

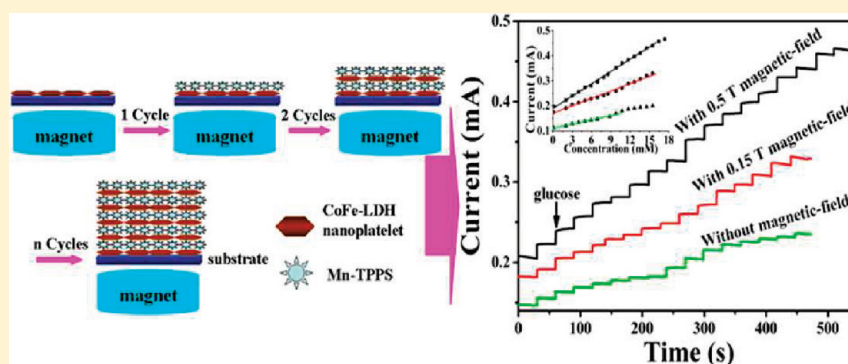
Magnetic-Field-Assisted Assembly of Layered Double Hydroxide/Metal Porphyrin Ultrathin Films and Their Application for Glucose Sensors

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S Supporting Information

ABSTRACT:



The ordered ultrathin films (UTFs) based on CoFe-LDH (layered double hydroxide) nanosheets and manganese porphyrin (Mn-TPPS) have been fabricated on ITO substrates via a magnetic-field-assisted (MFA) layer-by-layer (LBL) method and were demonstrated as an electrochemical sensor for glucose. The XRD pattern for the film indicates a long-range stacking order in the normal direction of the substrate. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of the MFA LDH/Mn-TPPS UTFs reveal a continuous and uniform surface morphology. Cyclic voltammetry, impedance spectroscopy, and chronoamperometry were used to evaluate the electrochemical performance of the film, and the results show that the MFA-0.5 (0.5 T magnetic field) CoFe-LDH/Mn-TPPS-modified electrode displays the strongest redox current peaks and fastest electron transfer process compared with those of MFA-0 (without magnetic-field) and MFA-0.15 (0.15 T magnetic field). Furthermore, the MFA-0.5 CoFe-LDH/Mn-TPPS exhibits remarkable electrocatalytic activity toward the oxidation of glucose with a linear response range (0.1–15 mM; $R^2 = 0.999$), low detection limit ($0.79 \mu\text{M}$) and high sensitivity ($66.3 \mu\text{A mM}^{-1} \text{cm}^{-2}$). In addition, the glucose sensor prepared by the MFA LBL method also shows good selectivity and reproducibility as well as resistance to poisoning in a chloride ion solution. Therefore, the novel strategy in this work creates new opportunities for the fabrication of nonenzyme sensors with prospective applications in practical detection.

INTRODUCTION

Glucose sensing is very essential in biotechnology, clinical diagnostics, and food industry, and significant research and development efforts have been devoted to prepare glucose sensors with high sensitivity, reliability, fast response, and good selectivity for in vitro or in vivo applications. Many techniques including Raman spectroscopy,¹ fluorescence,² electrochemiluminescence,³ and electrochemistry⁴ have been developed for this purpose. Electrochemical sensors for glucose have attracted much attention owing to the advantages of simplicity, high sensitivity, and excellent selectivity.⁵ Most previous studies on this subject involve the use of the glucose oxidase (GO_x), which catalyzes the oxidation of glucose to gluconolactone in the presence of oxygen, producing H_2O_2 simultaneously.⁶ However, the immobilization of enzyme

generally suffers from insufficient stability and loss of activity owing to the intrinsic nature of enzymes. For instance, the activity of GO_x is largely dependent on temperature, pH value, humidity, and toxic chemicals. To solve this problem, many nonenzymatic glucose sensors have also been explored in the hope of improving the stability and electrocatalytic activity toward the oxidation of glucose, such as noble-metal-based (containing Pt⁷ and Au⁸) and alloy-based (containing Pt, Ru, Pb, Au, and Cu)⁹ amperometric sensors, but the combination of good sensitivity and selectivity as well as resistance to poisoning was not well resolved. Therefore,

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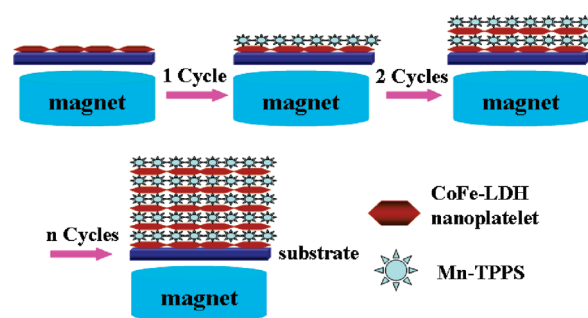
the development of suitable nonenzymatic electrochemistry sensors for glucose still remains a challenge.

