Yolk–Shell Nanocomposites of a Gold Nanocore Encapsulated in an Electroactive Polyaniline Shell for Catalytic Aerobic Oxidation

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ABSTRACT: Noble metal nanoparticles (NPs) have been widely applied in nanocatalysis owing to the benefits associated with their miniature size. However, improving their stability and reusability during catalytic applications still remains a great challenge. To this end, monodispersed gold@void@polyaniline yolk–shell nanocomposites (Au@void@PANI YSNs) were synthesized using bottom-up template-assisted methods. Au@SiO2 NPs, prepared from a modified sol–gel process, were used as templates for the thiol–ene click reaction with 4-vinylaniline (VAn) to immobilize the aniline moieties, which later performed as the initiation sites for the oxidative copolymerization of aniline from the outer surface of the Au@SiO2–VAn NPs with an electroactive PANI shell (Au@SiO2@PANI NPs). The silica layer sandwiched between the Au core and PANI shell was selectively removed by aqueous hydrofluoric acid to produce Au@void@PANI YSNs with a movable Au core. The electroactive PANI shell not only serves as a physical barrier that prevents the self-association of Au cores and provides a vacant cavity where chemical transformations take place on the Au cores in a controlled manner but also improves the activity and stability of Au cores due to the electrons delocalization and transfer from the Au d orbitals of the nanocores to the π-conjugated ligands of the PANI shell, as proved by the X-ray photoelectron spectroscopy results. The as-synthesized YSNs were found to perform as flexible and reusable heterogeneous catalysts with high catalytic efficiency for the aerobic oxidation of alcohol in aqueous solution. One may find the present study to be a general and effective way to fabricate monodispersed hollow nanomaterials in a controlled and green manner.

1. INTRODUCTION

Noble metal nanoparticles (NPs) on solid supports have been recognized as promising catalysts in various fields, including the fine chemicals industry and environmental protection.1–10 However, NPs with their miniature size usually undergo sintering or self-association during the catalytic reaction, leading to undesirable destruction of the active surface area for catalysis. In addition, the stability and reusability of NPs still remain a great challenge upon usage.11–14 To this end, sophisticated nanostructures were fabricated with a hollow cavity, in “yolk–shell” or “rattle-type” nanostructures, to create individualized nanoreactors around the catalytically active nanocores.15–22 These catalytic nanoreactors have several advantages in comparison with the conventional catalysts embedded in solid supports. Encapsulation of an individual nanocore into a solid but permeable shell creates a relatively homogeneous atmosphere and effectively prevents the functional nanocore from sintering or self-aggregation even under harsh reaction conditions. Furthermore, the interaction of catalytically active cores with the outer shells is more effective than that in the bulk form, leading to higher catalytic activity.

Among the various conducting polymers, polyaniline (PANI) has been of particular interest owing to its comparatively low cost, excellent chemical and thermal stabilities, tunable electrical conductivity, and interconvertible intrinsic redox states.23–25 These properties have enabled a broad spectrum of applications, including in the areas of batteries, catalysts, sensors, actuators, antistatic coating, corrosion protection of metal, biocompatible materials, electrochromic devices, and light-emitting devices.26–31 In light of the strong interaction between the amine groups and noble metal atoms on the surface of NPs, PANI, consisting of benzene rings and amine groups within the same repeat unit, will be an ideal stabilizer for noble metal cores. Control over the size of NPs with the catalytically active core, PANI polymer shell, and free space in between is still lacking but is of crucial importance for their applications as nanocatalysts.

In the present paper, we report a flexible, scalable, and robust template-assisted approach for the fabrication of yolk–shell nanocomposites (YSNs), encapsulating a movable Au core in the vacant space of an electroactive polymer shell (Au@void@PANI YSNs). The synthesis procedure consists of three major steps, as shown in Scheme 1. The most straightforward approach for the synthesis of YSNs is the template-assisted approach, where the core and two concentric shells with distinct chemical compositions are constructed from inside to outside in sequence, followed by selective removal of the template layer by dissolution or thermal decomposition. By
carefully selecting the shell compositions, this approach could be extended to the fabrication of various kinds of hollow or yolk−shell nanomaterials.

