Fabrication of Silver Yolk@Porous Janus Polymer Shell Nanospheres for Synergistic Catalysis

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\textbf{Abstract} Yolk-shell nanostructures have recently attracted tremendous research interests in various areas because of their unique structural merits. Currently, there is an urgent need for developing porous shells with multifunctional features to enhance their performance in various applications. Herein, advanced yolk-shell nanospheres have been facilely prepared by encapsulating silver nanoparticles with porous Janus polymer shells that consist of a hypercrosslinked polystyrene (xPS) outer layer and a tethered poly(acrylic acid) (PAA) brush lining. The xPS outer layer possesses well-developed porosity as mass diffusion pathways. More importantly, the tethered PAA brushes with customized carboxyl groups exhibit great affinity toward specific species (e.g., cationic dyes), leading to their enrichment from the bulk solution into the interior cavity. The unusual combination of highly porous outer layers with customizable inbuilt polymer linings in the porous Janus shells endows them with great promise for synergistically catalytic degradation of cationic dyes.

\textbf{Keywords} Yolk-shell nanostructure; Janus shell; Selective diffusion; Synergistic catalysis

\textbf{INTRODUCTION}

As an important class of functional materials characterized by the presence of internal void spaces between the cores and shells, yolk-shell nanospheres have recently attracted tremendous research interests in various areas.\textsuperscript{[1]} Especially, the appealing structures and tunable functionalities in both the yolks and shells render them very attractive as nanoreactors for numerous applications.\textsuperscript{[2]} The outer shells not only enable a homogeneous environment in the cavities but can also efficiently stabilize the inner yolks to avoid their aggregation, resulting in high stability. Moreover, the movable functional yolks with well-designed nanostructures feature a large number of surface active sites, thereby assuring high performance. In addition, the yolk-shell nanostructures can be tailored by employing different functional species as the yolk and shell materials, respectively, to maximize their performance.\textsuperscript{[3]} It is generally considered that the mass transfer property of the porous shells plays a very important role in achieving unprecedented performance for their applications. To date, various yolk-shell nanostructures made of different yolks and shells, including Fe\textsubscript{3}O\textsubscript{4}@mesoporous SiO\textsubscript{2}, metal@polymers, and metal@carbons, have been successfully fabricated, which demonstrate potential applications for adsorption, energy, catalysis, etc.\textsuperscript{[4–8]} Nevertheless, the previously reported porous shells of yolk-shell nanostructures are generally limited to a single component, and it is very difficult to achieve selective diffusion of specific molecules/ions across the porous shells, which may endow these materials with more functionalities and enhanced performance for various applications.

Janus nanostructures, comprising two hemistructures with different compositions and functionalities, are anisotropic in shape and surface chemistry, which allows them to provide particular sites for specific applications.\textsuperscript{[9–13]} It is reasonable to expect that the incorporation of specific functional species onto one side of the outer shells to construct porous shells with Janus nanostructures can not only maintain the pristine function of the shell, but bring great ability to further optimize their properties and thus enhance the performance of the yolk-shell nanostructures.\textsuperscript{[16]} Despite these fascinating features, there have been rare reports of yolk-shell structures with Janus polymer shells.

Herein, we report an efficient strategy for the synthesis of...
unusual yolk-shell nanospheres with unique porous Janus polymer shells and silver (Ag) nanoparticle yolks. The porous Janus polymer shell consists of a hypercrosslinked poly(styrene (xPS) outer layer and a tethered poly(acrylic acid) (PAA) brush lining. The xPS outer layer possesses well-developed porosity, which can provide pathways for mass diffusion. More importantly, the tethered PAA brushes with customized carboxyl groups exhibit great affinity toward specific species (e.g., cationic dyes), leading to their enrichment from the bulk solution into the interior cavities. As a result, for the as-obtained yolk-shell Ag@PAA-xPS nanospheres, the porous Janus PAA-xPS shells can work synergistically with the inbuilt Ag yolks to catalyse the degradation of cationic dyes.