An excellent electrochemical sensor for glucose needs two prerequisites: the physicochemical properties of the electroactive species and the fabrication of the electrode. Recent developments show that sensing units based on nanostructured films are capable of distinguished ability for detection of trace amounts of analyte,¹⁰ owing to the largely enhanced surface area and mass transport. Various methods have been reported to construct the electrochemical sensors, including drop-casting,¹¹ spin-casting,¹² sol-gel technique,¹³ Langmuir-Blodgett (LB),¹⁴ and layer-by-layer (LBL) electrostatic self-assembly.¹⁵ Recently, the use of external electric or magnetic field has attracted great interest as a powerful method to direct the assembly of nanocrystals and nanoparticles for tailoring the mechanical, optical, and electronic properties of materials.¹⁶ Controlled self-assembly of nanoparticles with field-assistance provides a convenient tool for the fabrication of electroactive species with high loading, desirable orientation, and anisotropic property, particularly when used with nanoparticles that are tailored to be intrinsically responsive.

Layered double hydroxides (LDHs) are layered anionic clays generally expressed by the formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{z+}(A^{n-})_{z/n} \cdot yH_2O$ (M^{II} and M^{III} are divalent and trivalent metals respectively; A^{n-} is the interlayer anion compensating for the positive charge of the brucite-like layers).¹⁷ Because of the specific layered structure and nanoscale size, LDH materials have been used as amperometric or potentiometric sensors via modification on the surface of electrodes with advantages of nontoxicity, high stability, and compatibility with many functional molecules.¹⁸ Recently, LDH materials containing magnetic transition metals (Fe, Ni, etc.) were also synthesized,¹⁹ which can be potentially used as sustainable and recycled catalysts and supports, adsorbents, and ion exchangers with easy manipulation by external magnetic field. This gives us impetus to take the challenge of fabricating electrochemical sensors based on magnetic-responsive LDH nanoparticles with the assistance of external magnetic-field, which exhibit fine-tuning ordered nanostructure and improved sensitivity and selectivity.

In our previous work, a LBL film with enhanced magnetic anisotropy was prepared via an external magnetic field.²⁰ In this work, we further report the fabrication of an electrochemical sensor for glucose by using the magnetic-field-assisted (MFA) layer-by-layer (LBL) method. The ordered ultrathin films (UTFs) based on CoFe-LDH nanoplatelets and manganese porphyrin have been fabricated via the MFA LBL method and were demonstrated as a good electrochemical sensor for glucose. Herein, the positively charged CoFe LDH nanoplatelets as building blocks were assembled alternately with negatively charged 5,10,15,20-tetrakis(4-sulfonatophenyl)porphinato manganese(III) (Mn-TPPS) on a pretreated ITO substrate with the assistance of an external magnetic field, and the direct electrochemistry behavior of the resulting MFA CoFe-LDH/Mn-TPPS was obtained. Moreover, the film-modified electrode exhibits excellent electrocatalytic performance for glucose with superior sensitivity, selectivity, stability, and response time compared with those assembled without MFA, owing to the coupling effect of interfacial electrostatic interactions and the external magnetic field. In addition, the obtained glucose sensor also exhibits excellent anti-interference property. Therefore, the MFA LBL technique in this work provides a promising approach for the fabrication of sensors with enhanced electrochemical behavior, which can be practically used in nonenzymatic sensing.

Scheme 1. Schematic Representation for the MFA LBL Assembly of the (CoFe-LDH/Mn-TPPS)_n Film



EXPERIMENTAL SECTION

Reagents and Materials. 5,10,15,20-tetrakis (4-sulfonatophenyl)-21H,23H-porphine manganese(III) was purchased from Sigma-Aldrich Co. $CoCl_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and NaOH are of analytical grade and used without further purification.

Preparation of CoFe-LDH. The CoFe-LDH nanoplatelets with narrow size-distribution and high crystallinity were prepared by a modified coprecipitation method. Typically, the pH of the aqueous solution (150 mL) containing $CoCl_2 \cdot 6H_2O$ (0.16 M) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.055 M) was adjusted to 8.0 with NaOH solution (1.5 M), and then it was aged in an autoclave at 130 °C for 24 h. The precipitate was centrifuged and washed three times with deionized water, and then it was filtrated using a membrane filter (0.2 μm , Millipore) to remove large LDH particles. The colloidal LDH suspension was thus obtained. Elemental analysis found for the resulting CoFe-LDH: Co, 36.1%; Fe, 12.0%; O, 46.0%; N, 3.01%; H, 2.81%.

