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Fabrication of Bimetallic Cu–Ag Nanoparticle-Decorated Poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol) and Its Enhanced Catalytic Activity for the Reduction of 4-Nitrophenol

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1. INTRODUCTION

The catalytic reduction of nitro derivatives has been a great challenge due to their toxic nature. Specifically, hydrogenation of 4-nitrophenol (4-NP) is extremely difficult due to its toxic, carcinogenic, and anthropogenic nature and excellent stability and solubility in water. This reaction has great importance due to its product 4-aminophenol (4-AP) properties as it is used as a hair-dye agent, corrosion inhibitor, antipyretics, photographic developer, and more importantly pharmaceutical intermediate materials. The common and efficient method to hydrogenate 4-NP is to use sodium borohydride as a reductant and noble metal catalyst Pd nanoclusters, Au25 nanoclusters, and Ag NPs. However, their catalytic ability is still under par to achieve the excellence in the domains of catalysis, and less abundance and high cost of noble metals restrict their applications.

The bimetallic system is expected to show not only the combination of the properties of two different metals but also new features because of the synergy between two metals. The synergistic effect of the bimetallic catalyst can exhibit higher catalytic activity even at low concentration when they are compared to their monometallic counterparts. Au–Ag bimetallic NPs, Pt–CeO2 nanocrystals, Au–Pt NPs, and Pd/Au bimetallic nanocrystals have been reported as heterogeneous system catalysts. It has been reported that bimetallic catalytic activity is mainly related to the size and dispersion. Smaller size bi-metallic NPs with high dispersion are better candidates for excellent catalytic activity due to their high surface to volume ratio. However, smaller size bimetallic nanocatalysts have the tendency to aggregate during their catalytic and electrolytic applications owing to their high surface energy, which can limit the initial catalytic activity and the selectivity of these bimetallic NPs. Hence, to stabilize these efficient catalysts, a variety of supporting materials have been used such as SiO2, carbon nanotubes, carbon spheres, and polymer NPs.

Among them, polymer supports for the stabilization of bimetallic NPs have been considered as suitable candidates.
Till now, various polymer substrates with different morphologies have been reported in the literature; however, one-dimensional support materials like polymer nanotubes have been very rarely reported. These potential one-dimensional nanotubes consisting of a high surface area have attained the attraction of researchers and are used in a variety of applications such as chemical sensors, optoelectrical nanodevices, drug carriers, NP carrier materials, and so on. Traditionally, one-dimensional polymer nanotubes are fabricated by two approaches: self-assembly technique or addition of a foreign template with a defined morphology. However, the self-assembly and template methods are involved in multistep syntheses. Therefore, achieving a facile method for the fabrication of one-dimensional polymer nanotubes through self-controlled dimensions under environment-friendly conditions is a task for the researcher. Polyphosphazenes are the novel genre of polymers with organic–inorganic nature and an inorganic (∼P=N∼) bone structure with a multiplicity of side functional groups, for example, organometallic, inorganic, or organic groups. These features of polyphosphazene hybrid materials make them promising candidates for the biomedical carriers and immobilizing the metal ions, which leads to the good dispersion of bimetalic NPs. Yan et al. reported the Ag–Au NPs impregnated over the PZS [poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol)] nanotube with rich −OH groups. These noble metal bimetallic NPs exhibited smaller size with high dispersion over PZS nanotubes and exhibited excellent catalytic activity or 4-NP reduction. However, there is still need to investigate these PZS materials as supports for non-noble bimetallic particles.

Herein, first, we prepared highly cross-linked PZS [poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol)] nanotubes with rich −OH groups on their surface. Afterward, using preprepared PZS nanotubes as additives, the PZS@Ag–Cu NP catalyst has been synthesized through a facile co-reductant technique in solution. The hydroxyl groups and abundant −OH groups of PZS nanotubes play a key role in the impregnation of ultratine and well-dispersed bimetallic NPs by providing various active sites for the coordination of metal ions. Through varying the feed of Ag and Cu precursors, AgNO₃ and Cu(NO₃)₂·H₂O, we obtained a series of bimetallic nanocatalysts. The outcomes exhibit that PZS@Ag–Cu NP composites display excellent catalytic ability for 4-NP reduction in contrast to their monometallic counterparts, even noble metal bimetallic NPs, owing to their good distribution, small size, and mainly the synergistic effect of two metals. Taking in account all of the abovementioned features, these non-noble bimetallic NP-supported PZS nanotubes have the ability for practical applications.