EXPERIMENTAL

Materials
tert-Butyl acrylate (tBA; Aladdin, 99%) and styrene (St; Aladdin, AR) were passed through alkaline alumina column before polymerization. CuBr was purified by stirring over glacial acetic acid, followed by filtration and washing for three times with ethanol and drying with N₂ flow overnight. The other chemicals were of analytical grade and used as received without further purification. Silver nitrate (AgNO₃), polyvinylpyrrolidone (PVP, M₉₀₀₀₀ = 5.5 × 10⁶), 3-aminopropyl triethoxysilane (APTES), N,N,N',N'-pentamethyldiethylenetriamine (PMDETA), 2-bromo-isobutyryl bromide, triethylamine, aluminum trichloride (AlCl₃), methylene blue (MB), rhodamine B (RhB), sodium borohydride, and dichloromethane were obtained from Aladdin. Tetraethyl orthosilicate (TEOS), ammonia water, ethylene glycol, isopropanol, hydrofluoric acid, carbon tetrachloride (CCl₄), methylene blue (MB), rhodamine B (RhB), sodium borohydride, and dichloromethane were obtained from Aladdin. Tetraethyl orthosilicate (TEOS), ammonia water, ethylene glycol, isopropanol, hydrofluoric acid, carbon tetrachloride (CCl₄), acetone, and tetrahydrofuran (THF) were obtained from Guangzhou Chemical Reagent Factory.

Preparation of Ag@SiO₂-g-PtBA Hairy Nanospheres
The Ag nanoparticles were first synthesized with an ethylene glycol reduction method as described previously. Then the Ag nanoparticles (60 mg) were dispersed in 180 mL of 2-propanol solution and ultra-sonicated for 15 min. After stirred at 40 °C for 5 min, 18 mL of H₂O and 10 mL of ammonia aqueous solution (25 wt%) were added into the solution. Then, 0.8 mL of TEOS in 20 mL of 2-propanol solution was injected dropwise for 1 h. After reacting for another 2 h, the as-obtained Ag@SiO₂ nanospheres were separated by centrifugation at 1.2 × 10⁴ r·min⁻¹ for 5 min and washed with ethanol for three times. Ag@SiO₂-g-PtBA hairy nanospheres were then prepared by St-ATRP. Typically, the above Ag@SiO₂ nanospheres were first modified by APTES to introduce amino functional groups on the surfaces. Subsequently, 1 g of Ag@SiO₂-NH₂ dispersed in 30 mL of anhydrous dichloromethane solution was added into a single-necked flask, and then filled with N₂ for 30 min. After adding 1.4 mL of triethylamine, the reactor was transferred into an ice-water bath, and then 1.2 mL of 2-bromo-isobutyryl bromide was added dropwise for 30 min. After stirring for 3 h, the reaction temperature was raised to 25 °C for 48 h, producing bromine-containing initiation sites on the surfaces (Ag@SiO₂-Br). The as-obtained Ag@SiO₂-Br nanospheres were then added into a Schlenk flask together with CuBr₂, PMDETA, and tBA with a molar ratio of 1/0.4/4.4/1000. After gently purging N₂ for 30 min, four molar equivalents of CuBr was added to the solution rapidly, followed by bubbling with N₂ for another 30 min. Then the flask was sealed and heated to 60 °C. The reaction was stopped by opening the flask and exposing the catalyst to air after reacting for 24 h. The product was isolated and purified by precipitation into an excess of methanol and centrifuged at 1.2 × 10⁴ r·min⁻¹ for 10 min, followed by drying at 40 °C overnight, producing Ag@SiO₂-g-PtBA hairy nanospheres.

Preparation of Ag@SiO₂-g-PtBA-b-PS Hairy Nanospheres
Ag@SiO₂-g-PtBA-b-PS hairy nanospheres were synthesized according to the following recipe: St/Ag@SiO₂-g-PtBA/CuBr/Br₂/PMDETA = 1000/1/4/0.4/4.4 (molar ratio). A Schlenk flask was firstly charged with Ag@SiO₂-g-PtBA, CuBr₂, PMDETA, and styrene. After gently purging N₂ for 30 min, CuBr was added to the solution rapidly. N₂ was bubbled for another 30 min to remove air completely. Then the flask was sealed and heated to 90 °C. After reacting for 24 h, the reaction was stopped by opening the flask and exposing the catalyst to air. The product Ag@SiO₂-g-PtBA-b-PS was isolated and purified by precipitation into an excess of methanol, washed by THF for three times, and centrifuged at 1.2 × 10⁴ r·min⁻¹ for 10 min, followed by drying at 40 °C overnight.