2. RESULTS AND DISCUSSION

2.1. Au and Au@SiO2−MTS Core−Shell NPs. Procedures for the template-assisted synthesis of monodispersed YSNs, comprising a gold core and an electroactive PANI shell (Au@void@PANI YSNs), are illustrated in Scheme 1. Common methods to fabricate YSNs involve soft template and template-free methods, Ostwald ripening and self-aggregation methods, and methods based on the galvanic replacement or the Kirkendall effect.15−22,32 These methods often require the use of highly toxic reagents (e.g., KCN), are restrained to specific nanostructures, and remain a great challenge to controlling the size and size distribution of the resultant NPs.15−22,32 An alternative method is selective etching of a sacrificial layer of core−double shell NPs. The template-assisted methods have proved to be general and effective methods for the synthesis of monodispersed hollow nanomaterials with a sophisticated structure, especially for the inorganic-polymer YSNs, in spite of their tedious synthetic processes.

Precise control over the size, shape, and size/shape distribution of nanocores is the prerequisite to developing monodispersed YSNs. Despite being an environmentally benign process and its ease of regulating the size of Au NPs, the Turkevich method usually suffers from a broad and undesirable size/shape distribution.33,34 This issue can be overcome by the rapid injection of a mixture of HAuCl4 (gold precursor), trisodium citrate (Na3Cit), and a trace amount of AgNO3 into boiling water.33 For the Turkevich method, the use of a Na3Cit/HAuCl4 feed molar ratio of 3.5:1 produces Au NPs with a minimal size.33,34 The Au NPs with an average diameter of 13 nm were obtained from the use of a Na3Cit/HAuCl4 molar ratio of 3.5:1, as confirmed by the transmission electron microscopy (TEM) image in Figure 1a. This approach effectively supplements the classical Turkevich method in terms of reproducibility and uniformity of the NP size and shape.

The thiol groups on the surface of Au@SiO2−MTS NPs will perform as coupling anchors for the surface-initiated thiol−ene click reaction for the introduction of aniline moieties.36−42 The absorbance of amphiphilic poly(vinylpyrrolidone) (PVP) stabilizers onto Au surfaces provides sufficient affinity for silica coatings on the single Au core. The respective TEM images of the so-obtained Au@SiO2−MTS NPs with two distinctive SiO2−MTS shell thicknesses of about 19 and 24 nm are shown in Figure 1bc, respectively. For each type of NP, a narrowly distributed and smooth concentric silica shell of lower image contrast encircling the Au core is clearly displayed. The silica shell thickness can be tuned by varying the tetraethyl orthosilicate (TEOS) feed volume. The average size, size distribution, and corresponding shell thickness of the Au@
SiO2−MTS NPs are calculated and summarized in Table 1. The X-ray photoelectron spectroscopy (XPS) wide-scan spectrum of the Au@SiO2−MTS-2 NPs is shown in Figure 2a. The dense and thick coverage of the SiO2−MTS shell on the Au@SiO2−MTS-2 NPs resulted in the signal eclipse of the underlying elements [Au 4f signal with a binding energy (BE) of ∼84 eV] in the XPS wide-scan spectrum.

### 2.2. Au@void@PANI YSNs

Introduction of aniline moieties onto the outer surface of the core−shell NPs allowed the subsequent fabrication of electroactive PANI outer shells via oxidative graft polymerization. Because of the incompatibility of aniline moieties with the radical polymerization and conventional coupling reaction, the use of a thiol−ene click reaction has recently attracted considerable interest and has been adopted as a complementary method for the synthesis of polymer nanocomposites. Thiol−ene click reactions proceed under mild reaction conditions with high efficiency and fast kinetics. 4-Vinylaniline (VAn) reacted with the thiol groups of the SiO2−MTS shell and was consequently clicked onto the shell surface (Scheme 1). The presence of a nitrogen signal in the XPS wide-scan spectrum of Au@SiO2−VAn NPs indicated that VAn had been successfully clicked onto the silica templates (Figure 2b).

