

Template-Free Synthesis and Characterization of Single-Phase Voided Poly(*o*-anisidine) and Polyaniline Colloidal Spheres

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Single-phase hollow poly(*o*-anisidine) colloidal spheres with uniform sizes were directly synthesized in dilute aqueous solution of *o*-anisidine in the presence of a small amount of an initiator, cupric acetate or basic cupric bromide, $\text{Cu}_2(\text{OH})_3\text{Br}$, under hydrothermal conditions. The void volume and size of hollow poly(*o*-anisidine) colloidal spheres can be readily tuned by varying the hydrothermal reaction time and adjusting the ratios between the starting reactants. The formation of voided poly(*o*-anisidine) results from a diffusion-related process driven by the relatively large concentration change between polymer core and solution as well as the high pressure and temperature under hydrothermal conditions. At the same time, the mesostructures of poly(*o*-anisidine) are dependent on reaction time, temperature, and monomer concentration. An extension of this one-pot synthetic method yields hollow polyaniline colloidal spheres.

Introduction

Hollow polymeric particles possess a high stability, low permeability and density, large surface area, great light scattering, and tunable particle diameter and shell thickness in comparison with the hollow organic vesicles formed from the self-assembly of amphiphilic molecules. Owing to these characteristics, hollow polymeric particles can serve as microreaction vessels, drug delivery vehicles, protective shells, and synthetic pigments in huge industrial scales.^{1–3} Currently, the hollow polymeric particles are available chiefly by means of templating approaches, which can be mainly classified into two categories: (i) a sacrificial core route and (ii) interfacial polymerization. The first concept involves coating core templates with polymers or directly polymerizing monomers around colloidal particles and thereafter removing the core by heating or chemical treatment. The earliest processes for producing hollow latex particles involve a two-stage core–shell emulsion polymerization, by which a structured latex with a carboxylated core polymer and one or more outer shells is prepared.^{4–6} The neutralization of the carboxylated core with base at appropriate temperatures causes the expansion of the particles and produces water-

or polyelectrolyte-filled hollow particles. Most recently, a number of alternative processes has been developed. In many cases, silica is an effective core material for its stability and facile core removal by etching with HF.^{7–10} Occasionally, gold nanoparticles, hydrocarbon nonsolvents, and polymers were used as core templates for hollow polymer nano- and microspheres.^{11–14} For the sacrificial core method, the tedious post-treatment tends to cause deformation and deterioration of the resulting hollow particles. Notable examples of the interfacial polymerization methods have been documented recently, which can be regarded as a soft template route. Hollow polymer capsules have been achieved via polymerization at the interface of miniemulsion or an inverse W/O emulsion followed by liquid droplet removal.^{15,16} Incorporation of hydrophobic monomers between the vesicle bilayer is possible to create hollow particles after polymerization in situ.¹⁷ The required compatibility between monomer and interface, however, limits the generality of this method. In addition, the hollow particles obtained by interfacial polymerization often have irregular shapes and/or a wide size distribution due to the instability and size polydispersity of the soft templates.

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On account that only limited approaches have been used to date and their drawbacks mentioned previously, more synthetic routes that are both simple and efficient are desirable for hollow polymeric particles. Herein, we introduce a new strategy for the one-pot synthesis of single-phase hollow poly(*o*-anisidine) colloids via hydrothermal polymerization without using any templates. To conduct this polymerization, a weak oxidant, cupric acetate ($\text{Cu}(\text{Ac})_2$), or basic cupric bromide ($\text{Cu}_2(\text{OH})_3\text{Br}$), produced by the reaction of $\text{Cu}(\text{Ac})_2$ with the cationic surfactant cetyltrimethylammonium bromide (CTAB) was used as the initiator. In particular, the diameter and size distribution of hollow poly(*o*-anisidine) colloidal spheres can be well-controlled by $\text{Cu}_2(\text{OH})_3\text{Br}$ through a cationic surfactant-assisted route. Other mesostructures of poly(*o*-anisidine) including porous and solid colloidal spheres are also obtained by simply varying the *o*-anisidine concentration or temperature. Likewise, we are able to synthesize hollow polyaniline colloids in a similar manner.