Preparation of Ag@PAA-xPS
To prepare Ag@PAA-xPS nanospheres, Ag@SiO₂-g-PtBA-b-PS hairy nanospheres were first Friedel-Crafts hypercrosslinked to produce Ag@SiO₂-g-PtBA-b-PS hairy nanospheres. Typically, 0.2 g of Ag@SiO₂-g-PtBA-b-PS was dissolved in 20 mL of CCl₄ in a three-necked flask equipped with a reflux condenser and heated to 75 °C. Subsequently, 1 g of AlCl₃ was added quickly to start the Friedel-Crafts hypercrosslinking reaction. The reaction was kept at 75 °C for 24 h under stirring and then terminated by adding the mixture of acetic acid and 3.7 wt% HCl solution (v/V = 3/1). Afterwards, the resulting Ag@SiO₂-g-PtBA-b-PS was dispersed in 20 mL of 4 wt% HF/ethanol/water solution (40% HF/ethanol/water = 1/3/6, v/V/v) for 15 min to remove the silica and then dried at 60 °C for 12 h, giving rise to the target product Ag@PAA-xPS nanospheres.

The control samples of yolk-shell Ag@xPS and hollow PAA-xPS nanospheres were prepared as described previously.

Structural Characterization
Molecular weights of PtBA and PtBA-b-PS grafted on the surfaces of Ag@SiO₂ nanospheres were analyzed with Waters Breeze gel permeation chromatography (GPC) by using THF as an eluent. The samples were pretreated with 40% HF ethanol/water solution (40% HF/ethanol/water = 1/3/6, v/V/v) for 15 min to remove the silica and then dried at 60 °C for 12 h, giving rise to the target product Ag@PAA-xPS nanospheres.

Catalytic Tests
Typically, RhB (25 mL, 0.4 g·L⁻¹) or MB (25 mL, 0.4 g·L⁻¹), sodium
borohydride (25 mL, 0.2 g·L\(^{-1}\)), and ethanol (2 mL) were put into an Erlenmeyer flask at 37 °C, and then the catalysts (20 mg) were quickly put into the above solution. At predetermined time intervals, 0.3 mL of solution was taken and diluted for UV-Vis test.

RESULTS AND DISCUSSION
The synthetic strategy of yolk-shell Ag@PAA-xPS is schematically illustrated in Fig. 1. Uniform Ag nanoparticles with an average diameter of 50 nm are first prepared with an ethylene glycol reduction method (Fig. S1, in the electronic supplementary information, ESI).[17] Condensed silica is further homogeneously coated on the surfaces of Ag nanoparticles via a modified Stöber method, producing monodispersed Ag@SiO\(_2\) nanoparticles with a nanoparticle in each nanosphere (Fig. 2a).[18] After introducing the bromine-containing initiation sites on the surfaces of Ag@SiO\(_2\), poly(t-butyl acrylate) (PtBA) molecular brushes are then successfully grafted from these modified surfaces via surface-initiated atom-transfer radical polymerization (SI-ATRP) (Fig. 2b). According to the gel permeation chromatography (GPC) trace, the grafted PtBA chains exhibit a number-average molecular weight (\(M_n\)) of 2.48 × 10\(^4\) with a polydispersity index (PDI, \(M_w/M_n\)) of 1.18 (Fig. 2c), indicating a well-defined molecular structure enabled by SI-ATRP. Subsequently, the PtBA chains on the surfaces of Ag@SiO\(_2\)-g-PtBA are used as initiation sites and PS chains are further grafted from the surfaces, producing Ag@SiO\(_2\)-g-PtBA-b-PS. \(M_n\) of as-obtained PtBA-b-PS chains is 7.64 × 10\(^4\), corresponding to a PDI of 1.23 (Fig. 2c). The result reveals that \(M_n\) of the grafted PS chains is 5.16 × 10\(^4\). SEM image (Fig. 2d) shows that the Ag@SiO\(_2\)-g-PtBA-b-PS nanoparticles inherit the distinct spherical morphology of Ag@SiO\(_2\). The average diameter is determined to be 256 nm (Fig. S2 in ESI).

