binding sites which are mainly responsible for their catalytic activity in various organic transformations. Given the range of applications in which silver is important, better control of its morphology, size and properties would have profound impact in academia and industries.

Hollow metal nanospheres are generally fabricated by coating the surfaces of colloidal particles (e.g., silica beads, polymer latexes etc.) with thin layer of desired metal precursors followed by selective removal of the colloidal templates through calcinations or wet chemical etching.⁴ Caruso et al. adapted different strategy which involves layer-by-layer adsorption of polyelectrolytes and charged metal colloids to form shell-like structures around colloidal template particles to hollow spherical particles.⁵ Mann and co-workers described a self-supporting porous framework of silver using dextran as a sacrificial template.⁶ Recently, there are few reports about the preparation of metal nanoparticles using soft templates and liposome.⁷ However, hollow spherical particles prepared by the above methods are associated with problems such as rough surfaces, polycrystallinity, non-uniformity in shell thickness, poorly defined composition, and difficulty in removing the colloidal templates without breaking the shells. More importantly, the hollow metal spheres obtained by these methods ranges from few hundred nanometers to a few micrometers and difficult to obtain hollow nanospheres of size less than 50 nm. Therefore, it is still a

challenging task to fabricate silver hollow nanospheres with a few tens of nanometer with uniform particle size.

Recently, a variety of inorganic hollow spherical nanospheres were reported using asymmetric triblock copolymeric micells with *core-shell-corona* architecture.⁸ The unique feature of these micelles is that the *core* acts as a template for void formation, *shell* domain serves as reaction site for inorganic precursors, and *corona* stabilizes the composite micelles. Herein, we report an efficient synthesis strategy for fabrication of uniform silver hollow nanospheres of size 29 ± 2 nm templated by micelles of poly(styrene-*b*-vinyl-2-pyridine-*b*-ethylene oxide) (PS-PVP-PEO) using AgNO₃ as metal source in the absence of external reducing agents under hydrothermal conditions. The poly(ethylene oxide) block similar to ethylene glycol effectively reduces AgNO₃ at elevated temperature^{7a} whereas the PVP domain acts as capping agent for metallic silver and subsequent shell formation. The synthesized silver hollow nanospheres acts as an efficient heterogeneous catalyst for Baeyer-Villiger oxidation, where various value-added lactones and esters can be prepared in one pot from their respective carbonyl compound in the presence of peroxides.⁹

The triblock copolymers with chain length of PS(20.1k) – PVP(14.2k) – PEO(26k) was purchased from Polymer Source Inc. and the number in the parentheses refer to molecular weights of respective blocks. In a typical preparation of micelles, the polymer was dissolved in a mixture of dimethylformamide (DMF) and water and dialyzed against water to obtain micelles



Scheme 1. Fabrication of silver hollow nanosphere using PS-PVP-PEO with concentration of 1 gL^{-1} (Experimental details, ESI[†]). Scheme 1 illustrates the typical formation of polymeric micelles and silver hollow nanospheres by redox reactions. Dynamic light scattering

and electrophoretic light scattering experiments of micelles revealed the values of hydrodynamic diameter D_h (63 ± 2 nm), and the ζ -potential (+ 41 mV), respectively. However, TEM observation of the micelles stained with phosphotungstic acid suggested a nearly monodispersed spherical micelles with average diameter *ca.* 38 ± 2 nm (Fig. 1A). The observed size discrepancy in the micelle particles's between DLS and TEM is due to the fact that the latter accounts for only the *core-shell* part and excludes the *corona* part of the micelles.⁸ The white contrast in the TEM image indicates hydrophobic PS-*core* whereas both PVP and PEO are hydrophilic domains. On addition of AgNO₃ (PVP/Ag = 7) to the micelle solution at pH 4 at room temperature, the transparent clear micelles turn to light brown color (Fig. S1, ESI[†]) during the commencement of nucleation and growth of nanoparticles and the PVP units serve as capping agent, whereas hydrophilic poly(ethylene-oxide) of the template micelles facilitates reduction of Ag⁺ to Ag. On treatment of the resulting colloidal suspension at elevated temperature (120 °C) under hydrothermal conditions further facilitates the reduction as well as assembly of nanostructures. The polyethylene glycol unimers reduce the silver ions and this reduction behavior of polyethylene glycol have already been well established for synthesis of silver nanostructures with different morphologies.^{7a} Therefore, polyethylene glycol domain of the template micelles play a dual role as stabilization of micelle architecture as well as reducing agents similar to polyvinyl alcohol (PVA) which simultaneously reduce metal ions and also acts as capping agents.¹⁰