Assembly of MFA CoFe-LDH/Mn-TPPS UTFs. The (CoFe-LDH/Mn-TPPS)_n multilayer UTFs were fabricated by applying the MFA LBL assembly technique. Prior to assembly, ITO substrates (3.0 cm $\times$ 1.0 cm) were cleaned by sonication in a series of solvents, acetone, ethanol, and deionized water, for 10 min each. Quartz glass slides were pretreated in a bath of methanol/HCl (1/1, v/v) and then concentrated H_2SO_4 for 30 min each to make the substrates surface hydrophilic and negatively charged. The overall process of MFA LBL deposition of (CoFe-LDH/Mn-TPPS)_n UTFs consists of a cyclic repetition of the following steps: (a) the pretreated substrate was immersed into the colloidal suspension of CoFe-LDH nanoplatelets for 10 min followed by washing with water and (b) the substrate was dipped into a Mn-TPPS aqueous solution (0.01 mg mL⁻¹) for 10 min and washed thoroughly. The whole procedure mentioned above was carried out with an external magnetic field perpendicular to the substrate, as shown in Scheme 1. The resulting films were finally dried in nitrogen gas flow.

Sample Characterization. X-ray diffraction (XRD) patterns were recorded by a Rigaku XRD-6000 diffractometer, using Cu K α radiation ($\lambda = 0.154$ nm) at 40 kV, 30 mA. The UV-vis spectra were collected with a Shimadzu U-3000 spectrophotometer. The morphology of thin films was investigated using a scanning electron microscope (SEM Hitachi S-4700) with the accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were recorded with Philips TECNAI-20 and JEOL JEM-2010 high-resolution transmission electron microscopes. The accelerating voltage was 200 kV. The surface roughness was studied using the atomic force microscopy (AFM) software (Digital Instruments, Version 6.12). The electrochemical measurements were performed using a CHI 660C electrochemical workstation (Shanghai Chenhua Instrument Co.). A conventional three-electrode system was used, including a modified ITO glass as the working electrode, a platinum foil as the auxiliary electrode, and a saturated Hg/HgCl₂ electrode as the reference electrode. All electrochemical measurements were carried out

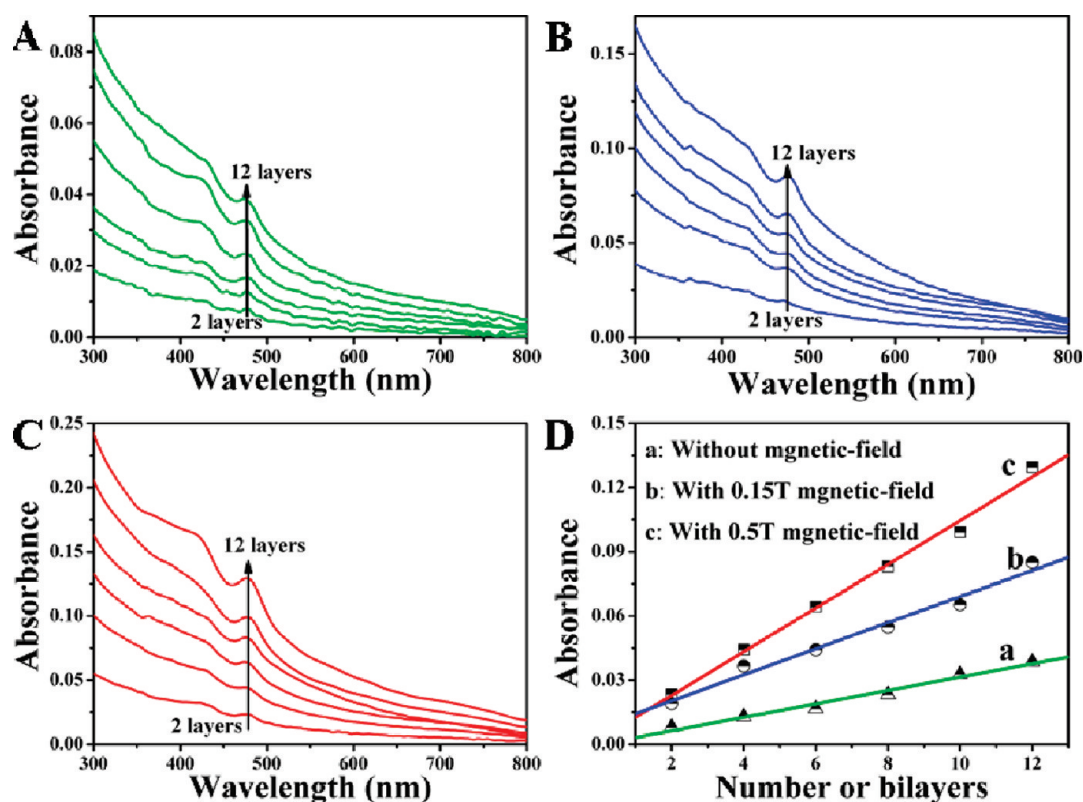


Figure 1. UV-vis absorption spectra of the MFA (CoFe-LDH/Mn-TPPS)_n ($n = 2-12$) UTFs with different magnetic field: (A) 0 T, (B) 0.15 T, (C) 0.5 T. (D) Absorbance of the MFA UTFs at 474 nm as a function of n .

in a NaOH solution (Milli-Q water, $>18 \text{ M}\Omega \text{ cm}$) at room temperature (ca. 20°C).