The aniline moieties on the Au@SiO2−VAn NPs can act as the anchoring and initiation sites for the surface-initiated oxidative polymerization of aniline in the presence of ammonium persulfate (APS) as the oxidant (Scheme 1). The TEM image of Au@SiO2@PANI-2 NPs in Figure 1d reveals a core−double shell hybrid nanoarchitecture with two concentric shells of distinctive image contrasts encircling the Au cores. With the increase in aniline feed volumes from 50 to 200 μL, the PANI shell thickness of the core−double shell NPs increases correspondingly from 7 to 29 nm, as shown in Table 1.

Removal of the silica sacrificial layer of the Au@SiO2@PANI core−double shell NPs by hydrofluoric acid (HF) etching resulted in the formation of HF-doped Au@void@PANI YSNs. Unlike in strong bases, the etching process of the silica layer by HF usually proceeds with high efficiency, fast kinetics, and formation of products with high water solubility. Excess HF was used to ensure total corrosion of the silica template layer. The YSN nanostructure with a hollow shell enclosing a movable metal core is clearly displayed in Figure 1e.f. The PANI shell with a thickness of 16 nm provides sufficient strength to sustain the hollow cavity (Figure 1e). Decrease in the thickness of the PANI shell to around 7 nm will lead to the deformation of hollow nanostructures, as shown in Figure 1f. The distinct Au 4f signal in the wide-scan spectrum of Au@void@PANI-1 YSNs suggests that the PANI shell thickness is comparable to the 8 nm probing depth of the XPS technique in organic matrices (Figure 2c). The electrons delocalization and transfer from the Au d orbitals to the π-conjugated ligands of the PANI shell have resulted in the shift of a normal Au 4f signal to a higher BE of 84.0 eV to a higher BE of 84.8 eV, as shown in Figure 2d. The interaction between the Au core and PANI shell can effectively stabilize the Au nanocores, making it difficult to lose additional electrons. Figure 2e–g describes the respective N 1s core-level spectra of the Au@void@PANI-1 YSNs in their neutral emeraldine (EM) base form, HF-protonated form, and fully reduced leucoemeraldine (LM) base form, respectively. The curve-fitted XPS N 1s core-level line

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Table 1. Size, Size Distribution, and Shell Thickness of the Gold, Gold@Silica Core−Shell, and Gold@Silica@Polymer Core−Double Shell NPs

| Sample          | D_ave (nm) | D_w (nm) | PDI (%) | Shell Thickness (nm) | CV (%) |
|-----------------|------------|----------|---------|----------------------|--------|
| Au              | 13         | 14       | 1.08    | 24                   | 5      |
| Au@SiO2−MTS-1   | 50         | 55       | 1.10    | 19                   | 17     |
| Au@SiO2−MTS-2   | 61         | 66       | 1.08    | 24                   | 14     |
| Au@SiO2−MTS-3   | 73         | 77       | 1.05    | 30                   | 12     |
| Au@SiO2@PANI-1  | 74         | 78       | 1.05    | 24 + 7               | 10     |
| Au@SiO2@PANI-2  | 92         | 98       | 1.07    | 24 + 16              | 13     |
| Au@SiO2@PANI-3  | 119        | 127      | 1.07    | 24 + 29              | 12     |

*D_ave is the number-average diameter, D_w is the weight-average diameter, PDI is the polydispersity index, and CV is the coefficient of variation (see Experimental Section). 2The shell thicknesses of the core−shell and core−double shell were determined from the TEM images. The Au@SiO2@PANI core−double shell NPs were prepared using Au@SiO2−MTS-2 as seeds.

