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Rapid Synthesis of Polyethylenimine-Protected Prussian Blue Nanocubes through a Thermal Process

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Polyethylenimine (PEI)-protected Prussian blue nanocubes have been simply synthesized by heating an acidic mixture of PEI, $FeCl_3$, $K_3Fe(CN)_6$, and KCl. The experiment results presented here demonstrate that the pH of the mixture plays an important role in controlling the shape and composition of the resultant product.

Prussian blue (PB) is known as one of the first reported mixed-valence compounds.[1] Reducing the PB size to nanoscale can facilitate the ion transfer in PB and modulate the magnetic property and thus promote practical applications in electrochromic displays,[2,3] molecular magnetic devices,[4,5] sensors,[6,7] energy storage, and batteries.[8] Many methods such as reverse microemulsion,[9,10] photoreduction,[11] and biomolecular matrix[12] have been used to successfully fabricate PB nanoparticles. However, reports on the synthesis of PB nanomaterials with controllable shapes and morphologies are scarce,[9,13–15] which are important for constructing functional devices and fine-tuning properties.

Organic polymers play an important role in the synthesis of nanomaterials. The selection of appropriate polymers not only leads to protection against aggregation but also leads to new attractive functions and therefore enlarges the application scope of nanomaterials.[16,17] Generally, organic-protected nanosized PB can be simply synthesized by directly mixing the solutions of Fe^{3+} cations and $[Fe(CN)_6]^{4-}$ anions in the presence of desired polymers.[4,18,19] Because of well-known poor solubility, PB nanoparticles are formed immediately after mixing. However, such a fast reaction process makes it difficult to control well the shape and morphology.

Polyethylenimine (PEI) with the functional group of amido has been studied in detail and used as the building block for the fabrication of functional thin solid films[20] and the vehicle for gene delivery.[21] Besides, PEI also presents the redox ability and has been used as a reductant to synthesize silver nanoparticles.[22] In this work, we report the rapid synthesis of PEI-protected PB nanocubes by simply heating the mixture of $FeCl_3$ and $[Fe(CN)_6]^{3-}$ in the presence of PEI.

In a typical synthesis, a 50 mL mixture of $FeCl_3$, $K_3Fe(CN)_6$, and KCl with $pH = 1.12$ was first prepared. A total of 3 mL of PEI (0.1254 g in 3 mL of water) was added into the mixture, and then the mixture was refluxed for 30 min. The mixture color gradually changed to dark blue, indicating the formation of PB. The product was centrifuged, washed with water several times, and then redispersed in water for further characterization. All pH values given here, unless mentioned otherwise, designate the freshly prepared mixture of $FeCl_3$, $K_3Fe(CN)_6$, and KCl. When the pH was below 1.5, the solution of Fe^{3+} changed to colorless, implying

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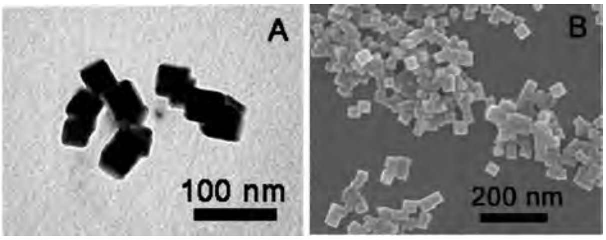

Figure 1. TEM (A) and SEM (B) images of the product obtained at pH = 1.12.

that hydrolysis of Fe^{3+} was prevented. Because hydrolysis of Fe^{3+} may have a negative effect on the synthesis of PB,[7] the pH of the mixture was adjusted below 1.5 to avoid hydrolysis of Fe^{3+}.

The UV−vis spectrum of the product obtained at pH = 1.12 shows a broad absorption band at 689 nm [Figure S1 in the Supporting Information (SI)], and the Fourier transform infrared (FTIR) spectrum displays a significant peak at 2087 cm^{-1} (Figure S2 in the SI). Both features are identical with the characteristic charge transfer and CN stretch mode in the $Fe^{2+}-CN-Fe^{3+}$ of PB,[4,23,24] indicating the formation of PB. Transmission electronic microscopy (TEM) and scanning electron microscopy (SEM) were employed to characterize the shape and morphology of the resultant PB, which reveal the cubic shape of PB and the average edge length of 50 nm (Figure 1). X-ray photoelectron spectroscopy (XPS) data demonstrate the presence of K, Fe, and N elements (Figure S3A in the SI), and inductively coupled plasma with optical emission spectrometry (ICP-OES) measurement confirms that the value for Fe/K is 4.25, indicating the existence of defects in PB frameworks.[4] Moreover, from the data of XPS and ICP-OES, the stoichiometry of the PB obtained at pH = 1.12 is confirmed as $K_{0.509}Fe_{1.164}[Fe(CN)_6]$. It is worth noting that the binding energy of N 1s appears at 401.3 and 399.5 eV, which suggests the presence of PEI on PB surfaces (Figure S4 in the SI).[25]