RESULTS AND DISCUSSION

Magnetic-Field-Assisted Assembly of the (CoFe-LDH/Mn-TPPS)_n Films. The suspension of colloidal CoFe-LDH nanoplatelets was obtained by using a modified coprecipitation method. The X-ray diffraction (XRD) pattern and FT-IR spectrum (Supporting Information, Figures S1-A and S1-B) of the CoFe-LDH powder sample indicate a well-defined nitrate-containing LDH ($\text{NO}_3\text{-LDH}$) with high crystallinity. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Supporting Information, Figures S1-C and S1-D) reveal that the individual CoFe-LDH nanoplatelets with particle size of 80–100 nm and an aspect ratio of 5–7 crystallize with a narrow size distribution. A clear Tyndall light scattering was observed, and the well-dispersed colloidal suspension was transparent and stable without any precipitation when stored in an N_2 atmosphere for more than 1 month.

Ultrathin films (UTFs) were fabricated by alternate assembly of CoFe-LDH nanoplatelets with manganese porphyrin anion (Mn-TPPS) by the MFA LBL method (Scheme 1). A magnetic field with different density (0, 0.15, and 0.5 T) was applied for the preparation of (CoFe-LDH/Mn-TPPS)_n UTFs, and the resulting films were denoted as MFA-0, MFA-0.15, and MFA-0.5 UTF, respectively. The MFA (CoFe-LDH/Mn-TPPS)_n ($n = 1-12$) UTFs were monitored by UV-vis absorption spectroscopy (Figure 1). The UTFs exhibit a strong absorption band at 474 nm attributed to the characteristic Soret band of Mn-TPPS, and the intensity correlates linearly with the increase of bilayer

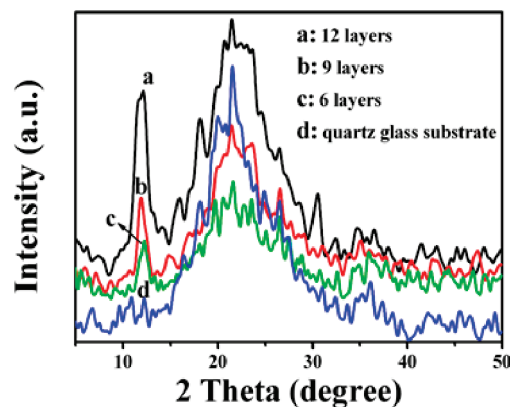


Figure 2. XRD patterns of the MFA-0.5 (CoFe-LDH/Mn-TPPS)_n UTFs ($n = 6, 9, 12$).

number n , indicative of a stepwise and regular deposition procedure with an almost equal amount of Mn-TPPS incorporated in each cycle. However, the slope of the plots (absorbance at 474 nm vs n , Figure 1D) becomes larger along with the increase of external magnetic density. This indicates that a more dense packing of building blocks in a bilayer cycle deposition was obtained for the MFA (CoFe-LDH/Mn-TPPS)_n UTFs with higher magnetic density, as a result of the enhancement of driving force including electrostatic interaction and magnetic attraction in the assembly process.

Morphological and Structural Characterization. The XRD patterns (Figure 2) for the obtained MFA-0.5 (CoFe-LDH/Mn-TPPS)_n ($n = 6, 9, 12$) UTFs exhibit the characteristic

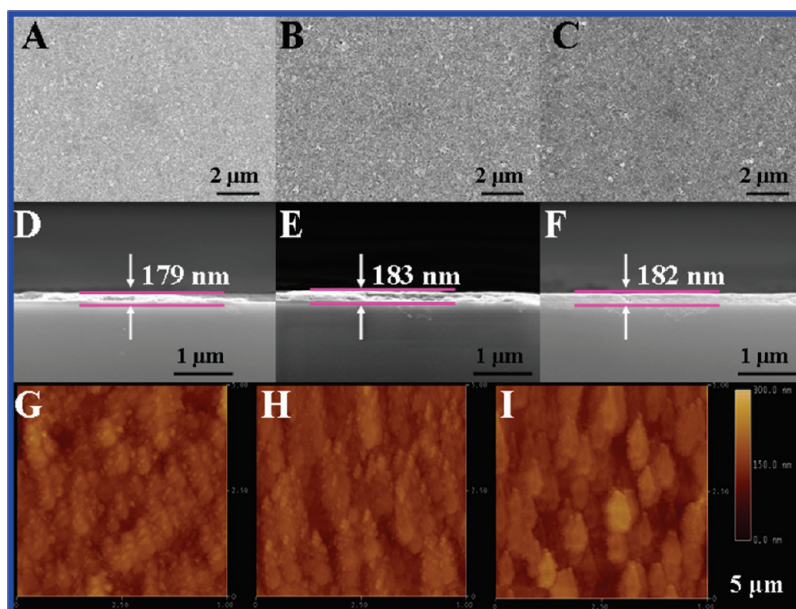


Figure 3. Top view and side view of SEM images and AFM images for the $(\text{CoFe-LDH/Mn-TPPS})_{12}$ UTFs assembled with different magnetic density: (A, D, and G) 0 T, (B, E, and H) 0.15 T, and (C, F, and I) 0.5 T.