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Figure 2. XPS wide-scan, N 1s, and Au 4f core-level spectra of the (a) Au@SiO2−MTS-2 core−shell, (b) Au@SiO2−VAn-2 core−shell NPs, Au@void@PANI-1 YSNs in their (c−e) neutral EM base form, (f) HF-protonated form, and (g) fully reduced LM base form.
shape of the Au@void@PANI-1 YSNs comprises two peak components with BEs at 398.2 and 399.4 eV for the respective quinonoid imine (−N=) and benzenoid amine (−NH−) units of the grafted PANI shell in their EM base form (Figure 2e).23,42−44,50,51 Protonation of the PANI shell by HF preferentially leads to the conversion of the −N= species to a comparable amount of the N+ species (Figure 2f).23,42,50,51 The predominance of C−N peak intensity at the BE of about 399.4 eV in Figure 2g is attributable to the conversion of PANI shells to the fully reduced LM state.

Figure 3 exhibits the respective thermogravimetric analysis (TGA) curves of the PANI homopolymers (curve a) and Au@void@PANI YSNs (curve b). The gross weight loss occurring at around 400 °C is associated with the thermal degradation of the PANI shells. On the basis of the weight remaining at 900 °C of these two samples, the weight content of Au nanocores in the Au@void@PANI YSNs is about 14 wt %.

2.3. Application of the Au@void@PANI YSNs in Aerobic Catalytic Oxidation of Alcohol. As a typical set of organic reactions in the fine chemicals industry, the chemical transformation of alcohols to aldehydes, ketones, and carboxylic acids usually requires stoichiometric consumption of toxic or corrosive substances, such as heavy metal ions in high oxidation states.32,52 The overoxidation and leakage of Au NPs during the catalytic applications largely promote the development of stable and reusable Au nanocatalysts for the chemical transformation of alcohols under mild conditions.54,55 In the present work, aerobic oxidation of 1-phenylethanol catalyzed by the Au@void@PANI YSNs in an aqueous solution and at room temperature was carried out (Scheme 2). The conversion reaches 90% at around 6 h and eventually exceeds 95% when the reaction time is prolonged to 24 h, as can be seen from the time course of the ketone yield in Figure 4A. The strong binding between the π-conjugated ligands in PANI shells and the Au NPs renders a more effective and comprehensive contact of reactants with Au cores. In addition, the catalytic YSNs can be facilely recycled by centrifugation and reused without significant loss of reactivity (yield loss within 2% after eight successive cycles; inset of Figure 4A). It has been reported that Au NPs are capable of activating O2 at the solid−liquid interface during the aerobic oxidation of alcohol in an aqueous solution.56 The PANI shells prevent the Au NPs from self-aggregation. No catalytic reduction of 1-phenylethanol was observed in the absence of YSNs. The stability of the YSNs is one of the most essential criteria governing their practical applications. The TEM image clearly displays the well-preserved rattle-type nanostructure with a hollow shell encircling a movable core, as shown in Figure 4B. The average diameter of the Au nanocores, as measured and calculated from Figure 4B, is about 13 nm, which is consistent with that obtained before the aerobic oxidation (Table 1). The inductively coupled plasma method also indicated that there was no conversion or leakage of the Au cores in the YSNs to the reaction solution during the catalytic applications. Thus, the synthesized YSNs can serve as a spatially confined reusable nanoreactor for catalytic applications.

3. CONCLUSIONS
Monodispersed Au@void@PANI YSNs, comprising a movable gold nanocore and an electroactive PANI shell, have been fabricated by selective removal of the silica template layer of Au@SiO2@PANI core−double shell NPs obtained from the combined sol−gel process, thiol−ene click reaction, and oxidative graft copolymerization. The Au@void@PANI YSNs exhibit desirable catalytic efficiency upon the usage of the aerobic oxidation of alcohols in an aqueous solution at room
temperature. Moreover, it can be facilely recycled from the reaction residue by centrifugation. The improved activity and stability have resulted from the unique YSN nanostructure, in which electrons delocalize and transfer from Au d orbitals of the core to the π-conjugated ligands of the PANI shell. Thus, the stable PANI shell protects the Au cores from self-aggregation. The versatile synthesis protocol for the YSNs of the present study opens up the possibility of designing a broad range of noble metal NPs encapsulated in an electroactive polymer shell. The YSNs can be used as a new class of nanoreactors for heterogeneous catalytic applications in a robust, confined, and controlled environment.