The crystal structure of the product obtained at pH = 1.12 was determined by powder X-ray diffraction (XRD) measurement, and the typical diffraction pattern is shown in Figure 2, which can be readily indexed as a PB face-centered-cubic (fcc) phase (space group $Fm3m$) with $a = 10.12$ Å.[13,26] The background is the result of an amorphous glass slice. The presence of strong and sharp peaks of [200] and [400] indicates that the PB nanocubes are primarily dominated by [100] planes.[26] It is accepted that the shape of the nanocrystals is related to the surface energy of different facets.[27] Here, the formation of PB nanocubes bounded by [100] under the condition of reflux indicates that the growth process of PB is mainly thermodynamics control because the intrinsic surface energy of [100] is lower than that of [111] in the case of fcc nanocrystals. It should be mentioned that PEI displays weak coordination interaction with Fe atoms, especially when pH < 2; it cannot significantly alter the surface energy of [100] and [111] during the growth process of PB nanocubes and further determine the final product shape.[9,28] In fact, the adsorption of PEI on PB surfaces should be dominated by electrostatic interaction owing to the fact that PB is negatively charged and PEI is positively charged in acidic solutions.[3] Moreover, by adding aniline to the mixture of $FeCl_3$ and $K_3Fe(CN)_6$ at room temperature or adding PEI to the boiling mixture of $FeCl_3$ and $K_3Fe(CN)_6$, PB nanoparticles can be immediately obtained with irregular shapes, suggesting that the slow reaction process is a key factor in forming PB nanocubes here.

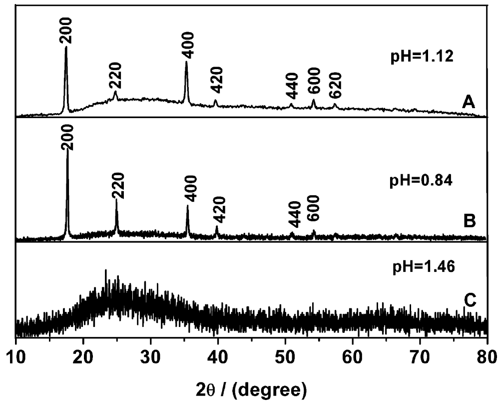

Figure 2. XRD patterns of the products obtained at pH = 1.12 (A), 0.84 (B), and 1.46 (C).

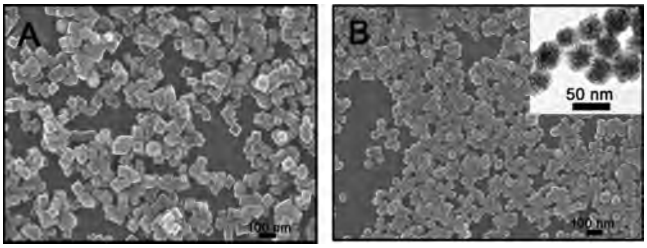

Figure 3. SEM images of the products obtained at pH = 0.84 (A) and 1.46 (B). The inset in part B is the the TEM image of the product obtained at pH = 1.46.

Early work reported the successful synthesis of silver nanoparticles by heating the mixture of Ag^+ and PEI,[29] which suggests that Ag has a more positive redox potential than PEI. Because the redox potential of Fe^{3+}/Fe^{2+} is more positive than that of Ag^+/Ag^0, it is reasonable that Fe^{3+} should be reduced to Fe^{2+} by PEI upon reflux, and the resultant Fe^{2+} immediately reacts with $[Fe(CN)_6]^{3-}$ to yield the PB nanocubes. However, this is not true in our system because no PB nanoparticles are formed by adding $[Fe(CN)_6]^{3-}$ to the mixture of PEI and Fe^{3+}, which has been first refluxed for 30 min and cooled to room temperature. Moreover, the reaction between $[Fe(CN)_6]^{3-}$ and PEI was studied by UV−vis spectroscopy (Figure S5 in the SI). It is evident that the absorption band of $[Fe(CN)_6]^{3-}$ at 420 nm disappears after the reaction with PEI upon reflux for 10 min, indicating that $[Fe(CN)_6]^{3-}$ is reduced to $[Fe(CN)_6]^{4-}$

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by PEI. After the addition of Fe^{3+}, the mixture of $[Fe(CN)_6]^{3-}$ and PEI, which has been first refluxed for 30 min and cooled to room temperature, displays the characteristic blue color of PB, implying the formation of PB nanoparticles. Therefore, the route to generating PB nanocubes can be deduced; that is, $[Fe(CN)_6]^{3-}$ is selectively reduced to $[Fe(CN)_6]^{4-}$, which, in turn, reacts with Fe^{3+} to yield PB nanocubes, as described below.

$$[Fe(CN)_6]^{3-} \xrightarrow{PEI} [Fe(CN)_6]^{4-} \xrightarrow{Fe^{3+}} PB \qquad (1)$$

