Hexagonal BiPO₄ nanorods thin films with remarkable photoelectrocatalytic (PEC) performance were successfully fabricated on FTO substrates via cathodic electrodeposition. Chronoamperometry, linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were used to study the photoelectrochemical properties of these materials. The photoelectrocatalytic capability was evaluated by the degradation of methyl blue (MB). The film deposited in 40 min has the best catalytic activity and good stability with the 30 h degrading experiment. The photocurrent was increasing because the concentration of MB was being degrading. The CV analysis which reveals a potential shift and the increasing anodic and cathodic peak currents with increasing scan rate proves a diffusion-controlled process. The hydrosol radicals are the main active species that can oxidize the adsorbed organic pollutants.

Hence, they act as a powerful tool to degrade organic dyes in aqueous media.

Characterization.— The obtained products were analyzed by X-ray diffraction (XRD; Bruker D8 Advance) with Cu-Kα radiation (λ = 0.15406 nm) in scan range of 10°–80° to determine the phases and structures. The views of the materials were investigated by using field emission scanning electron microscopy (FESEM) using a Zeiss field emission electron microscope. The photoelectrocatalytic activity has been regarded as an ideal means of curbing environmental organic dyes pollution in aqueous solution using different semiconductor electrodes. Moreover, the applied potential can enhance charge separation and facilitate the transfer of photo-generated electron. In our previous work, the BiPO₄ film prepared by hydrothermal process has performed remarkable photoelectrocatalytic activity. However, a more facile way to synthesize more stable film still needs to be explored.

In this paper, the BiPO₄ nanorods were first synthesized by a one-step cathodic electrodeposition approach on FTO substrates from precursor solution. Structure, morphology and the electrochemical performance were characterized as well. The photoelectrocatalytic activity was evaluated by the degradation of MB.

Experimental

Electrochemical deposition.— All chemical reagents were of analytical purity without further purification. All electrochemical de-
studies were performed at different scan rates of 2 ~ 50 mV/s in a potential range between 0.6 and −0.6 V vs. SCE.

The photocatalytic activities were evaluated by the decomposition of MB under UV light (λ = 254 nm). The quartz electrolytic cell was filled with 10−5 M MB solution. The filtrates were analyzed by recording variations of the maximum absorption band (663 nm for MB) using a TU - 1810 UV-vis spectrophotometer. The BiPO4 thin films served as the working electrode. Prior to the irradiation, the prepared composite electrodes were magnetically stirred in the dark for 20 min to reach an absorption-desorption equilibrium.

Results and Discussion

Structure and morphologies of the BiPO4 thin films.— XRD patterns of the BiPO4 thin films electrodeposited with a current density of 0.3 mA/cm2 at 70 °C in different time are shown in Fig. 1. The XRD patterns are found to match well with the hexagonal phase of BiPO4 (JCPDS no. 15-0766) with lattice constants a = 6.982 Å and c = 6.476 Å. No other phase can be assigned to the patterns except FTO substrate. The high and sharp peaks indicate that BiPO4 nanorods are well crystallized. The peaks (mark with #) in the XRD patterns can be indexed as (100), (101), (110), (111), (200), (102), (112), (211), (212) and (203) of hexagonal phase of BiPO4. The remained XRD peaks are ascribed to the tetragonal structure of SnO2 (designated as *).

The morphologies of the products synthesized under different times were viewed by SEM. Figs. 1b–1d show the typical low-magnification SEM images of the as-prepared BiPO4 thin films, and it is seen that a large quantity of nanorods were successfully synthesized on the FTO substrates. It also shows the amount of the BiPO4 nanorods in the surface morphology of FTO increases with the increasing of deposition time. The inset figures in Figs. 1b–1d are the high-magnification SEM images, showing that these nanorods have a diameter of 400–800 nm, a length of 1000–2000 nm and a well-defined hexagonal morphology, which is successfully obtained via a template-free cathodic electrodeposition.