4. EXPERIMENTAL SECTION

4.1. Materials. TEOS (98%), (3-mercaptotributyl)-trimethoxysilane (MTS, 95%), 2,2-dimethoxy-2-phenylaceto-phenone (DMPA, 99%), VAn (97%), APS ((NH4)2S2O8, ≥98%), aniline (≥99.5%), PVP (Mw = 10 000 g/mol), and phenylethanol (98%) were obtained from Sigma-Aldrich Chem. Co. and used as received without further purification. Ammonium hydroxide solution (13.2 M, 37 wt %), hydrochloric acid (HCl, 37 wt %), potassium bicarbonate (K2CO3, ≥99%), HF (48 wt %), and N-methyl-2-pyrrolidinone (NMP, reagent grade) were obtained from Merck Chem. Co. and used as received without further purification. PANI was obtained according to the methods reported in the literature.23,24 All glassware and stirring bars were cleaned with aqua regia, consisting of 37 wt % hydrochloric acid (75 vol %) and 65 wt % nitric acid (25 vol %), and then rinsed thoroughly with ultrapure water before use.

4.2. Synthesis of the Au@SiO2−MTS Core−Shell NPs via a Sol−Gel Reaction. Preparation of monodispersed quasispherical gold NPs (Au NPs) was carried out using procedures reported earlier.33−35 About 20 mg of Au NPs with an average diameter of 13 nm were stabilized by PVP (Mw = 10 000 g/mol), concentrated, and stored in 40 mL of ultrapure water.

The incorporation of a silica template layer on the PVP-stabilized Au NPs was performed via the sol−gel reaction with TEOS. In a typical synthetic procedure, the above-mentioned Au NP aqueous solution was mixed with ethanol (160 mL) and ammonium hydroxide solution (13.2 M, 5 mL), with the aid of ultrasonic sonication for 30 min. About 0.2 mL (0.9 mmol) of TEOS was added dropwise to the reaction mixture under vigorous stirring. The reaction was allowed to proceed at room temperature for 24 h. After the reaction, the Au@SiO2 NPs were isolated by centrifugation and purified by three cycles of redispersion/washing/centrifugation in a mixture of ethanol and water of equal volume ratio. The purified Au@SiO2 NPs were dried under reduced pressure for future use.

About 30 mg of Au@SiO2 NPs were dispersed into a mixture of ethanol (80 mL), water (20 mL), and ammonium hydroxide solution (13.2 M, 2.5 mL). The reaction mixture was sonicated for 30 min. About 0.3 mL of MTS (1.26 mmol) was introduced dropwise into the mixture before sealing the flask in an argon atmosphere. The reaction mixture was stirred vigorously over a reaction period of 24 h, to introduce the thiol groups onto the surface of silica templates. After the reaction, the Au@SiO2−MTS NPs were isolated by centrifugation and purified by three cycles of redispersion/washing/centrifugation in a water and ethanol mixture of equal volume ratio. The purified NPs were dried in a vacuum oven at room temperature for 24 h. The involvement of initial TEOS volumes of 0.2, 0.3, and 0.4 mL in sequence in the sol−gel reaction produces Au@SiO2−MTS core−shell NPs with shell thicknesses of 19, 24, and 30 nm, respectively.

4.3. Synthesis of the Au@SiO2−PANI Core−Double Shell NPs via the oxidative graft polymerization. In a typical thiol−ene click reaction, about 35 mg of Au@SiO2−MTS NPs were dispersed into 30 mL of ethanol with the aid of sonication for 15 min. DMPA (246 mg, 1.77 mmol) and VAn (200 μL, 1.77 mmol) were then introduced into the mixture. The mixture was stirred and daged with purified argon stream for 20 min, sealed, and subjected to UV irradiation for 1 h. The Au@SiO2−VAn NPs were extracted thrice with ethanol to dissolve bound reactants. The Au@SiO2−VAn NPs were dried under reduced pressure for future use.