As a kind of conducting/electronic polymer, the parent polyaniline and its derivatives are of great technological importance because of their high potential applications in microelectronic and optical devices.^{18,19} Thus far, intensive efforts have been made to develop techniques for the synthesis of polyaniline with various dimensions, morphologies, and architectures to meet the demand for the design and construction of devices.^{20–23} The activity in the production of voided polyaniline spheres is increasing now.^{24–26} Hybrid structures of polyaniline are simultaneously produced using the previous methods to become hollow polyaniline particles.^{24–26} In addition, the control over the size and dispersity of voided particles remains challenging, and the molecular structures of the hollow polyaniline spheres need to be further studied.^{24–26} To our knowledge, no techniques have been developed for the direct one-pot fabrication of hollow colloids of polyaniline and its derivatives. In terms of the oxidation potential of the aniline dimer (0.5 V),²⁷ the polymerization of aniline and its derivatives (e.g., 2-methylaniline, *o*-anisidine, and 2,5-dimethoxyaniline) can easily be accomplished at ambient temperature in the presence of transition metal salt oxidants, such as FeCl_3 , HAuCl_4 ,^{28,29} AgNO_3 ,³⁰ and CuCl_2 .^{31,32} In particular, the Cu^{2+} ion is expected to play a unique role in initiating the polymerization

of aniline and its derivatives as a result of its weak oxidizing ability and the coordination of the Cu^{2+} and amine groups (NH_2 -).

Experimental Procedures

All chemicals were obtained from commercial sources and used as received. The deionized water used throughout this work was degassed by bubbling with dry N_2 for 1 h.

Method I: Using $\text{Cu}(\text{Ac})_2$ as the Initiator. A total of 8 mL of an aqueous solution of $\text{Cu}(\text{Ac})_2$ (0.05 M) was loaded into a 40 mL Teflon-lined stainless steel autoclave. Afterwards, 32 mL of an aqueous solution of *o*-anisidine (0.025 or 0.10 M) was transferred to the autoclave, and almost immediately, the reaction mixture turned dark green due to the coordination of Cu^{2+} and *o*-anisidine. In the case of polymerizing 0.10 M *o*-anisidine in the autoclave, 0.4 mmol of cupric acetate was directly dissolved in 40 mL of an aqueous solution of 0.10 M *o*-anisidine. The autoclave was sealed and maintained at 180 °C for 7–11 h (or at 150 or 120 °C for 10 h) and subsequently cooled to ambient temperature naturally. The resulting stable poly(*o*-anisidine) colloidal solution was poured off and centrifuged at 4500 rpm for 5 min to isolate poly(*o*-anisidine). The poly(*o*-anisidine) precipitate was collected and redispersed in ethanol by sonication.

Similarly, 0.015 M aniline and 0.075 M $\text{Cu}(\text{Ac})_2$ were used to make hollow polyaniline particles. The polymerization of aniline was carried out at 180 °C for 4 h under hydrothermal conditions.

Method II: Using Cupric Bromide, Basic $\text{Cu}_2(\text{OH})_3\text{Br}$ as the Initiator. In a typical synthesis, 8 mL of an aqueous solution of $\text{Cu}(\text{Ac})_2$ (0.05 M) was loaded into a 40 mL Teflon-lined stainless steel autoclave. CTAB (1.6 mmol) was then added into the autoclave. A color change pattern from initially clear to visibly turbid and then to cloudy was gradually observed, suggesting the formation of $\text{Cu}_2(\text{OH})_3\text{Br}$ due to the reaction between CTAB and $\text{Cu}(\text{Ac})_2$ ($2\text{Cu}(\text{Ac})_2 + \text{CTAB} + 3\text{H}_2\text{O} \rightarrow \text{Cu}_2(\text{OH})_3\text{Br} + 3\text{HAc} + \text{CTA}^+\text{Ac}^-$, see Supporting Information). The yield of $\text{Cu}_2(\text{OH})_3\text{Br}$ is in proportion to the amount of $\text{Cu}(\text{Ac})_2$ when CTAB is in excess. Simultaneously, the anionic exchange leads to the production of cetyltrimethylammonium acetate. A total of 32 mL of an aqueous solution of 0.025 M *o*-anisidine was subsequently transferred to the autoclave. Without stirring the mixture, the autoclave was sealed and maintained at 180 °C for 7–11 h and then cooled to ambient temperature naturally. Poly(*o*-anisidine) was isolated by centrifugation and decantation. Finally, the product was ultrasonically dispersed in ethanol.

