Electrochemical Controllable Synthesis of Bismuth Hexacyanoferrate(II) Nanoplates and Its Application in Electrocatalysis

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A facile electrochemical approach was developed for the controllable synthesis of bismuth hexacyanoferrate(II) (BiHCF(II)) nanoplates. The composition, morphology, and structure of the as-prepared BiHCF(II) nanoplates were characterized by the techniques such as infrared spectrum, thermogravimetry, inductively coupled plasma mass spectroscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectrum, powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and selected area electron diffraction. The formula of the prepared BiHCF(II) nanoplates could be assigned to KBi[Fe(CN)6]·xH2O. It was observed that the nanoplates and their flowerlike aggregations could be obtained in the electrolytes containing different concentration of HNO3. The nanoplates were prepared at the potential for 0.2 V (versus SCE) and could be further grown to a good single-crystalline hexagonal microstructure at 0.6 V. To the best of our knowledge, the structures have not been reported before. The modified Au electrode by the BiHCF(II) nanoplates showed good electrochemical properties, especially with a stable anodic response over the pH range from 2.0 to 11.0. Also, the electrode possesses prominent electrocatalytic activity toward the reduction of hydrogen peroxide.

1. Introduction

As an important class of mixed-valence compounds, metal hexacyanoferrates (MHCFs, including hexacyanoferrate(II) and hexacyanoferrate(III) compounds) have aroused considerable interest because of their attractive electrocatalytic, electrochromic, ion-exchange, ion-sensing, and photomagnetic properties.1–4 The electrochemical properties and applications of transition-metal hexacyanoferrates have been widely studied, especially in glucose oxidase electrodes as the effective catalysts for hydrogen peroxide.5,6 For the main group metal hexacyanoferrates, reported work mainly focused on the IIIA and IVA metal elements. Although bismuth and its compounds have been studied recently because of their unique qualities, until now, to the best of our knowledge, no reports were involved on the electrochemical preparation and electrocatalytic properties for the bismuth hexacyanoferrate(II) (BiHCF(II)).

In the past decades, there has been considerable interest in the preparation and the properties of the nanostructural materials. Therefore, it is a new challenge for synthetic and material scientists to have control over nanocrystalline morphologies and the size of MHCFs or to create advanced and functional building blocks for the development of innovative nanomaterial and smart nanodevices. Since Mann and co-workers first synthesized the steady MHCFs nanocrystals,7–9 efforts have been focused on ferromagnetic MHCFs to achieve superparamagnetic coordination nanoparticles.10 Although some reports involved the synthesis of hexacyanoferrate nanoparticles,7–14 the methods mostly rely on photoinducing or the protection by organic materials.10c–e The products are mostly cubic, and the shape- and size-dependent properties of MHCFs have been rarely reported. Generally, in alkaline solutions the strong interaction between metal ions and hydroxyl ions (OH−) can form M(OH)x, and result in the destruction of the M−CN−Fe bond so that the MHCFs are unsteady. For analytical applications, the reported MHCFs modified electrodes are usually used in acidic solutions, which may restrict the applications in bioelectroanalysis. Therefore, controlling the growth of MHCFs under spatial confinement is a promising subject,15–18 and it is now eagerly desired to investigate the other unexpected properties of MHCFs, such as the stability in alkaline solutions and high electrochemical catalytic property in nanosized regime.19–21