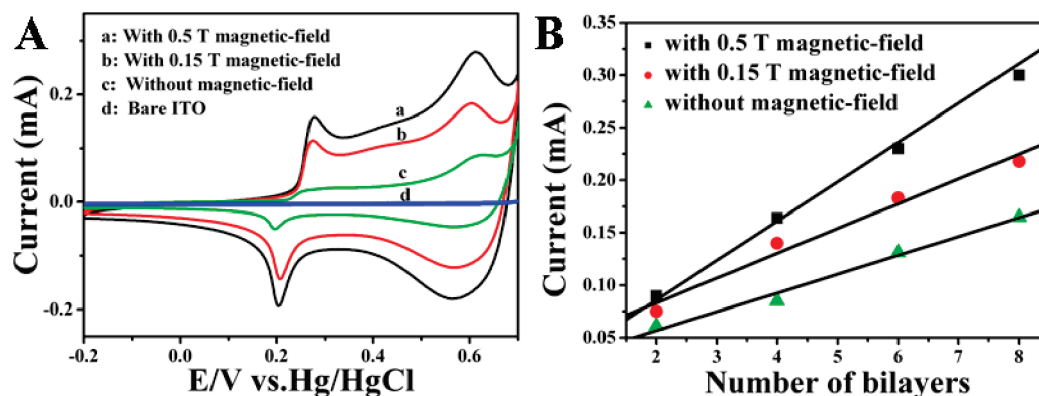


Figure 4. (A) Cyclic voltammograms (CVs) of the $(\text{CoFe-LDH/Mn-TPPS})_6/\text{ITO}$ electrodes assembled with different magnetic field in 0.1 M NaOH solution at 0.1 V s^{-1} : (a) MFA-0.5 T, (b) MFA-0.15 T, (c) MFA-0 T, and (d) a bare ITO. (B) The anodic peak current of the MFA UTFs at 0.6 V as a function of n .

reflection of the LDH structure with the (001) peak appearing as narrow, symmetric, strong lines at $2\theta = 11.4^\circ$, and both its intensity and symmetry increase successively upon increasing deposition cycle. Moreover, the absence of any nonbasal reflections ($h, k \neq 0$) at high angle is as expected for an extremely well c -oriented assembly of LDH nanoplatelets (the peak at $2\theta = 15^\circ \sim 35^\circ$ is assigned to amorphous reflection of the quartz substrate).²¹ The surface morphology and thickness of MFA $(\text{CoFe-LDH/Mn-TPPS})_n$ UTFs assembled with different magnetic density were further investigated by SEM and AFM. Top view of SEM images of the MFA $(\text{CoFe-LDH/Mn-TPPS})_{12}$ UTF (Figure 3A,B,C for 0, 0.15, 0.5 T) show that the film surface is continuous and uniform. Side-view of SEM images display rather close thickness of the MFA-0, MFA-0.15, and MFA-0.5 UTFs (Figure 3D–F), indicating that MFA assembly did not give rise to additional increase in film thickness in each cycle. Therefore, it can be concluded that the packing of LDH nanoplatelets and the

arrangement of Mn-TPPS are more condense and uniform in the MFA UTFs, since they show enhanced UV-vis absorbance compared with 0 T magnetic density (Figure 1). The AFM images reveal that the value of the root-mean-square (rms) roughness is ~ 27.5 , 28.1 , and 29.6 nm for MFA-0, MFA-0.15, and MFA-0.5, respectively (Figure 3G,H,I). Moreover, the AFM images show a more ordered arrangement of the LDH nanoplatelets for the MFA-0.5 than for MFA-0.15 and MFA-0 UTF. The rms roughness value of MFA-0.5 UTFs with different bilayer number increases slowly from 24.7 nm ($n = 6$) to 29.6 nm ($n = 12$) (Supporting Information, Figure S2), indicating a relatively smooth surface for these MFA-0.5 UTFs.

Electrochemical Behavior of the $(\text{CoFe-LDH/Mn-TPPS})_n$ UTFs. Figure 4A shows the cyclic voltammograms (CVs) of different electrodes in 0.1 M NaOH solution at a scan rate of 0.1 V s^{-1} . No electrochemical response was observed for the bare ITO (curve d). The MFA-0.5 (curve a), MFA-0.15 (curve b), and

MFA-0 (curve c) (CoFe-LDH/Mn-TPPS)₆ UTF modified ITO electrodes show two pairs of redox peaks, corresponding to the redox process of cobalt (0.56 and 0.60 V) and iron (0.22 and 0.28 V), respectively. Both the anodic and cathodic peak currents increase significantly upon increasing magnetic density, which is related to the higher loading of LDH nanoplatelets with stronger magnetic density. The redox current presents consistent enhancement with the increase of bilayer number *n*, also demonstrating an ordered and regular film growth procedure (Figure 4B and Supporting Information, Figure S3). Moreover, compared with the MFA-0 and MFA-0.15 electrode, the MFA-0.5 electrode shows the maximum redox peak current with the same bilayer number, in agreement with the UV-vis absorption spectra (Figure 1D).