TEM images were obtained from the samples prepared by dropping the poly(*o*-anisidine) colloidal solutions in ethanol onto carbon-coated copper grids at an accelerating voltage of 100 kV. The mean size of the poly(*o*-anisidine) particles was estimated by measuring the diameters of at least 200 individual particles. SEM images were taken at a 15 kV accelerating voltage.

Results and Discussion

In analogy to the aniline/ $\text{Cu}(\text{II})$ system described in ref 31, the oxidative polymerization reaction did not occur in dilute solutions of *o*-anisidine and Cu^{2+} under ambient conditions due to the weak oxidizing ability of the Cu^{2+} ion. Instead, an *o*-anisidine–copper(II) complex was formed. This determines that a long induction time is required to initiate

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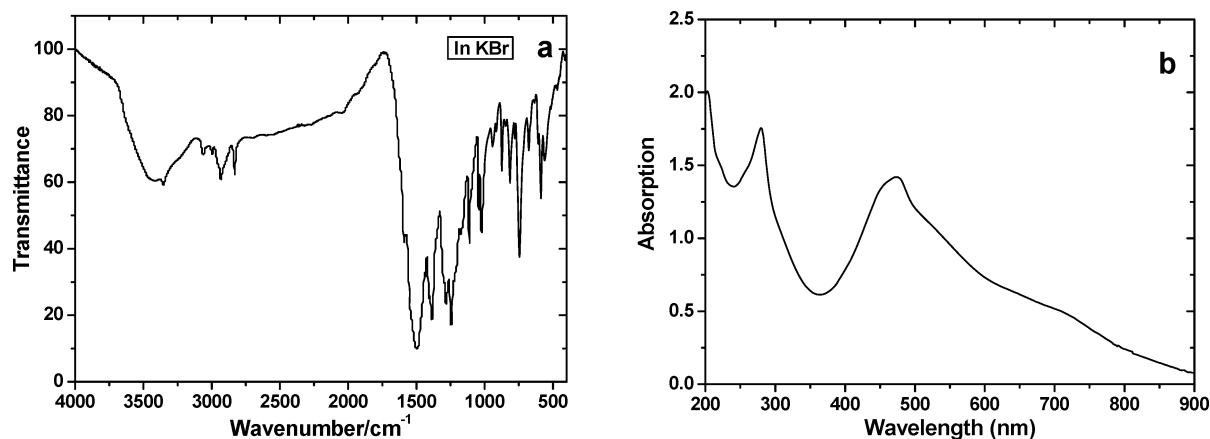


Figure 1. (a) FTIR spectrum of hollow poly(*o*-anisidine) particles isolated by centrifugation in KBr pellet. (b) UV-vis spectrum of hollow poly(*o*-anisidine) colloids in ethanol.

the polymerization of *o*-anisidine, which ensures that the polymerization reaction can proceed at a designated temperature. In our experiments, to implement the polymerization of *o*-anisidine, the reaction should be carried out at temperatures above 110 °C under hydrothermal conditions. Ultimately, a colloidally stable dispersion in solution is obtained at each monomer concentration after completion of the polymerization.

Figure 1a shows the FTIR spectrum of poly(*o*-anisidine) synthesized with 0.02 M monomer *o*-anisidine and 0.01 M initiator Cu(Ac)₂ at 180 °C after 10 h of polymerization reaction. First, the N-H stretching peaks are observed at 3300–3500 cm⁻¹. Second, the absorption bands related to the quinoid ring and stretching of the benzenoid ring appear at 1595 and 1490 cm⁻¹, respectively. The bands at 1284 and 1245 cm⁻¹ originate from C-N and C-O stretching absorptions, respectively. Third, the bands at 1386, 2830, and 2932 cm⁻¹ are due to the -CH₃-substituted group, while the bands at 3000 and 3055 cm⁻¹ can be assigned to the C-H stretch of the benzenoid ring. Finally, the bands at 1000–400 cm⁻¹ are associated with the *o*-substituted aromatic rings. Figure 1b presents the corresponding UV-vis spectrum of poly(*o*-anisidine). The shoulder peaks seen in the region of 300–350, 500–600, and 700–750 nm can be attributed to the π - π^* transition of benzenoid rings (inter-band transition), the exciton transition of the quinoid ring, and the polaron- π^* transition, respectively.^{33–36} The peak centered around 470 nm is probably due to the polaron- π transition.³⁷ Thus, we assume that the produced poly(*o*-anisidine) is in an emeraldine base form. At the same time, Cu²⁺ ions are reduced to Cu₂O during the polymerization process (see Supporting Information).