Herein, a facile amperometric method is developed to synthesize the BiHCF(II) nanoparticles. By altering the acidity of solutions, different shapes such as nanoplates and the flowerlike aggregations of the BiHCF(II) particles could be fabricated on a large scale. The structure and composition of the BiHCF(II) nanoplates were characterized with infrared spectrum (IR), thermogravimetry (TG), X-ray powder diffraction (XRD), inductively coupled plasma mass spectroscopy (ICP-MS), energy-dispersive X-ray spectrum (EDS), and X-ray photoelectron spectroscopy (XPS) techniques. The morphology and structure of the final products were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected area electron diffraction (SAED), respectively. It was found to be a fast, convenient route for the preparation of different shapes and sizes of the BiHCF(II). The electrochemical behaviors of the BiHCF(II) nanoplates are investigated. To the best of our knowledge, the nanoplates and the flowerlike aggregations of MHCFs have not been reported before. The modified electrode with the BiHCF(II) nanoplates showed the good electrochemical properties, steady anodic response in alkaline solutions, and prominent electrocatalytic activity toward the reduction of hydrogen peroxide.

2. Experimental Section

2.1. Materials and Characterization. Bismuth nitrate (Bi(NO3)3·5H2O), potassium hexacyanoferrate(III) (K3[Fe-
(CN)₃], potassium nitrate (KNO₃), nitric acid (HNO₃), and hydrogen peroxide (H₂O₂) were purchased from Shanghai Chemical Reagent Co. All reagents were of analytical grade and used without further purification, and distilled water was used throughout.

IR spectroscopy was carried out on a Bruker IFS66 Fourier transform infrared (FTIR) spectrometer (Bruker Co.) with KBr (FTIR grade) pellet in the single-beam mode over the range of 400–4000 cm⁻¹ at room temperature. The TG curves were recorded in a Shimadzu TGA-50 instrument. A model ELAN 9000 (Perkin-Elmer, U.S.A.) was used for the ICP-MS measurements. Powder XRD measurement was performed on a Shimadzu XD-3A X-ray diffractometer at a scanning rate of 4°/min in the 2θ range from 10 to 60° with graphite monochromatized Cu Kα radiation (λ = 0.15418 nm) and nickel filter. The XPS patterns were recorded on an ESCALAB MK II X-ray photoelectron spectrometer by using nonmonochromatized Mg Kα X-ray as the excitation source and choosing C1s (284.6 eV) as the reference line. The SEM images and EDS spectra were carried out on an S-3000 N (Hitachi, Japan) scanning electron microscope with EX-250 (Horiba, Japan) operating at 20 kV. TEM and SAED images were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of 200 kV. The samples used for TEM and SAED observations were prepared by dispersing the products in ethanol followed by ultrasonic vibration for 30 min and then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon.

Electrochemical experiments were carried out on a CHI 660B electrochemical workstation (Chenhua, Shanghai, China) at room temperature. A traditional three-electrode configuration containing 5.0 mM Bi(NO₃)₃, 5.0 mM K₃[Fe(CN)₆], and 0.1 M KNO₃ with different acidity, and the potential was kept at a certain value for given times. Then, the ITO electrode was gently washed with doubly distilled water to remove the adsorbed salts. The ITO slide with deposited BiHCF(II) was scraped from the ITO glide by a stainless steel knife.

2.3. Preparation of BiHCF(II) Nanoplates-Modified Au Electrodes. Polycrystalline gold disk electrodes (99.99%, 3.0 mm diameter) were polished with a fine grade of polishing paper. They were further polished down to a mirror surface with 0.05 µm alumina slurry on microcloth pads, followed by ultrasonic rinsing with acetone and water successively. The cleaned electrode was dried with a stream of nitrogen before use. Electrodeposited BiHCF(II) nameplates on Au electrode were the same as those on ITO. After the deposition of the BiHCF(II) nanoplates, the modified electrode was rinsed with doubly distilled water thoroughly and then played into a 0.1 M KNO₃ solution, followed by a cyclic potential scan in the potential range of −0.2−0.6 V at 50 mV/s until the recorded i~ E curves did not change anymore. The electrochemical properties of the BiHCF(II) nanoplates and its catalytic properties to hydrogen peroxide were all performed on the modified electrode.