2. RESULTS AND DISCUSSION

PZS nanotubes were synthesized and successfully decorated with Ag–Cu NPs. Herein, we mainly focused on the fabrication of stabilized bimetallic Ag–Cu NPs over PZS nanotubes. First, using a modified in situ template mechanism, HCCP and BPS as co-monomers, and TEA as the acid acceptor, cross-linked organic–inorganic PZS nanotubes with enriched −OH groups were formed. The as-prepared PZS nanotubes were immediately used as a support for loading non-noble bimetallic Ag–Cu NPs by a co-reduction method. Lastly, the catalytic activity of the as-synthesized PZS@Ag–Cu NPs was explored via employing a model reaction, reduction of 4-NP to 4-AP using NaBH₄ as a reductant.

Figure 1a,b shows the SEM results of the PZS nanotubes fabricated by the precipitation polymerization method. The PZS nanotubes look like short rods with an outer diameter of 400 nm mostly entangled with each other probably owing to the existence of hydroxyl groups on the surface. Transmission electron microscopy (TEM) images reveal that the PZS nanotubes are hollow from inside, rendering the tubular structure with an inner diameter of 400 nm. However, it is important to mention that most of the nanotube ends are closed; it could have resulted due to the higher power applied on the reaction system during ultrasonic irradiation.

Afterward, the as-prepared PZS nanotubes were utilized as supports for the in situ co-reduced series of bimetallic Ag–Cu NP-stabilized nanotubes using NaBH₄ as a reductant. The nanotubes decorated with a series of bi-metallic Ag–Cu NPs were examined through TEM. Figure 1c,d shows the TEM results of the PZS nanotubes fabricated by the precipitation polymerization method. Figure 1e–g illustrates the successful decoration of the Ag NPs and Cu NPs over PZS nanotubes. The average diameter of the Ag NPs and Cu NPs NPs was in the range of 10–15 nm for both. The TEM images of AgₓCu₋ₓ NPs are revealed in Figure 1h–j, when x = 0.5, 0.4, and 0.3, respectively. It can be observed that bimetallic NPs have been equally dispersed on the outer wall of nanotubes and did not change the morphology of the PZS nanotubes. All bimetallic NPs with different ratios along with
Ag NPs and Cu NPs NPs have not been aggregated during in situ co-reduction of sodium borohydride on nanotubes, and their uniform monodispersed distribution over PZS nanotubes suggests that the nanotubes with abundant hydroxyl groups provide more sites for the coordination of even non-noble bimetallic NPs.

PXRD was used to further reveal the crystalline properties of Ag–Cu NPs@PZS composite nanotubes shown in Figure 2A. Figure 2A demonstrates the X-ray diffraction (XRD) pattern of PZS nanotubes which contain only wide diffraction bands at a 2 theta (2θ) value of (16.8°), indicating PZS nanotubes. However, the XRD spectrum of the PZS nanotubes decorated with Ag NPs shows four discrete peaks at 38.2, 44.3, 64.5, and 77.6°, which have been reported as characteristic peaks for the face-centered cubic (fcc) peaks of the Ag crystals (JCPDF no. 5-7709). As for the PZS@Cu NP composites, the diffraction peaks at are at 43.3°, 27.6°, and 31.8° detected in bi-metallic NPs, which can be referred to precipitated AgCl during the fabrication process of PZS@Cu NPs NPs and Cu NPs NPs have not been aggregated during in situ co-reduction of sodium borohydride on nanotubes, and their uniform monodispersed distribution over PZS nanotubes suggests that the nanotubes with abundant hydroxyl groups provide more sites for the coordination of even non-noble bimetallic NPs.

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As shown in Figure 2B, the synthesis of Ag–Cu NPs was further confirmed via Fourier transform infrared spectroscopy (FTIR). The distinctive peaks for the hydroxyl (phenolic) group can be noted at 3431 and 3093 cm−1 of the PZS nanotubes. The peaks at 1292 and 1152 cm−1 were observed. The new peak at 941 cm−1 could be ascribed to phenolic (phenol) to verify the successful condensation of 4-nitrophenol (4-NP) and NaBH4 as a reductant. The catalytic reaction can be considered finished when the absorbance peak at 400 nm completely disappeared from the spectrum. Furthermore, the monometallic catalyst Cu NPs@PZS also exhibited catalytic activity under the same conditions and successfully reduced 4-NP. All of these catalytic reactions have been performed under the same reaction conditions, and the amount of catalyst used was 0.05 mg. There is no peak appearing in UV-spectra other than that at 298 nm, which connotes that reduction of 4-NP gives the byproduct.24
The time for PZS@Cu NPs is 35 min to accomplish the reaction presented in Figure 4c, while PZS@Ag NPs have been reported to complete the reaction within 50 min with same conditions applied. However, the bimetallic catalyst Ag\(^{-}\)Cu NPs@PZS reduces 4-NP in a much shorter time. These results suggest that the catalytic activity of Ag\(^{-}\)Cu NPs is boosted in contrast to that of monometallic Ag NPs@PZS and Cu NPs@PZS nanocomposites. The rate of catalytic ability can be calculated via pseudo-first-order kinetics with respect to the reactant 4-NP considering a much high amount of borohydride ions than that of 4-NP.\(^{25}\) The rate constant is calculated by the following equation