The mesostructures of poly(*o*-anisidine) synthesized with 0.02 M *o*-anisidine and 0.01 M Cu(Ac)₂ at 180 °C over a different hydrothermal reaction period were examined by scanning electron microscopy (SEM) and transmission

electron microscopy (TEM). SEM investigations display a view of discrete and regular spherical poly(*o*-anisidine) particles with diameters of 240–400 nm (Figure 2a). A closer look at the polymeric spheres in Figure 2a reveals that a number of poly(*o*-anisidine) microspheres has an opening, implying that they are hollow in the interior. TEM observations reveal that these microspheres exclusively have single, regular, well-centered circular voids inside them (Figure 2b). In multiple TEM studies, it was found that the mean diameter of the hollow poly(*o*-anisidine) particles was 305 nm, which does not differ significantly for the different concentration of Cu(Ac)₂ and hydrothermal reaction time. However, as shown in Figure 2b–d, increasing the hydrothermal reaction period from 7 to 10 to 12 h decreases the void volume of the hollow particles from 35 to 10% to microvoids accordingly. It can be inferred that the polymer chains around the spheres ramp into the interior of the voided particles as the polymerization reaction time increases. The decrease in the size of the voids in hollow particles with an increasing hydrothermal reaction time is presumably due to the swelling of the polymer shells.

The acid dopant level has a significant impact on the morphology of poly(*o*-anisidine). Figure 2e shows the TEM image of hollow poly(*o*-anisidine) particles obtained using 0.001 M HCl dopant in the initial reaction mixture after a polymerization period of 7 h. Four probe pressed-pellet conductivities for the hollow poly(*o*-anisidine) particles made in the presence of 0.001 M HCl are in the range of 0.002–0.01 S/cm. The conductivities for the hollow poly(*o*-anisidine) particles made without HCl are anticipated to be lower for the small amount of dopant present. Increasing the concentration of HCl or polymerization period leads to the granular growth of poly(*o*-anisidine). At the same time, we are able to extend this approach to synthesize hollow polyaniline colloids. Figure 2f exhibits the TEM image of hollow polyaniline particles with a 175 nm mean diameter and 30 nm mean shell thickness.

SEM and TEM studies manifested that hollow poly(*o*-anisidine) colloids were also yielded with basic cupric bromide as the initiator (Figure 3). The SEM image displays that regular spherical poly(*o*-anisidine) particles obtained at 180 °C after a hydrothermal reaction period of 11 h have a comparatively sharp size distribution (relative SD of 15%),

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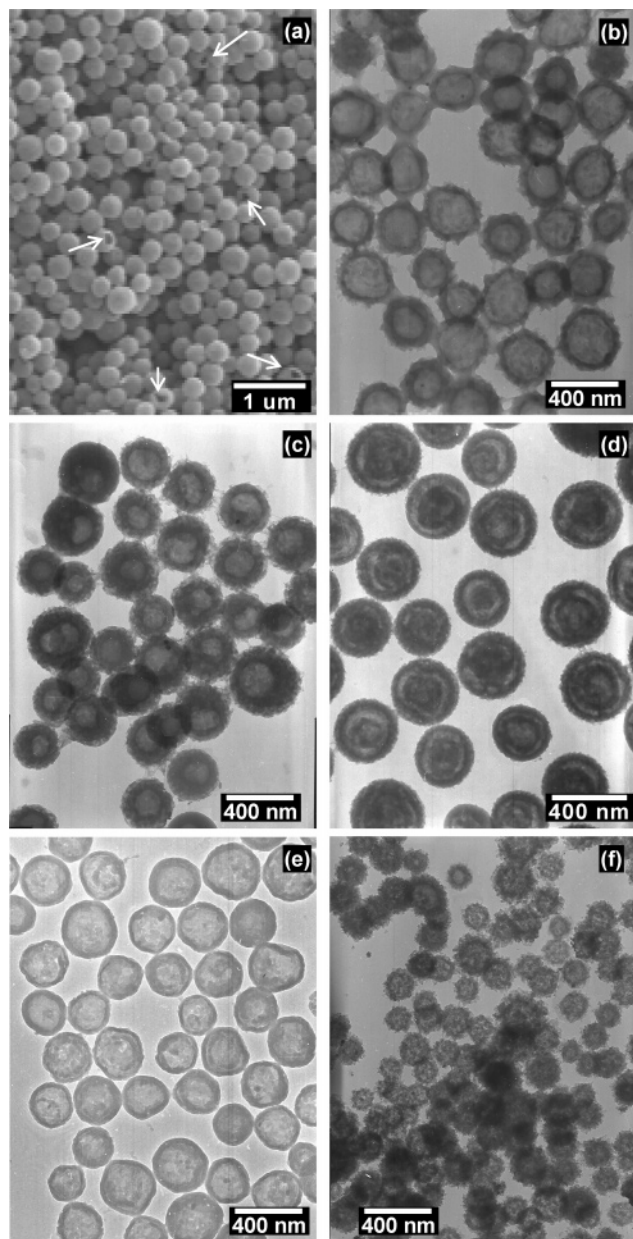