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** Schematic illustration for (a) fabrication of Ag@PAA-xPS and (b) its applications for catalysis.

![Fig. 2](https://example.com/fig2.png)

**(a)** TEM image of Ag@SiO\(_2\); (b) SEM image of Ag@SiO\(_2\)-g-PtBA; (c) GPC traces of the cleaved linear polymer chains from the Ag@SiO\(_2\)-g-PtBA and Ag@SiO\(_2\)-g-PtBA-b-PS nanospheres; (d) SEM image of Ag@SiO\(_2\)-g-PtBA-b-PS; (e) SEM and (f) TEM images of Ag@PAA-xPS.

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To obtain interior cavities and well-developed porosity in the polymer shells, the Ag@SiO$_2$-g-PtBA-b-PS nanospheres then undergo a Friedel-Crafts hypercrosslinking reaction with anhydrous aluminium chloride (AlCl$_3$) as the catalyst and carbon tetrachloride (CCl$_4$) as the solvent and crosslinker to produce Ag@SiO$_2$-g-PAA-xPS,$^{[18]}$ followed by etching the SiO$_2$ egg whites with the HF solution. Notably, the inner PtBA chains are hydrolysed and transformed to PAA linings in the hypercrosslinking process due to the strong acidity of AlCl$_3$, giving rise to the target product yolk-shell Ag@PAA-xPS nanospheres (Fig. 2e). This result is confirmed by the Fourier transform infrared (FTIR) spectra which demonstrate the disappearance of tert-butyl characteristic bands (1369 and 1390 cm$^{-1}$) and the shift of carbonyl stretching band from 1730 cm$^{-1}$ for PtBA to 1717 cm$^{-1}$ for PAA (Fig. S3 in ESI).$^{[20]}$ Benefiting from the robust crosslinking bridges, the porous polymer shells are very stable upon etching the SiO$_2$ components,$^{[21]}$ leading to the formation of uniform yolk-shell nanospheres with an average diameter of 261 nm (Fig. 2f and Fig. S4 in ESI). No aggregates or free Ag nanoparticles outside the shells are observed, further indicating the good integrity and stability of the porous polymer shells.

The pore structure of yolk-shell Ag@PAA-xPS is quantified by N$_2$ adsorption-desorption isotherms. As illustrated in Fig. 3(a), a sharp increase of the nitrogen uptake at low relative pressure is observed, suggesting the presence of abundant micropores. Meanwhile, the steep hysteresis loop at high relative pressure indicates the coexistence of mesopores and macropores. According to the DFT pore size distribution curve, the size of micropores is 1.3 nm, while the meso-/macropores range from 2 nm to 126 nm (Fig. 3b). The micropores can be attributed to the hypercrosslinked structures of PS outer layers, while the meso-/macropores are derived from the cavities formed by removing SiO$_2$ egg whites and the interspaces of interconnected yolk-shell nanospheres. The Brunauer-Emmett-Teller surface area ($S_{\text{BET}}$) of yolk-shell Ag@PAA-xPS is measured to be 172 m$^2$·g$^{-1}$. Notably, $S_{\text{BET}}$ of Ag@SiO$_2$-g-PtBA-b-PS and Ag@SiO$_2$-g-PAA-xPS is 21 and 61 m$^2$·g$^{-1}$, respectively (Fig. S5 in ESI). The results demonstrate that both hypercrosslinking reaction and silica etching are crucial for the high surface area of yolk-shell Ag@PAA-xPS.

The unusual yolk-shell nanostructures with unique porous Janus polymer shells and noble-metal yolk make Ag@PAA-xPS a very attractive candidate as nanoreactors for catalytic reactions.$^{[22]}$ For demonstration, the catalytic degradation of dye molecules by Ag nanoparticles with the presence of NaBH$_4$ is chosen as a model reaction. As an important class of industrial products, dyes are commonly used in various industries, such as printing and dyeing in textiles, paper, and paints. However, the inevitable release of these dyes into waters, even below 1 ppm, can cause serious environmental and biological problems, which has a great influence on our health and lives. The catalytic degradation of harmful dyes into less toxic small molecules via noble metal-based nanocatalysts is regarded as an efficient, green, and economical method for environmental treatment.$^{[23,24]}$