\[
\ln\left(\frac{C_t}{C_0}\right) = -kt
\]

where \(t\) denotes the reaction time, \(C_0\) symbolizes the initial concentration of 4-NP before the reaction starts, \(C_t\) is the concentration of 4-NP at \(t\) time, \(k\) denotes the rate constant. Furthermore, we prepared a series of bimetallic NPs by varying

![Figure 4. UV−visible spectra of 4-NP reduction; without a catalyst (a), with a catalyst (b), PZS@ Cu NPs (c), PZS@Ag\(_{\text{0.5}}\)−Cu\(_{\text{0.5}}\) NPs (d), PZS@Ag\(_{\text{0.6}}\)−Cu\(_{\text{0.4}}\) NPs (e), and PZS@Ag\(_{\text{0.7}}\)−Cu\(_{\text{0.3}}\) NPs (f).](image)

![Figure 5. Pseudo-first-order plot (a) and \(\ln(\frac{C_t}{C_0})\) vs time plot (b) for the reduction of 4-NP.](image)
the ratio of Ag and Cu to investigate the synergetic effect of Cu and Ag and to optimize the catalytic activity of the Ag–Cu@PZS nanotubes. All obtained samples exhibit a linear relationship with ln(C0/Ct) versus reaction time.

The nature of bimetallic NPs was precisely tuned by adjusting the mole ratio of Ag/Cu. It is obvious that all bimetallic nanocomposites show better catalytic activity than monometallic nanocomposites, suggesting the synergistic effect of Cu and Ag species. Ag0.7–Cu0.3 NPs have the highest catalytic activity in comparison to the rest of the two bimetallic NPs. We compiled the varying tendency of rate constant values of different catalysts to determine any correlation effect existing between Cu and Ag content ratios in the bimetallic catalyst. Cu contents of 0.5 and 0.3% have almost the same rate constant value. However, Ag0.6–Cu0.4 NPs@PZS composites show the highest catalytic activity for the reduction of 4-NP among three catalysts. These results are better than those of even noble monometallic catalysts and bimetallic catalysts, reaching values as high as 8.93 × 10−3 s−1 (as shown in Figure 5 and Table S1 within the Supporting Information).

The abovementioned analysis can conclude that the superior catalytic activity of the bimetallic catalyst in the reduction of 4-NP is mainly due to the nature of the bimetallic catalyst structure consisting of PZS nanotubes. The remarkable catalytic activity can be mainly referred to two points. First, the structure effect, size effect, and composite effect resulting from the intimate interaction existing between two metals played the key role in the performance of bimetallic nanocomposites. Second, the synergetic electronic effect existing in the bimetallic catalyst: the transfer of electrons can happen from Ag to Cu, which increases the electronic density on the surface of the bimetallic Ag–Cu NPs@PZS catalyst, which improves the catalytic activity.

To investigate the recyclability of bi-metallic NPs, the catalyst with higher catalytic activity, Ag0.6–Cu0.4 NPs@PZS composites, was utilized for the reduction of 4-NP to 4-NA over six cycles, as shown in Figure 6. It was assumed that the reduction of 4-NP could reach 84% after six cycles. These results indicate that the obtained Ag0.6–Cu0.4 NPs@PZS composite exhibits good reusability.

3. CONCLUSIONS

We have successfully demonstrated a facile and rapid method to fabricate Ag–Cu NPs@PZS composites. The presence of a higher heteroatom content and large amount of hydroxyl groups in polyphosphazene nanotubes could increase the surface wettability to provide ultrafine Ag–Cu bimetallic NPs with a particle size of 11 nm with good dispersion. Through tuning the content ratio of the Ag and Cu precursors, a series of bimetallic NPs are synthesized, and bimetallic catalysts showed higher catalytic activity compared to their monometallic NP counterparts. We also noticed that the catalytic ability of bimetallic NPs was remarkably boosted when the copper content was 0.3% in Ag–Cu NPs and the rate constant value for reduction of 4-NP was 8.93 × 10−3 s−1. These results suggested that a significant synergistic electronic effect influenced by the content ratio of Ag to Cu in the bimetallic NPs plays a key role in their catalytic ability. Furthermore, the reusability of bimetallic NPs over PZS nanotubes was recorded 84% after six cycles. We believe that these non-noble bimetallic nanocatalysts have good use in the future for other applications and domains due to their cost effectiveness, facile fabrication, excellent catalytic activity, and efficient reusability.