3. Results and Discussion

3.1. Characterization. Typical IR spectrum of the BiHCF(II) sample is shown in Figure 1. As Prussian blue (PB, ferric hexacyanoferrate(II), Fe₄[Fe(CN)₆]₃·xH₂O) and other metal hexacyanoferrate(II), the BiHCF(II) IR spectrum has a sharp stretching vibration peak of the CN group (ν(CN)) around 2056 cm⁻¹, which indicates the typical asymmetric CN vibration of ferrocyanide. Two peaks appeared at 594 and 455 cm⁻¹, respectively, in the BiHCF(II) spectrum, corresponding to the stretching mode of ν(MC) and bending mode of δ(MCN). A broadband at around 3383 cm⁻¹ and a sharp peak at 3560 cm⁻¹ show that there are two types of stretching vibrations of the OH group, indicating that there are two types of H₂O in the structure. One is the interstitial water or zeolitic water, and the other is the water coordinated to Bi, corresponding to the broad adsorptive band occurring at approximately 3383 cm⁻¹, which results from the association of water due to the H-bonding; this is similar to the case of PB. The other is the water coordinated to Bi, corresponding to the peak at 3560 cm⁻¹. The peak at around 1600 cm⁻¹, which is assigned to the bending vibrations of the OH group in water, splits into two peaks at 1598 and 1630 cm⁻¹. This indicates that there are two kinds of OH groups in the BiHCF(II); the peak at 1598 cm⁻¹ corresponds to the bending vibration of the interstitial water, and the peak at 1630 cm⁻¹ corresponds to the bending vibration of the coordinated water. The weak peak at 1384 cm⁻¹ can be assigned to the stretching mode of few NO₃⁻ ions that adsorbed on the BiHCF(II). The IR spectrum

![Figure 1. IR spectrum of the as-prepared BiHCF(II).](Image)

![Figure 2. TG curves of the BiHCF(II) deposited at different potentials: (a) 0.2 V; (b) −0.4 V.)](Image)
of the as-prepared product shows that the BiHCF(II) is a metal hexacyanoferrate(II) compound.

Figure 2 shows the TG curves of the BiHCF(II) prepared at 0.2 V and −0.4 V. In the TG curves, it can be observed that both coordinated and zeolitic waters are weakly bonded, and the material begins to evaporate the crystal water at a relatively low temperature, which is under 100 °C, and the mass loss corresponds to up to 25% of the sample weight. This easy dehydration may be related to the framework of the BiHCF(II), which facilitates the removed water molecules released from the solid. It seems that the dehydration process is accompanied by the decomposition of a small sample fraction. The TG curve of the BiHCF(II) samples show a slight but continued weight loss up to 330 °C, where a pronounced evolution of a gaseous species is observed. Because ferricyanides decompose at lower temperature, only ferrocyanides remain stable up to above 300 °C. TG curves also indicate the as-prepared products are all hexacyanoferrate(II) compounds, and it is consistent with the IR results.

The elemental composition of the obtained BiHCF(II) was first detected by ICP-MS technique. Results showed that the composition of the BiHCF(II) had no distinct difference with the deposition potentials. For example, when the BiHCF(II) was deposited at 0.2 and −0.4 V for 500 s, the atomic ratios of bismuth and iron were 1.10:1 and 0.93:1, respectively; if the EDS was selected, the atomic ratios were 1.03:1 and 0.98:1 (see Supporting Information). These results indicate that the atomic ratio of Bi and Fe in BiHCF(II) is close to 1.