Figure 1B shows the TEM image of the polymer/silver composite micelles and the average size of the particles were found be 51 ± 3 nm. The thermal analyses (TG/DTA) of polymer/silver composite particles revealed about 13 wt.% weight loss for as-synthesized samples (Fig. S2, ESI[†]). It is worth to note that a part of organic polymers was washed away during initial centrifugation and washing with ethanol. The polymer/silver composite particles were further extracted with dimethylformamide or toluene at 100 °C for 12 h under stirring to remove the remaining polymeric template and obtain template-free silver hollow nanospheres. The formation of Ag nanocrystals was characterized by UV-vis spectra which illustrate the Plasmon resonance peak intrinsic to silver nanoparticles at different period of time (Fig. S3, ESI[†]).¹¹ After commencement of reaction at room temperature (at 2 hour), the solution gave a weak peak centered at 418 nm suggesting presence of very little Ag nanoparticles (Fig. S3, A). Further treatment of reaction solutions at elevated temperature (110 °C) for 8 h resulted in very high intensity peak with similar band width indicating substantial increase in the concentration of Ag nanoparticles (Fig. S3, B) and further extended period of reaction did not increase absorption peak intensity (Fig. S3, C). Thus Ag particles formation and their distribution appears to depend on varying extent of chemical reaction as well as a digestive processes at high temperature.¹²

Fig. 1C shows TEM image of Ag hollow nanospheres and average particle size and void space diameter were found to be 29 ± 2 nm and 15 ± 1 nm, respectively. The wall thickness estimated from TEM observation was approximately 7 ± 0.5 nm. The PS block core size estimated from TEM image (white contrast) was found to $25 \text{ nm} \pm 1 \text{ nm}$ (Fig. 1A) and size of the composite particle increases to 51 ± 3 nm on treatment with AgNO₃; however, after solvent extraction of the composite particles in DMF, the particle size shrinks and the void space diameter was found to be 15 ± 1 nm, resulting in shrinkage of about 40 % of initial size similar to metal oxide hollow nanospheres.¹³ The versatility of this method was also demonstrated by tuning void

volume and shell thickness. The void volume expanded to 21 ± 1 nm using polymer with increased PS block length (45k) whereas the shell thickness increased to 11 ± 0.5 nm by using high silver precursors, PVP/Ag = 15 (Fig. S4 & Experimental section; ESI[†]). Though the polymer micelles, Ag/polymer (Fig. 1 A & B) are less prone to aggregation, the final Ag-hollow particles exhibit pronounced agglomeration (Fig. S5, ESI[†]) due to very high free-energy of nanoparticles. The high resolution TEM image (Fig. 1D) reveals that the silver hollow nanoparticles are highly crystalline and the fringe spacing of 2.4, 2.0, and 1.4 Å correspond to the (111), (200), and (220) planes, respectively of face-centered cubic structure.¹⁴ The well-resolved interference fringe patterns confirm the single crystalline structure of silver hollow nanospheres. The selected area electron diffraction pattern (SAED, Fig. 1D, inset picture) from the same nanoparticles also indicates its high crystallinity. The powder XRD pattern (Fig. S6, ESI[†]) also exhibits (111), (200) and (220) peaks and all the diffraction peaks can be indexed to cubic face centered silver (JCPDS 04-0783) and no obvious impurity phase, such as Ag₂O is detected.¹⁵ The BET surface area estimated from nitrogen adsorption isotherms was found to be $67 \text{ m}^2 \text{ g}^{-1}$. High BET surface area of the synthesized hollow nanoparticles has motivated us to explore their catalytic activity in Baeyer-Villiger (BV) oxidation reaction under liquid-phase reaction conditions.

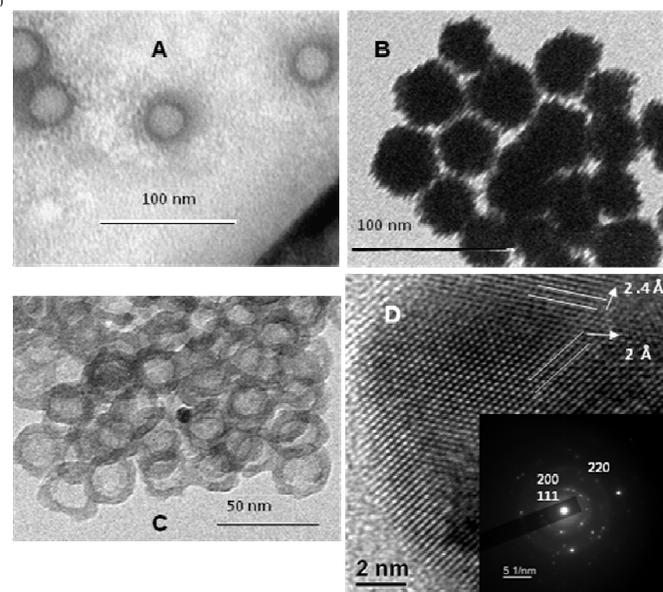
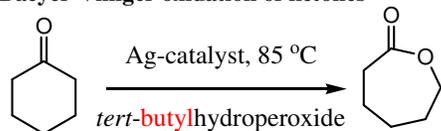


Fig.1. TEM images of nanoparticles: (A) PS-PVP-PEO micelle; (B) Ag/polymer composite particles; (C) Ag hollow nanospheres and (D) HRTEM and SAED of sample C.