The control experiments were carried out at pH = 0.84 and 1.46 to examine the influence of pH on the synthesis of PB nanocubes. In the case of pH = 0.84, a blue product is obtained, indicating the formation of PB. The UV−vis spectrum shows a broad absorption band at 700 nm (Figure S1 in the SI), and the FTIR spectrum displays a peak at 2084 cm^{-1} (Figure S2 in the SI). XRD patterns can be readily indexed to the PB fcc phase with $a = 10.06$ Å. XPS data show the existence of K, Fe, and N elements (Figure S3B in the SI), and ICP-OES measurement confirms that the value of Fe/K is 7.83, indicating fewer defect sites than those in PB obtained at pH = 1.12.[4] The corresponding stoichiometry is determined as $K_{0.286}Fe_{1.238}$ $[Fe(CN)_6]$. An SEM image (Figure 3A) shows that the product obtained at pH = 0.84 is a nanocube with broader size distribution than that obtained at pH = 1.12. It should be pointed out that the slight differences in UV−vis, FTIR, and XRD data between the products obtained at pH = 1.12 and 0.84 may be related with their different stoichiometries and particle sizes,[4] while, in the case of pH = 1.46, surprisingly, a slight yellow product is obtained and the corresponding UV−vis spectrum shows no absorption peak in the range of 350−800 nm, suggesting that no PB is formed (Figure S1 in the SI). The FTIR spectrum obviously shows a peak at 2050 cm^{-1} associated with the linear nonbridging stretch mode of CN (Figure S2 in the SI),[30] further demonstrating that no PB-type structure is formed. No XRD diffraction patterns can be observed, suggesting that the product is noncrystal (Figure 2C). The SEM image clearly reveals that the product is a monodisperse nanosphere with a mean diameter of 50 nm (Figure 3B), and the TEM image shows that the nanosphere is an aggregate of small nanoparticles.[31] The product contains Fe and N but no K elements as characterized by XPS (Figure S3C in the SI). Binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ appear at 711.2 and 724.7 eV, respectively, which are identical with that of Fe in Fe_2O_3.[32] The peak at 708.3 eV can be assigned to Fe $2p_{3/2}$ of $[Fe(CN)_6]^{4-}$ (Figure S6A in the SI). The peaks of N 1s at 401.3 and 399.5 eV imply the existence of PEI,[25] and the peak at 397.4 eV indicates the presence of $[Fe(CN)_6]^{4-}$[25] (Figure S6B in the SI). From the above-mentioned results, the nanosphere obtained at pH = 1.46 may be an aggregate of the hydrolysis product of Fe^{3+} mediated by PEI. Because of its dissociation in an acidic solution,[26] $[Fe(CN)_6]^{4-}$ produced during the redox reaction between $[Fe(CN)_6]^{3-}$ and PEI may form a complex with PEI (such as $[PEI-Fe(CN)_5]^{4-}$). Therefore, the existence of $[Fe(CN)_6]^{4-}$ in the nanosphere is reasonable. It should be mentioned that the exact phase of the hydrolysis product of Fe^{3+} in our system is unclear now; further exploitation is needed.

Evidently, the pH value plays an important role in the synthesis of cubic PB nanoparticles. It should be reminded that the pH values given in our work designate the freshly prepared mixture of Fe^{3+}, $[Fe(CN)_6]^{3-}$, and KCl. After the addition of PEI, the pH changes from the initial values of 0.84, 1.12, and 1.46 to 1.00, 1.47, and 2.85, respectively. At pH = 2.85, PEI can form a complex with Fe^{3+} because PEI is partially protonated, while at pH = 1.46 and 1.00, PEI cannot coordinate with Fe^{3+} because it is fully protonated. However, the coordination between PEI and Fe^{3+} does not seem to be the predominant factor responsible for the different product obtained at various pHs. We heat the mixture of Fe^{3+} and PEI at pH = 2.85 and find hydrolysis of Fe^{3+} (Figures S7 and S8 in the SI), indicating that coordination between PEI and Fe^{3+} is not strong enough to prevent hydrolysis of Fe^{3+}. Hydrolysis of Fe^{3+} at pH = 1.47 and 1.00 is not observed (Figure S7 in the SI). Therefore, the pH-dependent hydrolysis of Fe^{3+} on the pH value may be responsible for the obvious pH-dependent synthesis of cubic PB nanoparticles.

In summary, we present a new chemical route to synthesizing PEI-protected PB nanocubes with uniform size distribution. This method is simple, reproducible, and rapid. The adsorbed PEI enables PB to form a complex with other functional materials through electrostatic and coordination interaction and even chemical reaction.[33,34] Coupled with the interesting properties of the PB, these nanocubes may benefit the construction of functional nanodevices and find application in optics, analysis, and magnetism. Moreover, considering the fact that PB nanocubes are readily dissolved in an alkaline solution, they may be used as hard templates to fabricate hollow nanocubes.[35]

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Supporting Information Available: Detailed experimental section, FTIR, XPS, and UV−vis data of the products obtained at different pHs, and the TEM image of the product obtained at pH = 1.46. This material is available free of charge via the Internet at http://pubs.acs.org.

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