The product was also characterized by XPS for the evaluation of its composition and purity. The XPS spectra of the BiHCF(II) prepared at 0.2 V is shown in Figure 3. Figure 3a is the wide-scan XPS spectrum, and peaks of Bi, Fe, C, N, and O are observed. Unfortunately, there is no peak of K in the XPS spectra. However, in the EDS spectra of BiHCF(II) the peak of potassium can be observed (see Supporting Information, Figure S1). The peaks for O can be attributed to coordinated water. The high-resolution XPS spectra of Bi(4f) and Fe(2p) are shown in Figure 3b and Figure 3c, respectively. The two strong peaks taken for the Bi region at 157.0 and 162.0 eV are assigned to the Bi(4f) binding energy. The Fe(2p) peak appears at 708.3 eV, which is characteristic of Fe(II); there is no evidence of Fe(III) existing. The peak areas of Bi(4f) and Fe(2p) are measured, and quantification of the peaks gives the atomic ratio of Bi/Fe to be approximately 1.2:1; this is approximate to the ICP-MS and EDS results. According to the results above, the as-prepared BiHCF(II) is a stoichiometric compound, and the formula may be KBi[Fe(CN)6]·xH2O.

Powered XRD pattern of the BiHCF(II) deposited at 0.2 V for 500 s in the electrolyte containing 1.0 M HNO3 is shown in Figure 4. The sharp and narrow diffraction peaks indicate the product has highly preferential orientation. Figure 4 shows that the obtained products crystallize in the hexagonal space group $P6_3/m$ with measured lattice constants of $a = 7.172$ Å and $c = 13.521$ Å. To the best of our knowledge, there is no literature on bismuth hexacyanoferrate(II), and only two are found on...
bismuth hexacyanoferrate(III) with monoclinic space group \(P_2_1/m\) \((a = 7.420 \, \text{Å}, \ b = 13.67 \, \text{Å}, \ \text{and} \ c = 7.421 \, \text{Å})\) and orthorhombic space group \(Cmcm\) \((a = 7.449 \, \text{Å}, \ b = 12.85 \, \text{Å}, \ \text{and} \ c = 13.67 \, \text{Å})\). 26, 27 On the basis that the atomic radii of \(\text{Bi}^{3+}\) and \(\text{Ln}^{3+}\) ions are approximately equal, 28 and XRD patterns of \(\text{Ln}-\text{K} \) ferrocyanides correspond to a hexagonal unit, it may be interpreted that bismuth hexacyanoferrate(II) has a similar XRD mode with the \(\text{Ln}-\text{K} \) ferrocyanides. Through careful inspection of the JCPDs of lanthanide ferrocyanides, we find that almost all of the detected peaks are indexed as the hexagonal \(\text{YbHCF} \) (JCPDs 43–0767) with the lattice constants of \(a \) and \(c\) of 7.239 and 13.42 Å, respectively; the lattice constants of as-prepared is comparable to that of hexagonal \(\text{YbHCF} \). However, there is slight variation between the two XRD patterns and lattice contents, which can be attributed to the tiny difference in the radii of \(\text{Bi}^{3+}\) and \(\text{Yb}^{3+}\) ions.

Figure 5 shows the typical SEM images of the \(\text{BiHCF(II)}\) fabricated at 0.2 V for 500 s in electrolytes containing different nitric acid. As shown in Figure 5, the irregular nanoparticles, nanoplates, and their flowerlike aggregations can be obtained in the electrolytes containing 0.19, 1.00, 1.75, and 2.25 M \(\text{HNO}_3\), respectively. The side length of a crystal shows a positive relationship with \(\text{HNO}_3\) concentration, while its thickness decreases from 400 to 80 nm in the acidity range from 0.19 to 1.00 M and keeps almost invariable to more concentrated \(\text{HNO}_3\). Furthermore, the nanoparticles can self-assemble into flowerlike aggregations once the \(\text{HNO}_3\) concentration reaches 1.75 M.