In order to further verify the redox process of CoFe-LDH/Mn-TPPS film, CVs of the MFA-0.5 (CoFe-LDH/Mn-TPPS)₆-modified ITO electrode were carried out in NaOH solution with various concentrations (Supporting Information, Figure S4). Negative shifts in both anodic and cathodic peak potential were observed upon increasing the concentration of OH[−], indicating that OH[−] plays a key role in the redox process of cobalt and iron. The effect of scan rate on the electrochemical response of the MFA-0.5 (CoFe-LDH/Mn-TPPS)₆ film is shown in Figure 5. It was found that a linear relationship between the anodic (or cathodic) peak current and the potential sweep rate was obtained, indicating a surface-controlled process.²²

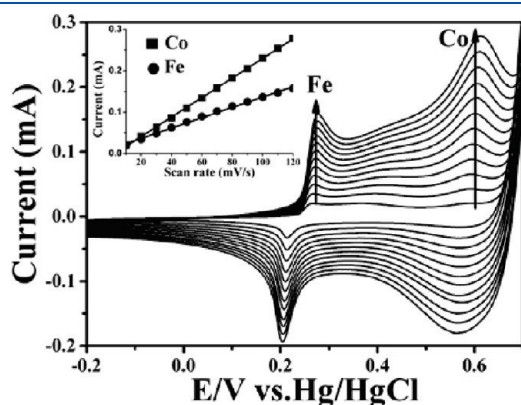


Figure 5. CVs of the MFA-0.5 (CoFe-LDH/Mn-TPPS)₆-modified ITO electrode with scan rate ranging from 0.01 to 0.1 V s^{−1}. (Inset) Plots of peak current vs scan rate in 0.1 M NaOH.

The electrochemical impedance spectroscopy (EIS) study provides information about the interfacial properties of surface-modified electrodes. The semicircle diameter of EIS equals the electron transfer resistance (*R*_{et}), which controls the electron transfer kinetics of the redox probe at the electrode interface. In this work, *R*_{et} reflects the restricted diffusion of the redox probe through the multilayer system, which relates directly to the accessibility of the underlying electrode or the film permeability. Figure 6 shows the typical EIS for the MFA (CoFe-LDH/Mn-TPPS)_{*n*}-modified electrodes in 0.1 M KCl solution containing the redox probe Fe[(CN)₆]^{4−/3−}. The semicircle-like shape with smaller diameter was observed for MFA film modified electrode (Figure 6A) relative to the bare ITO, which indicates a conducting effect of the CoFe-LDH in facilitating the electron-transfer process at the electrode interface. Furthermore, the electron-transfer resistance (*R*_{et}) decreases significantly as the magnetic density increases from 0 to 0.5 T, implying that the more ordered structure of the MFA film allows for much easier electron transfer. As shown in Figure 6B, the diameter of the semicircle decreases significantly as the bilayer number (*n*) increases from 2 to 6, while it turns to increase with a further increase of *n* from 6 to 10, resulting from the hindrance effect on the redox couples along with the stepwise deposition of CoFe-LDH/Mn-TPPS UTF. As a result, the film with *n* = 6 was chosen as the optimum electrode for amperometric determination of glucose in the next section.

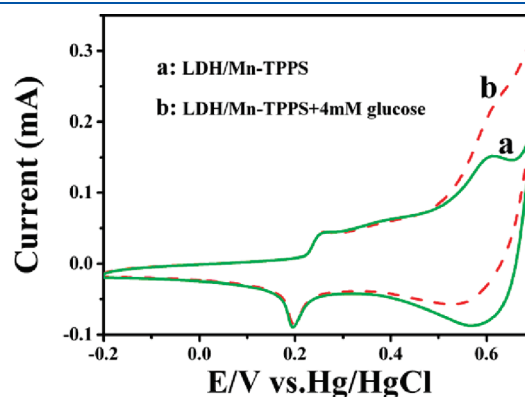


Figure 7. CVs of the MFA-0.5 (CoFe-LDH/Mn-TPPS)₆ electrode in (a) 0.1 M NaOH solution and (b) 0.1 M NaOH + 4 mM glucose. Scan rate 0.1 V s^{−1}.