Significantly, HRTEM images were further demonstrated to observe the fine structure of BiPO4 nanorods composite. The results in Fig. 2a shows that two different distinct areas could be found with d spacing 0.349 nm and 0.606 nm, which corresponds to the (110) plane and (100) plane of BiPO4, respectively. The SAED dotted pattern illustrates the as-prepared BiPO4 particles to be single crystalline in Fig. 2b. By carefully measuring the lattice parameters and comparing with the data in JCPDS with the SAED pattern, the d-spacing is obtained as 0.606 nm, 0.349 nm and 0.307 nm, corresponding well to the (100), (110) and (111) crystallographic plane of hexagonal BiPO4.

Fig. 3a shows the Raman pattern of the BiPO4 nanorods film. The Raman analysis demonstrates that the BiPO4 nanorods are well crystallized with hexagonal structure. To further investigate the surface elemental composition and oxidation state of the product, X-ray photoelectron spectroscopy (XPS) analysis was performed and the surveys are shown in Fig. 3b. In the high resolution XPS spectra of the resulting film, the double broad peaks with higher binding energy of 159.4 eV and 164.7 eV are consistent with the characteristic Bi 4f 7/2 and Bi 4f 5/2, respectively, with a peak separation of 5.3 eV (Fig. 3c). This indicates the existence of a trivalent oxidation state for bismuth. The peak in Fig. 3d of P 2p locates at 132.9 eV suggests that the P in the sample exists in the oxidation state of P5+. As shown in Fig. 3e, the O may be fitted to two types of chemical states: crystal lattice oxygen and adsorbed oxygen. The peak at 352.1 eV is assigned to the adsorbed oxygen, while the peak at 530.6 eV is related to crystal lattice oxygen, and the results are in line with previous reports on BiPO4. The UV-vis diffuse reflectance spectra of BiPO4 nanorods coated on FTO glass showed a bandgap at around 2.94 eV (Fig. S1).

Electrochemical characterization.— Fig. 4a displays the chronocamperographs of the BiPO4 thin film, showing an effective charge transfer process under UV light illumination and 1 V bias. The BiPO4 thin film depositing in 40 min presents the highest photocurrent, indicating that the 40 min film has the highest separation efficiency of photogenerated electron-hole pairs. The value of the photocurrent of the linear sweep voltammogram for the BiPO4 thin film electrodeposited in 40 min is larger than the others (Fig. 4b) at −1.5 V bias potential. These results confirm that the film deposited in 40 min has optimal PEC performance.
LSVs both in the dark and under 1 mW/cm² illumination are also performed on the BiPO₄ thin film in 0.1 M phosphate buffer at pH 7 with and without the addition of 0.1 M sodium sulfite (Na₂SO₃) (Fig. 4c). As expected for an n-type semiconductor, the BiPO₄ thin film serves as a photocathode and generates anodic photocurrent through the consumption of photoinduced holes for water at the semiconductor/electrolyte interface. The photo-assisted BiPO₄ thin film yields the greatest cathodic shift of the onset potential for PEC water oxidation, which is ∼600 mV at 4.60 V vs. SCE. When sulfite was added, the anodic photocurrent density increased. It increases to 3.51 mA/cm². This is because of the sulfite, and the anodic photocurrent generated is exclusively ascribed to the oxidation of sulfite, which is kinetically easier than water oxidation. Thus, the substantial enhancement in photocurrent in the presence of sulfite demonstrates that the water oxidation photocurrent on the BiPO₄ thin film is mainly limited by poor kinetics for water oxidation. Thus, the combination of photoirradiation and applied bias potential is an effective way to improve photocatalytic efficiency. The applied bias potential not only can separate the holes and electrons but also can directly electrolyze MB. Thus, MB can be effectively degraded.