Figure 6 shows the SEM images of \(\text{BiHCF(II)}\) deposited at 0.6 V for 500 s in 1.0 M \(\text{HNO}_3\) solution. While the deposition potential changes from 0.2 to 0.6 V and keeps the deposition time fixed, the yield of the \(\text{BiHCF(II)}\) decreases, as shown in Figure 6a. However, the sizes change from hexagonal nanoplates to hexagonal microplates (Figure 6b); the crystal side length of a microplate is about 1.8 \(\mu\text{m}\) and the thickness is about 170 nm.
The size and morphology of the microplates were also analyzed by TEM. Figure 7a reveals that the product consists of hexagonal microplates, which confirms the morphology of hexagonal microplates observed in Figure 6. The side length of the microplates is about 1.7 µm, which is approximately equal to the SEM observation. The minor difference among the side lengths in a microplate is caused by the orientation not being absolutely perpendicular to the sample measured by TEM, which is in accordance to the SEM images (Figure 6). The fragmentized plates are produced by the tempestuous ultrasonic vibrating in the process of preparing TEM sample. As observed in the TEM image, there are some irregular holes in the hexagon, which may be caused by the irradiating of the high energy electron beam; this indicates the BiHCF(II) hexagon may be unstable. The crystallography of the hexagonal BiHCF(II) was further proven by SAED, transmission electron diffraction performed in a set of such hexagon leads to a pattern is shown in Figure 7b. The SAED pattern shows that BiHCF(II) nanoplate is a single-crystal hexagon and it matches the XRD result.

The formation process of BiHCF(II) on the electrode surface can be expressed as the following electrochemical–chemical reaction:

\[
\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-} \quad (\text{electrochemical reaction}) \quad (1)
\]

\[
\text{Fe(CN)}_6^{4-} + \text{Bi}^{3+} + \text{K}^+ + x\text{H}_2\text{O} \rightarrow \text{KBi[Fe(CN)}_6]^{4+} \cdot x\text{H}_2\text{O} \quad (\text{chemical reaction}) \quad (2)
\]

Although the exact effect of the electrolytes acidity in the size- and morphology-controlled preparation of BiHCF(II) is
not clear, according to the results the nanoparticles, nanoplates, and their flowerlike aggregations can be fabricated through adjusting the acidity of solutions so we can believe that the acidity may play a main role in the morphology-controlling process. To explore the influence of solution acidity, we also prepared some transition-metal hexacyanoferrates such as cobalt hexacyanoferrate and nickel hexacyanoferrate in different acidity conditions. Experimental results showed that the morphologies of these transition-metal hexacyanoferrates were almost unchangeable with the acidity. That is, the influence of acidity on the morphology of BiHCF(II) is a exceptional example in the preparation of MHCFs. Glass carbon and gold electrodes were also used to deposit the BiHCF(II) nanoplates; the morphology and size of the prepared BiHCF(II) were accordant with that of an ITO electrode, which indicated the electrode materials had no evident influence on the size and morphology. All the results above demonstrate that the morphology and size-controlled synthesis of BiHCF(II) could be carried out by modulating the experimental parameters, suggesting that the adopted method was an effective approach to the preparation of the BiHCF(II) materials.

3.2. Electrochemical Properties of the BiHCF(II) Nanoplates. To investigate the applications of the BiHCF(II), the nanoplates were chosen as an example to explore the electrochemical properties. Cyclic voltamograms obtained at 0.1 M KNO₃ is shown in Figure 8. As shown in Figure 8a and 8b, when the scan rate is under 200 mVs⁻¹, the potentials of anodic and cathodic peaks do not change with scan rates. The anodic and cathodic peak currents are directly proportional to scan rate, and the ratio of anodic and cathodic peak currents almost keeps constant, suggesting facile charge transfer kinetics over this range of sweep rate. For sweep rates above 200 mV s⁻¹, the peak separations begin to increase clearly (Figure 8c), the plot of peak current versus scan rate deviates from linearity, and the peak current becomes proportional to the square root of the sweep rate (Figure 8d), indicating diffusion behavior in charge transport at these sweep rates.