4. EXPERIMENTAL DETAILS

4.1. Materials.

All chemicals such as tetrahydrofuran (THF), ethanol, copper nitrate (Cu(NO3)2·6H2O), silver nitrate (AgNO3), 4,4′-sulfonyldiphenol (BPS), sodium acetate (CH3COONa), sodium borohydride (NaBH4), triethylamine (TEA), and 4-NP were acquired from Beijing Chemical Co., Ltd, while hexachlorocyclotriphosphazene (HCCP) was sublimed twice, recrystallized with petroleum ether, and used without further treatment (as shown in Scheme 1).

Scheme 1. Scheme for the Synthesis of PZS@Au–Cu NPs

Figure 6. Reusability of the PZS@Ag0.6–Cu0.4 NPs composites as catalysts for the reduction of 4-NP by NaBH4.

4.2. Synthesis of PZS Nanotubes. The facile fabrication of the PZS nanotube is prepared by an in situ template route. 50 mL of THF with 120 mg of HCCP was mixed dropwise with 250 mg of BPS solution in 50 mL of THF. The reaction mixture was agitated for 1 h in an ultrasonic bath before adding 360 μL of TEA dropwise. The reaction mixture was agitated in an ultrasonic bath at 40 °C for 10 h. The mixture color turned milky from transparent, indicating the formation of PZS nanotubes. The solid yielded was rinsed three times with ethanol and water, alternatively. The resultant product was dried in vacuum overnight at room temperature (as shown in Scheme 1).
4.3. Synthesis of PZS@Ag–Cu NP Composite Nanotubes. The PZS@Ag–Cu NP composite nanotubes were synthesized through an in situ co-reduction method. 10 mg of the PZS nanotube solution was dispersed in 10 mL of distilled water and agitated ultrasonically for 30 min. After sonication, 0.1 mL of AgNO$_3$ solution (20 mM) and 0.1 mL of copper nitrate solution (20 mM) were dropwise added into PZS nanotubes, and the reaction mixtures were magnetically stirred for 30 min. 0.01 wt% of sodium borohydride was added to the reaction in the presence of 2.5 mL of sodium acetate solution (50 mM) and stirred for 5 min. The mixture color immediately changed from milky to brownish, confirming the synthesis of Ag–Cu NPs. The mixture was centrifuged and washed with water and then vacuum-dried overnight at room temperature. The powder product was named as PZS@Ag$_{0.5}$–Cu$_{0.5}$ NPs composite nanotubes. The other PZS@Ag$_{0.6}$–Cu$_{0.4}$ NPs and PZS@Ag$_{0.7}$–Cu$_{0.3}$ NPs were prepared by the same method by only varying the ratio of AgNO$_3$ and copper nitrate amount of volume. For comparison, PZS@Ag nanotubes and PZS@Cu nanotubes were fabricated by adding 0.2 mL of AgNO$_3$ solution (20 mM) and copper nitrate (20 mM), respectively.

4.4. Catalytic Activity. Typically, a freshly synthesized aqueous solution of sodium borohydride ($7.5 \times 10^{-3}$, 1.0 mL) was added in the aqueous solution of 4-NP ($1.0 \times 10^{-7}$ mol L$^{-1}$, 1.7 mL) in the quartz cell [path length (l) = 1 cm]. The mixture color immediately turned from light yellow to yellowish green on adding NaBH$_4$. 0.1 mL of catalyst (1.0 mg mL$^{-1}$) was added into the reaction mixture, and the catalytic activity was immediately monitored using UV–visible spectroscopy through recording time-dependent absorbance spectra of the reaction mixture in the scanning range (200–600 nm) at room temperature.

4.5. Characterization. The morphology of the PZS@Ag–Cu NP composite nanotubes was investigated via TEM images with an H-800 type Hitachi instrument. Furthermore, the composites were well-characterized for the powder XRD (PXRD) spectra via a diffractometer (XRD-6000). Fourier transform infrared (30 co added) spectra were taken via a Bruker Vector-22, using KBr to make sample pellets. UV–visible absorption spectra were acquired using a Lambda 3600 UV–visible spectrophotometer (PerkinElmer, Inc., USA). The surface morphology of the samples was investigated using a JEOL JSM-6701F scanning electron microscope.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06786.

Comparison of the obtained reaction constant (K) with different catalytic systems for the reduction of 4-NP (PDF)

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