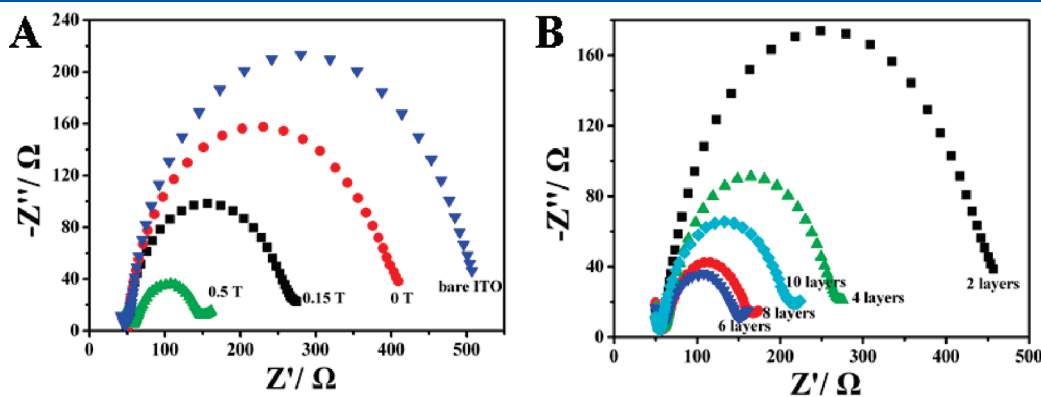


Figure 6. Electrochemical impedance spectra: (A) the MFA (CoFe-LDH/Mn-TPPS)₆ UTFs with different magnetic density and (B) the MFA-0.5 (CoFe-LDH/Mn-TPPS)_{*n*} UTF (*n* = 2–10) modified electrodes in the presence of 5 mM Fe[(CN)₆]^{4−/3−} in 0.1 M KCl solution.

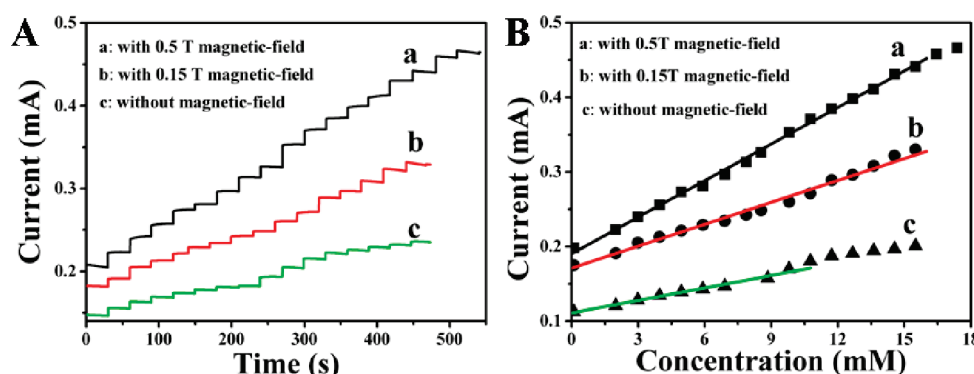
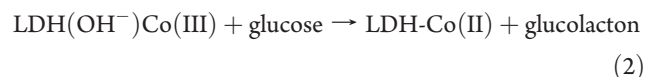


Figure 8. (A) Current–time curves measured at +0.6 V for the (CoFe-LDH/Mn–TPPS)₆ electrode with successive addition of glucose in 0.1 M NaOH: (a) MFA-0.5, (b) MFA-0.15, (c) MFA-0. (B) Calibration curves for the three modified electrodes.

Enhanced Performance for an Amperometric Glucose Sensor. The electrocatalytic activity of the MFA-0.5 (CoFe-LDH/Mn–TPPS)₆ UTF modified electrode toward oxidation of glucose in an alkaline solution is shown in Figure 7. Compared with curve a, the CV (curve b) presents an unchanged Fe³⁺/Fe²⁺ redox current peak but a significantly increased Co²⁺/Co³⁺ anodic current peak with the addition of glucose. This is attributed to the electrocatalytic effect of the Co²⁺/Co³⁺ redox couple for the oxidation of glucose. The oxidation of glucose at platinum in alkaline solutions has been well-understood.²³ On the basis of the results in this work and previous reports,²⁴ the electrocatalytic behavior of the (CoFe-LDH/Mn–TPPS)₆ UTF for the oxidation of glucose can be tentatively expressed as follows:



The (CoFe-LDH/Mn–TPPS)₆/ITO gives a couple of well-defined reversible redox peaks at 0.56 and 0.6 V corresponding to Co²⁺/Co³⁺ (Figure 4A). When applying a potential of 0.6 V to the electrode, the Co(II) species is oxidized to Co(III). The glucose molecule in aqueous solution diffuses from the bulk solution to the electrode surface and is oxidized to glucolacton by the Co(III) species; Co(II) species regenerates simultaneously. The schematic illustration for the electrooxidation of glucose at the (CoFe-LDH/Mn–TPPS)₆ electrode in alkaline condition is shown in Scheme S1 (Supporting Information).