Herein, because of the acidic characteristic of PAA brush linings, Lewis basic dyes, e.g., rhodamine B (RhB) and methylene blue (MB), are chosen for demonstration (Fig. S6 in ESI). It is well known that the acidic PAA chains have a strong interaction with the cationic dyes, which can result in their enrichment in the interior cavities. As shown in Fig. 4(a), the original color of RhB aqueous solution is deep pink with the presence of NaBH$_4$. After the addition of yolk-shell Ag@PAA-xPS, the pink color is rapidly faded and the aqueous solution is colorless within only 15 min, suggestive of high catalytic activity. In order to demonstrate that such a color change of the aqueous solution results from the catalytic degradation of RhB molecules by the Ag catalysts, the yolk-shell Ag@PAA-xPS after reaction of 60 min is collected and then dispersed in the strong polar dimethyl sulfoxide (DMSO) solvent, which has great ability to elute the adsorbed molecules and release them into the bulk solution. As shown in Fig. S7 (in ESI), the DMSO solution remains colorless, indicating no RhB molecules remaining in the yolk-shell Ag@PAA-xPS. Contrarily, the DMSO solution dispersed with hollow PAA-xPS without Ag nanoparticles is deep pink again because of the release of adsorbed RhB molecules from the PAA-xPS shells. The results demonstrate that all the RhB molecules can be degraded in the yolk-shell Ag@PAA-xPS nanoreactor.

Fig. 4(b) shows the time-dependent ultraviolet-visible (UV-Vis) absorption spectra of the degradation of RhB molecules in the presence of yolk-shell Ag@PAA-xPS. RhB exhibits a characteristic ultraviolet-visible (UV-Vis) absorption peak at a wavelength of 553 nm, which sharply descends after the ad-
dition of yolk-shell Ag@PAA-xPS, in accordance with the digital photos of Fig. 4(a). The time-concentration curve reveals that 91.4% of RhB molecules are degraded by the yolk-shell Ag@PAA-xPS within only 2 min, and almost all the RhB molecules (97%) disappear within 15 min (Fig. 4d). In contrast, the concentration of RhB molecules remains unchanged without the addition of any catalysts. It should be noted that the PAA brush linings play a critical role in the superior activity of yolk-shell Ag@PAA-xPS toward the RhB degradation. As shown in Figs. 4(a) and 4(c), substantial RhB molecules still remain in the aqueous solution after reaction for 60 min when yolk-shell Ag@xPS is used as the catalyst. Fig. 4(d) reveals that only 75% of RhB molecules are degraded by the yolk-shell Ag@xPS within 2 min, and the concentration of RhB is almost unchanged from then on, indicating that the catalytic performance of yolk-shell Ag@xPS is greatly limited when the bulk concentration of RhB molecules is relatively low. The results demonstrate that the acidic PAA brush linings with strong interaction with the cationic dyes facilitate the diffusion of RhB molecules through the porous shells and enrich them in the internal cavities, and thus work synergistically with Ag yolks for the efficient degradation of RhB molecules. As shown in Fig. 5b in (ESI), all the MB molecules can be degraded within only 15 min by the yolk-shell Ag@PAA-xPS, much faster than the yolk-shell Ag@xPS catalyst, revealing the universality of yolk-shell Ag@PAA-xPS catalyst for the degradation of Lewis basic dyes.

CONCLUSIONS

In summary, we have demonstrated a simple yet efficient strategy for the fabrication of novel yolk-shell structure by encapsulating noble metal nanoparticles with porous Janus polymer shells. The porous Janus polymer shell is obtained by the Friedel-Crafts hypercrosslinking of PBA-b-PS brushes grafted from the surfaces of SiO₂ nanospheres, which produces a crosslinked PS outer layer with well-developed porosity and a tethered PAA brush lining with abundant carboxyl groups. The crosslinked PS outer layer provides abundant pathways for mass diffusion, while the tethered PAA brushes exhibit great affinity toward specific species (e.g., cationic dyes), leading to their enrichment from the bulk solution into the interior cavities. Benefitting from these fascinating features, the yolk-shell Ag@PAA-xPS holds great promise for both efficient catalytic degradation of cationic dyes. Our findings could open an avenue for the design and fabrication of novel yolk-shell Janus nanostructures and provide an opportunity to boost their performance.

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Electronic Supplementary Information

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