Figure 2. SEM (a) and TEM (b–e) images of poly(*o*-anisidine) synthesized after a hydrothermal reaction period of (a and b) 7 h, (c) 10 h, (d) 12 h, and (e) 7 h at 180 °C. Arrows in panel a point to the openings of the colloidal spheres. Parent solution concentrations: (a–e) 0.02 M *o*-anisidine and 0.01 M Cu(Ac)₂ and (e) 0.001 M HCl. (f) TEM image of polyaniline synthesized with 0.015 M aniline and 0.075 M Cu(Ac)₂ after a hydrothermal reaction period of 4 h at 180 °C.

while their diameters are in the range of 140–280 nm (Figure 3a). The TEM micrographs reveal that the nearly monodisperse particles have a well-defined interior cavity and nearly constant shell thickness (Figure 3c). The average outside diameter and shell thickness are 225 and 25 nm, respectively, that is, the void volume is 50%. This particular polymerization allows us to make a range of particle diameters and void fractions by simply varying the concentrations of Cu(Ac)₂ and CTAB. Figure 3b,d shows that the smallest hollow poly(*o*-anisidine) particles have a mean outer diameter of 115 nm with a 30% void fraction, while the largest have a mean outer diameter of 340 nm with a 65% void fraction. This size variation trend can also be seen when CTAB is replaced by tetradecyltrimethylammonium bromide. Never-

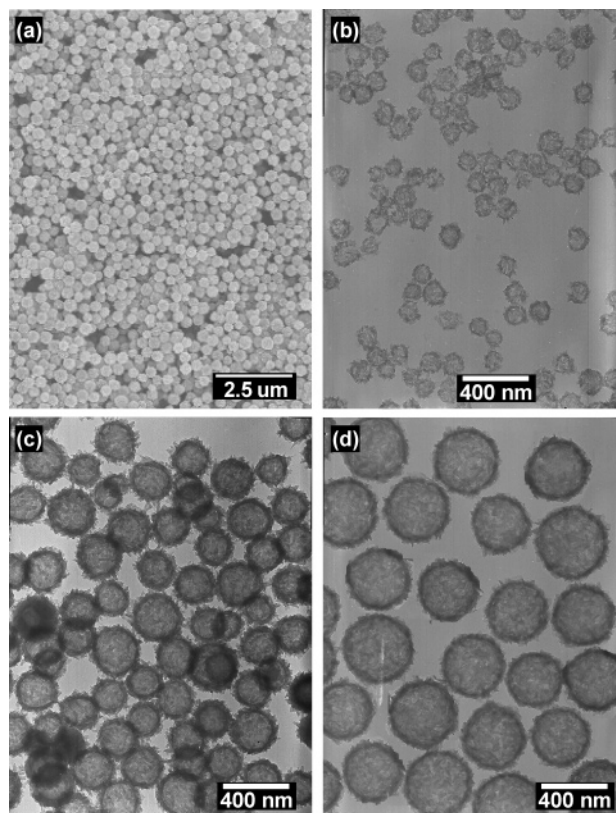


Figure 3. SEM (a) and TEM (b–d) images of poly(*o*-anisidine) synthesized at Cu(Ac)₂ and CTAB concentrations of (a and c) 0.01 and 0.04 M, (b) 0.01 and 0.02 M, and (d) 0.02 and 0.04 M, respectively. The *o*-anisidine concentration is maintained at 0.02 M. The reaction is performed at 180 °C under hydrothermal conditions.