About 25 mg of the Au@SiO2−VAn core−shell NPs and 100 μL (1.1 mmol) of aniline were added to 10 mL of 1 M HCl under vigorous stirring. About 250 mg (1.1 mmol) of APS was dissolved in 2 mL of 1 M HCl and introduced dropwise into the reaction mixture at 0 °C. The oxidative graft copolymerization was allowed to proceed under stirring for 8 h. The use of excess NaOH (1 M) renders the conversion of the PANI shell to the neutral EM base form. The resulting Au@SiO2−PANI NPs were isolated by centrifugation and purified by three cycles of redispersion/washing/centrifugation in NMP to dissolve the adsorbed oligomers and homopolymers. The purified Au@SiO2−PANI NPs were dried under reduced pressure until a constant weight was obtained. Au@SiO2−PANI core−double shell NPs of 7, 16, and 29 nm in PANI shell thickness were...
synthesized via oxidative graft polymerization using initial aniline feed volumes of 50, 100, and 200 μL, respectively.

4.4. Preparation of the Au@void@PANI YSNs by HF Etching. Au@void@PANI YSNs were prepared by selective etching of the silica sacrificial layer from the Au@SiO₂@PANI NPs by HF corrosion. About 40 mg of Au@SiO₂@PANI NPs were introduced into 10 mL of HF (24 wt %). The reaction was allowed to proceed under stirring at room temperature for 12 h. The YSNs were separated by centrifugation and dialyzed in ultrapure water for one week to remove the excess HF and SiF₄. Finally, the Au@void@PANI YSNs were recovered via lyophilization. Interconversion of the protonated PANI shells to the EM base by reaction with a strong base (e.g., NaOH) and subsequent EM base to fully reduced LM base by reaction with reducing agents (e.g., hydrazine) was carried out according to the methods reported in the literature with a slight modification.²³,²⁴,²⁵

4.5. Catalytic Aerobic Oxidation of Alcohol. Aerobic oxidation of alcohol is catalyzed by Au NPs in an aqueous solution.²⁶ For the aerobic catalytic oxidation of alcohol using the Au@void@PANI YSNs, 1-phenylethanol (12.2 mg, 0.1 mmol) and K₂CO₃ (41.4 mg, 0.3 mmol) in ultrapure water (5 mL) were introduced into a 25 mL reaction flask. The Au@void@PANI YSN suspension (1 mL, 10 mg/mL) was added to the solution. The aerobic oxidation was carried out under stirring at 25 °C. The reaction mixture (6 mL) was taken out at fixed periods, diluted with 1 mL of 1 M HCl, and extracted three times with ethyl acetate (5 mL). After being dried over magnesium sulfate, the combined organic layer was collected by filtration and diluted with ethyl acetate to about 30 mL in total. The product was studied by gas chromatography (GC, Agilent, 7890A-5975C, USA), and the reaction yield was obtained from the calibration curve.

4.6. Materials Characterization. The morphology of the NPs was studied by a field emission TEM (JEOL JEM-2100F). Surface compositions of the NPs were determined by XPS measurements on a Kratos AXIS Ultra DLD spectrometer equipped with a monochromatized Al Kα X-ray source (1486.71 eV photons). Thermal stability of the YSNs was analyzed by TGA. Each sample was heated from 25 °C to about 900 °C, with a heating rate of 10 °C/min, in a dry nitrogen atmosphere in a Shimadzu DTG-60AH TGA-DTA Analyzer. The polydispersity index (PDI) of the NPs was determined by

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PDI = \frac{D_w}{D_n} \quad D_n = \sum_{i=1}^{k} n_i D_i / \sum_{i=1}^{k} n_i \]

\[
D_w = \sum_{i=1}^{k} n_i D_i^{1.4} / \sum_{i=1}^{k} n_i \]

where Dₙ denotes the number-average diameter, Dₘ denotes the weight-average diameter, and Dₙ denotes the measured diameter of the NPs. The average diameter of each sample was calculated based on the Dₙ of random selection of at least 100 NPs in the TEM images. Coefficient of variation (CV) denoted as the ratio of standard deviation (δ) to the mean (Dₙ), or CV = δ/Dₙ, was introduced to estimate the error in the NP size.

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**Notes**

The authors declare no competing financial interest.

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