Catalytic measurement—Photocatalysis, electrocatalysis, and photoelectrocatalysis of MB at the bias potential of 3 V (and 1.5 V see Supporting Information Fig. S3) are respectively performed. The variation of relative concentration of MB (c/c₀) as a function of reaction time is shown in Fig. 5a. It is clear that MB can be photocatalytically degraded.

The radius of the arc on the EIS Nyquist plot reflects the reaction rate occurring at the surface of electrode. The arc radius on the EIS Nyquist plot of the BiPO₄ thin film is smaller than that of film under UV irradiation (Fig. S2(A)). The sizes of the arc radius are reduced by combination of photoirradiation and applied bias potential of 0.5 and 1.0 V (Fig. S2(B)). As shown in Fig. S2(C), it is the smallest at the 2.0 V bias potential combined with photoirradiation, which suggested that a more effective separation of photogenerated electron-hole pairs and faster interfacial charge transfer occurred on the BiPO₄ thin film. At the bias potential of 1.0 V, the size of the arc radius of the film deposited in 40 min is the smallest. These photoelectric characteristics prove that the combination of photoirradiation and the applied bias potential is an effective way to improve photocatalytic efficiency. The applied bias potential not only can separate the holes and electrons but also can directly electrolyze MB. Thus, MB can be effectively degraded.

Figure 3. (a) Raman spectrum of the BiPO₄ nanorods synthesized by cathodic electrodeposition (b) Survey XPS spectrum obtained from the surface of the BiPO₄ thin film. XPS spectra of (c) the Bi 4f peaks, (d) the P 2p peak, and (e) the O 1s peak from the spectrum in (b).
Figure 4. (a) Chronoamperographs of the BiPO4 thin films depositing 30 min, 40 min and 60 min at 1.0 V vs. SCE in 0.1 M NaCl aqueous solution, (b) Linear sweep voltammograms of the BiPO4 thin films (scan rate = 10 mV/s), (c) Current-potential characteristics of the BiPO4 thin films obtained under UV light in (1) 0.1 M KH2PO4 and (2) 0.1 M KH2PO4 with 0.1 M Na2SO3, both at pH 7. 1’ and 2’ are the corresponding LSVs obtained in the dark, (d) The EIS plane at the BiPO4 thin films under UV light and the applied bias potential of 1.0 V vs. SCE.

degraded using the BiPO4 nanorods film, and it can also be degraded via the electro-oxidation process at the bias potential of 1.5 or 3 V. However, only 3% MB is degraded under UV light without BiPO4. Clearly, the largest degradation rate of MB is attained when both applied potential (EC) and UV-light irradiation (PC) are introduced. It is consistent with the conclusions of the Chronoamperographs, LSVs and EISs.

Fig. 5b shows the PEC degradation efficiencies of MB by different BiPO4 thin films with 3 V bias potential (and 3.5 V see Supporting Information Fig. S4). According to the experimental results, the as-prepared BiPO4 thin films at 3.0 V reveal the significant degradation of MB as a function of UV illumination time. After 5 h under UV irradiation, the relative concentrations of MB remain 35.0%, 19.6% and 59.9%, respectively corresponding to depositing time of 30 min, 40 min and 60 min. On the other hand, when applying 3.5 V bias potential, the relative concentrations are 55.3%, 30.2% and 33.7% (Fig. S3). It clearly demonstrates that the 40 min depositing electrode have best photoelectrocatalytic performance at bias potential of 3 V and 3.5 V.

Also, after five recycles for the photodegradation of MB by the combination of UV light irradiation and electro-oxidation with 3.0 V, the film do not exhibit any significant loss of activity, as shown in Fig. 5c, confirming that the BiPO4 nanorods are not photocorrod during the photocatalytic oxidation of the pollutant molecules. To test the stability of the sample during the photocatalytic process, we compare the XRD patterns before and after 5 recycles of the reaction (Fig. S5). After reaction, no obvious change has been observed, indicating its good stability.