The Baeyer-Villiger oxidation is a very important organic reactions for production of industrially important lactones and esters from their corresponding carbonyl compounds in the presence oxidizing agents.¹⁶ Scheme 1 depicts the Ag hollow nanospheres catalyzed Baeyer-Villiger oxidation under liquid phase conditions and data for various cyclic and acyclic substrates are given in Table 1. Among the solvents toluene, THF, and acetonitrile (entries 1–3) employed, acetonitrile exhibited consistently good activity consistent with earlier reports¹⁷ and therefore used as solvent for subsequent investigation. The anhydrous *tert*-butylhydroperoxide (TBHP) exhibited higher reactivity than benzaldehyde/O₂ system under similar conditions (entries 3 and 4) for conversion of cyclohexanone to ϵ -caprolactone. It is likely that the exposed silver surface atoms may be poisoned and/or converted to Ag₂O in presence of oxygen

results in diminished reactivity. Entries 5 and 6 exhibit difference in migratory aptitude of substituted cyclohexanones; 2-methylcyclohexanone yields 7-methyloxepan-2-one as the sole product whereas 3-methylcyclohexanone leads mixture of lactones (ca. 6-methyloxepan-2-one and 4-methyloxepan-2-one) similar to literature reports.¹⁸ Cycloheptanone forms the corresponding lactone at high turn-over number (entry 7). The acyclic methyl ethyl ketones and isobutyl methyl ketone also lead to formation of corresponding ester in very high yields (entries 8 and 9). Entry 10 shows the activity of Ag nanoparticles of size 8 ± 1 nm that exhibits lower activity than Ag hollow particles possibly due to presence of PVP stabilizer (Fig. S7 ESI[†]). Furthermore, we have also scrutinized the micron-sized Ag hollow nanoparticles (entry 11, Fig. S8, ESI[†]) synthesized by layer-layer technique realized lower activity due to less catalytic binding sites of larger particles. We have recycled the catalyst for cyclohexanone oxidation for 5 repetitive cycles after activating the catalyst with nitrogen containing 5 % H₂ at 120 °C for 3 h and Ag particles also retain the crystallinity (Fig. S9 ESI[†]). In the fifth cycle the conversion and TON were nearly maintained compared to the pristine catalysts under similar conditions (entry 12).

Table 1. Baeyer-Villiger oxidation of ketones^a



Entry	Substrates	Conversion, mole %	TON
1 ^b	Cyclohexanone	63.8	10.4
2 ^c	Cyclohexanone	78.3	12.7
3 ^d	Cyclohexanone	98.8	16.1
4 ^e	Cyclohexanone	83.0	13.5
5	3-methylcyclohexanone	93.2	15.0
6	4-methylcyclohexanone	95.6	15.4
7	Cycloheptanone	91.7	14.9
8	Ethyl methyl ketone	96.5	15.6
9	Methyl isobutyl ketone	92.8	15.0
10 ^f	Cyclohexanone	74.7	12.1
11 ^g	Cyclohexanone	74.5	13.0
12 ^h	Cyclohexanone	98.1	15.8

^aReaction conditions: ketone = 3 mmol (0.28 g); tert-butylhydroperoxide = 3.3 mmol (70 % anhydrous solution), acetonitrile = 5 mL, 10 wt % catalysts with respect to substrate, 0.1 mmol naphthalene was used as internal standard, Reaction time = 4 h and temperature 85°C and the reaction was carried out in N₂ atmosphere. ^btoluene solvent; ^cTHF solvent; ^dacetonitrile solvent; ^ebenzaldehyde/O₂ as oxidant; ^fDense silver nanoparticles (8 ± 1 nm) as catalysts; ^ghollow silver microsphere as catalysts; and ^hreused catalyst after 5 cycles.

In conclusion, we have demonstrated novel strategy for efficient and simple fabrication of silver hollow nanospheres using PS-*b*-PVP-*b*-PEO polymeric micelles with core-shell-crown architectures. The present method enables us to prepare hollow spherical particles of size less than 30 nm with high crystallinity, size tenability, and monodispersity. The silver hollow particles efficiently catalyze various cyclic- and acyclic-ketones to the corresponding lactones and esters at high yields under liquid-phase conditions, suggesting future potential of this unique Ag nanoarchitecture in efficient catalysis.

Notes and references

- ^aSRM Research Institute, SRM University, Kattankulathur, Chennai, 603203, India, E-mail: sasadharan.m@res.srmuniv.ac.in.
^bDepartment of Material Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India, E-mail: msab@iacs.res.in
[†] Electronic Supplementary Information (ESI) available: [Preparation of micelles and hollow nanospheres. TEM, SEM, XRD, TG-DTA, and UV-visible data]. See DOI: 10.1039/b000000x/
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