theless, in both cases, the growth time (hydrothermal treatment of 7–11 h) has no noticeable effect on the diameter and shell thickness of the hollow poly(*o*-anisidine) particles. Our studies further demonstrate that the diameter of the hollow poly(*o*-anisidine) particles does not change if different amounts of the isolated Cu₂(OH)₃Br are used as the initiator. At this time, the polymerization of *o*-anisidine is performed through a solid–liquid reaction. It has been established that components in polymerization, such as initiator type and level, monomer type, and surfactant, all influence the final morphology of polymer.^{38,39} One possible hypothesis is that the cationic surfactant might play a certain role in controlling the growth of hollow polymeric particles, although the exact mechanism responsible for the diameter changes of the hollow poly(*o*-anisidine) particles is still not clear. The hollow polymeric particles described previously can maintain their regularly spherical shape after mechanical treatment and heating to 150 °C, thus suggesting that they are highly robust and stable.

The mesostructure evolution of poly(*o*-anisidine) particles takes place if the monomer concentration or polymerization reaction temperature is varied. Observations by SEM reveal that poly(*o*-anisidine) microspheres with comparatively rough or smooth surface are obtained after 10 h of hydrothermal reaction at 180 °C when the concentration of *o*-anisidine is increased to 0.08 or 0.10 M (Figure 4a,c). The corresponding

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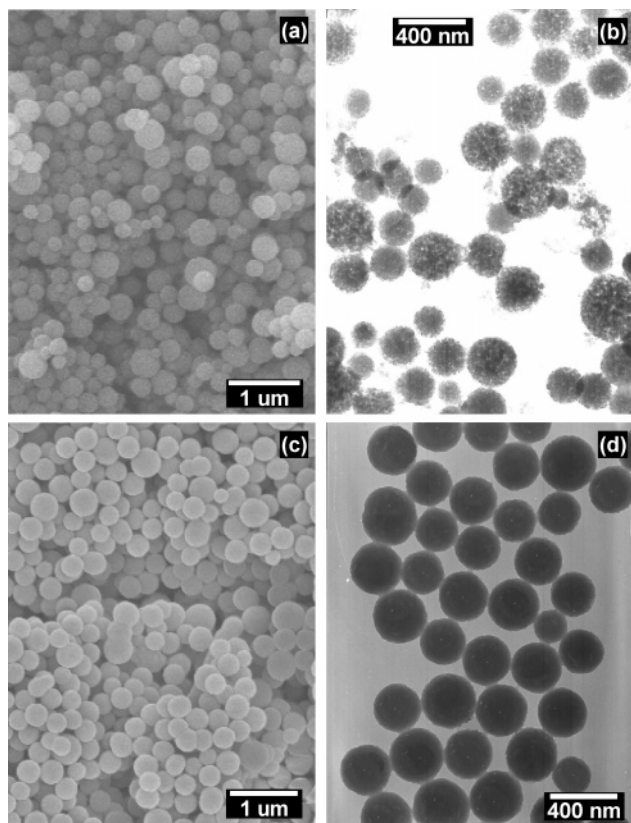


Figure 4. SEM (a and c) and TEM (b and d) images of poly(*o*-anisidine) synthesized with $\text{Cu}(\text{Ac})_2$ as the initiator at 180°C at an *o*-anisidine concentration of (a and b) 0.08 and (c and d) 0.10 M.

TEM micrographs in Figure 4b,d reveals that porous microspheres and solid microbeads are yielded, respectively. Alternatively, such porous microspheres and solid microbeads are formed if 0.02 M *o*-anisidine is polymerized for 10 h at 150 and 120°C , respectively. The FTIR and UV-vis spectra of all the mesostructured poly(*o*-anisidine) particles formed at different temperatures, monomer concentrations, and over different polymerization periods of time are identical to those shown in Figure 1a,b, indicating that they have the same emeraldine base structures.

To understand the void formation, we monitored the mesostructural evolution of poly(*o*-anisidine) synthesized with 0.02 M *o*-anisidine and 0.01 M $\text{Cu}(\text{Ac})_2$ at 180°C with time. Figure 5 shows the TEM images of poly(*o*-anisidine)

obtained after 2, 4, and 6 h of hydrothermal reaction. After 2 h of polymerization, poly(*o*-anisidine) is in the form of solid nanospheres (Figure 5a). In increasing the reaction time to 4 h, small voids appear near the peripheries of most nanospheres (ca. 80%) (Figure 5b). At this point, the polymer core and the polymer on the periphery of the nanospheres tend to become separated by a clear gap. At the same time, the rest (20% poly(*o*-anisidine) nanospheres) already has the same hollow structure as that shown in Figure 2b. A polymerization period of 6 h causes a further separation of polymer core from peripheral polymer within ca. 50–60% nanospheres, leading to the appearance of large voids (Figure 5c). At this stage, the ratio of hollow poly(*o*-anisidine) nanospheres increases to 40–50%.