The oxidative species in the photocatalytic process can be detected through the trapping experiments of radicals and holes. As shown in Fig. 5d, under UV light irradiation the photodegradation of MB is scarcely restrained by the addition of a hole scavenger EDTA while it is obviously inhibited when tBuOH (hydroxyl radicals scavenger) is added. This indicates that hydroxyl radicals are the main active species that can oxidize the adsorbed organic pollutants. A possible mechanism for the photoelectrocatalytic degradation of MB over BiPO4 film was illustrated in Fig. S7. As pattern showed, BiPO4 particles generate and separate electron/hole pairs under UV irradiation and applied bias. Then, photogenerated holes in the valence band combine with hydroxide (OH$^-$) to produce hydroxyl radical (·OH), which can directly break the ring structure of MB molecules and convert them into CO2 and H2O.

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The CV analysis is carried out for the BiPO4 sample which exhibits two anodic peaks and two cathodic ones corresponding to the reverse reactions. The reduction peaks around $-0.8$ V vs. Hg/HgO are corresponding to the reduction of Bi(III) to Bi metal and the oxidation peaks around $-0.2$ V vs. Hg/HgO are corresponding to the oxidation of Bi metal to Bi(III) at 50 mV s$^{-1}$, respectively. Moreover, there is a potential shift and an increasing current with increasing scan rate in the range of 2–50 mVs$^{-1}$, which shows further insight into electrochemical performance as shown in Fig. 5f. The cathodic and anodic peak current is linearly proportional to the square root of scan rates (inset of Fig. 5f). This is a characteristic of a diffusion controlled process limited by the diffusion of either NaCl or the reaction intermediates.47

Mott–Schottky (MS) analysis was carried out using the SP-150 BIO-LOGIC science workstation. MS plots of the
Conclusions

In summary, a novel hexagonal BiPO₄ nanorods with space group P3121(152) has been synthesized on FTO for the first time via cathodic electrodeposition technique. Simultaneously, the amount of the nanorods increases with the deposited time. The d-spacing of 0.606 nm, 0.349 nm and 0.307 nm in HRTEM and SAED are well matched to the (100), (110) and (111) crystallographic plane of hexagonal BiPO₄. The BiPO₄ thin film shows a notable photo response of current under UV illustration, while EIS are radius of the 40 min depositing sample appears to be the smallest. The PEC degradation of MB is much more efficient than the sum of the electrochemical degradation and photocatalytic process. Particularly, the 40 min depositing film exhibits the best photoelectrocatalytic performance at bias potential of 3 V and 3.5 V. Moreover, the film maintains high photoelectrocatalytic activity in 5 recycles of PEC degradation. The photocurrent is increasing during per degradation reaction. In addition, the main oxidative species are determined to be hydroxyl radicals. A potential shift and the increasing anodic and cathodic currents with increasing scan rate in the range of 2–50 mV s⁻¹ prove a diffusion-controlled process. Moreover, the as-prepared BiPO₄ is a typical n-type semiconductor. These results also indicate that it is possible to synthesize other nonmetal oxy-acid salts materials with superior photoelectrocatalytic activity by cathodic electrodeposition.

Figure 5. (a) 10⁻⁵ M MB degradation profiles of the BiPO₄ film under conditions of (PC): photocatalysis, (without and with BiPO₄) (EC): electrocatalysis, (PEC): photoelectrocatalysis with applied potential of 3 V vs SCE and UV light irradiation. (b) Photocatalytic properties of the BiPO₄ films deposited in 30 min, 40 min, and 60 min. (c) Cycling runs in the photoelectrocatalytic degradation of the BiPO₄ film. (d) System of photodegradation of MB by the BiPO₄ film. (e) Chronoamperographs of the BiPO₄ film. (f) Cyclic voltammograms of the BiPO₄ film in 0.1 M NaCl, at pH 7, using different scan rates.
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