The stability of the nanoplate-modified Au electrode was also examined. After 100 cycles of repetitive scans in 0.1 M KNO₃ solution, no changes were observed in peak height and peak-to-peak separation, indicating a good stability. It is probably due to the higher affinity of the complex for K⁺ ion. Generally, MHCFs are redoxactive only in acid media (pH < 7), which has restricted its applications in bioelectrochemistry. However, when the pH values vary from 2.0 to 11.0, the cathodic peak potential changes with pH but the anodic peak potential keeps stable. The anodic and cathodic peak current are all altering a small amount with pH; when the pH is 11.0, the anodic peak current is about 70% of that in pH 7.0 solution, as shown in Figure 9. This property differentiates from most of the other MHCFs.5,29–31 In alkaline solutions, the strong interaction between metal ions and hydroxyl ions (OH⁻) usually forms M(OH)ₓ, thus leads to the destruction of the M–CN–Fe bond and the instability of MHCFs in alkaline solutions. However, BiO⁺ is the steady form of bismuth ion in alkaline solution, and the solubility of BiOOH is bigger than that of most transition-metal hydroxyls. This may account for the unusual stability of BiHCF(II) in alkaline solutions.

3.3. Electrocatalysis of the BiHCF(II) Nanoplates. Cyclic voltammograms of the BiHCF(II) nanoplate-modified electrode in a 0.1 M KNO₃ solution (pH 7.0) toward the reduction of H₂O₂ are shown in Figure 10a. The reductive potential of hydrogen peroxide starts at approximately 0.37 V. It is more positive than that of other MHCFs,13,29–34 and the cathodic peak current increases greatly with the addition of H₂O₂. This demonstrates that the reduction of H₂O₂ on this modified electrode has lower overpotential, that is, the BiHCF(II) nanoplates are a good electrocatalyst toward the reduction of H₂O₂. Figure 10b shows the amperometric response of bare Au, ITO, and their BiHCF(II) nanoplate-modified electrodes at a potential of 0.10 V in solutions containing different concentration of H₂O₂. At 0.10 V, the bare electrodes have no amperometric response to H₂O₂ at all, and the modified electrodes all
show good amperometric response. When the modifying parameters and electrodes area are the same, the modified-Au electrode has a faster response time and bigger cathodic current, compared to the BiHCF(II) nanoplate-modified ITO electrode. Therefore, a H2O2 sensor can be fabricated by modifying the BiHCF(II) nanoplates on an Au electrode. In the insert of Figure 10b, the calibration curve of the H2O2 sensor under optimal experimental conditions showed a linear response to H2O2 concentration in the range of 0.6–200.0 µM; the detection limit and sensitivity of this sensor are 0.07 µM and 156.0 µAmM⁻¹cm⁻², respectively. The observed electrocatalytic reduction of H2O2 was close to those previously reported nanosized PB-modified electrodes. These results showed the BiHCF(II) nanoplate-modified Au electrode was a good choice for H2O2 sensing.

4. Conclusions
In conclusion, we successfully prepared the BiHCF(II) nanoplates with different shapes. The prepared sample is close to a stoichiometric compound of KBi[Fe(CN)₆]·xH₂O. It was found that the proper acidity selection was very important in controlling the morphology of the BiHCF(II). In the electrolytes containing 1.0 M HNO₃, the deposited BiHCF(II) has a hexagonal structure, and the size is influenced by deposition potential. The prepared BiHCF(II) nanoplate-modified Au electrode has good electrochemical properties. Because of the special character of bismuth ion and big solubility of BiOOH, BiHCF(II) nanoparticles showed a stable anodic response in alkaline solutions. On the basis of the lower overpotential of BiHCF(II) nanoplates to the reduction of hydrogen peroxide, a good sensor of H₂O₂ has been fabricated. The fast response, high sensitivity, low detection limit, and broad linear response to H₂O₂ concentration of this sensor can provide potential applications in bioelectroanalysis.

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Supporting Information Available: EDS spectra of the BiHCF(II) nanoparticles prepared at 0.2 V and −0.4 V. The material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes
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