FTIR and UV-vis analyses prove that the poly(*o*-anisidine) obtained during the course of 2–6 h of hydrothermal reaction has the same emeraldine base structure as the previously discussed hollow particles because the corresponding optical profiles are identical to those shown in Figure 1. Apparently, the macromolecular structure effect on the void formation can be ruled out. It is plausible to postulate that the changes of the polymeric morphology are related to the equilibrium between polymer growth and diffusion. In the initial stage of hydrothermal polymerization, the growth of poly(*o*-anisidine) is dominant before the monomer is exhausted. This gives solid polymeric structures. In addition, growing regular spherical poly(*o*-anisidine) particles is associated with isotropic growth, possibly due to the precursors, the complex of *o*-anisidine and Cu^{2+} , having symmetric molecular structures. The growth rate of poly(*o*-anisidine) decreases over time as the amount of monomer consumed gradually increases. After complete conversion of the monomer, however, the diffusion of the polymer becomes prominent. Thus, we believe that the generation of resulting hollow structures results from the outward diffusion of the inner polymer of the initially produced solid poly(*o*-anisidine) nanospheres. High temperature and a comparatively dilute solution favor such outward diffusion. The molecule mobility increases at high temperatures. On the other hand, the relatively large difference in the concentration of the polymer between core and solution offers a driving force for the outward diffusion of the core polymer. The core poly(*o*-anisidine) molecules diffused into

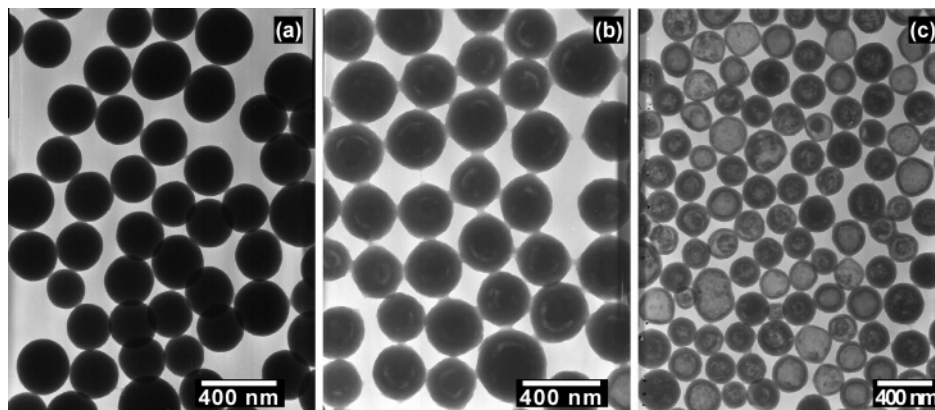


Figure 5. TEM images of poly(*o*-anisidine) colloids synthesized with 0.02 M *o*-anisidine and 0.01 M $\text{Cu}(\text{Ac})_2$ after a hydrothermal reaction period of (a) 2 h, (b) 4 h, and (c) 6 h at 180°C . After each designated period of reaction time, the autoclave was promptly cooled to ambient temperature using cold water ($2\text{--}4^\circ\text{C}$) to quench the hydrothermal reaction.

solution may grow into new hollow colloidal spheres since no other structures of poly(*o*-anisidine) can be found by TEM investigations.

In summary, we performed the polymerization of *o*-anisidine and aniline initiated by weak oxidants, cupric acetate and basic cupric bromide, in their dilute aqueous solutions under hydrothermal conditions. This unique polymerization route is very effective in synthesizing high quality hollow poly(*o*-anisidine) and polyaniline colloidal spheres. Furthermore, this approach allows control over the size and morphology of hollow poly(*o*-anisidine) particles. Hence, we may extend the method to produce other hollow polyaniline derivative colloids without the aid of templates. The dependence of the formation of the hollow structures

on reaction time, temperature, and concentration of monomer demonstrates the diffusion of the polymer.

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Supporting Information Available: Detailed characterization of Cu₂O nanoparticles and XRD pattern of copper hydroxide bromide. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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