The amperometric response and CV behavior of the MFA (CoFe-LDH/Mn–TPPS)₆ UTF modified electrode for the successive addition of glucose in 0.1 M NaOH solution are presented in Figure 8A and Supporting Information, Figure S5, respectively. For all the MFA (CoFe-LDH/Mn–TPPS)₆ electrodes, the amperometric signal responds rapidly to the change in glucose concentration. As shown in Figure 8B and Supporting Information, Table S1, compared with the MFA-0 and MFA-0.15 (CoFe-LDH/Mn–TPPS)₆ electrode, the MFA-0.5 (CoFe-LDH/Mn–TPPS)₆ electrode exhibits a wider linear range (0.1–15 mM; $R^2 = 0.999$), lower detection limit (0.79 μM), and higher sensitivity (66.3 $\mu\text{A mM}^{-1} \text{cm}^{-2}$). Furthermore, the glucose sensing performance of the electrode is also superior to those reported previously, such as PtPb-CNTs²⁵ and porous gold.²⁶ The high sensitivity in this work implies that the MFA

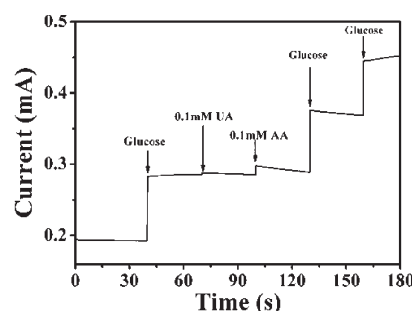


Figure 9. Amperometric response of glucose (4 mM) in the absence and presence of 0.1 mM UA and AA at the MFA-0.5 (CoFe-LDH/Mn–TPPS)₆-modified electrode. Electrolyte, 0.1 M NaOH; applied potential, +0.6 V.

electrode possesses a good electrocatalytic activity toward the glucose oxidation. Moreover, the high loading and dense packing of LDH nanoplatelets on the electrode with the MFA LBL method not only increase the active species for the glucose but also facilitate the electron transfer process on the electrode.

Uric acid (UA) and ascorbic acid (AA) present in physiological fluids are the most important interferences for the direct electrochemical oxidation of glucose on different electrodes especially nonenzymatic sensors.²⁷ Therefore, in the present work, the influence of electrochemical interferences UA and AA for glucose on the response of MFA (CoFe-LDH/Mn–TPPS)₆ electrode was evaluated. Figure 9 represents the chronoamperometric responses of glucose (4 mM) in the presence of UA (0.1 mM) and AA (0.1 mM) in 0.1 M NaOH solution at the MFA-0.5 (CoFe-LDH/Mn–TPPS)₆-modified electrode. It is observed that the addition of UA and AA does not influence the current response of glucose significantly, demonstrating that the modified electrode selectively catalyzes the oxidation of glucose in the presence of UA and AA.

It was reported that chloride ion imposed a serious poisoning effect on the metals or alloy electrocatalysts (such as Pt and Pt alloy), leading to the loss of their activity toward the oxidation of glucose.²⁸ The poisoning effect of chloride ion on the CoFe-LDH/Mn–TPPS catalyst was therefore examined by adding a high concentration of chloride ion into the supporting electrolyte. The CV features of the MFA-0.5 (CoFe-LDH/Mn–TPPS)₆ electrode in 0.1 M NaOH solution containing 4 mM glucose with (curve a) and without (curve b) 0.5 M NaCl are almost identical (Supporting Information, Figure S6). This demonstrates

that chloride ion has no observable poisoning effect on the CoFe-LDH catalyst. Therefore, the electrocatalyst can be widely used for the practical glucose sensing, even in the presence of a high concentration of chloride ion, which is an advantage over those noble-metal catalyst reported previously.²⁹

The (CoFe-LDH/Mn-TPPS)₆-modified electrode exhibits good measurement stability from 10 times of test using one electrode, with a relative standard deviation (RSD) of less than 0.8% (Supporting Information, Figure S7-A). The long-term stability of the MFA-fabricated electrode was determined by storing the sensor at room temperature and monitoring the response current every week for 4 mM glucose. After 1 month, the current maintained ~98% of its initial response (Supporting Information, Figure S7-B). The good stability and long lifetime of the glucose sensor relates to the ordered long-range stacking of LDH nanoplatelets in the MFA films, resulting from the coupling effect of interfacial electrostatic interaction and the external magnetic field in the fabrication process.

CONCLUSIONS

In summary, a facile and effective MFA LBL method to fabricate (CoFe-LDH/Mn-TPPS)_n UTFs by using LDH nanoplatelets and manganese porphyrin anion as building blocks was reported. The structural and morphological studies show that the MFA film is continuous and uniform with long-range stacking order in the normal direction of the substrate. The coupling effect of interfacial electrostatic interaction and the external magnetic field gives rise to dense packing of LDH nanoplatelets on the substrate compared with single electrostatic assembly. The MFA-0.5 (CoFe-LDH/Mn-TPPS)₆-modified electrode demonstrates the maximum redox current peaks and the fastest electron transfer process compared with those of MFA-0 and MFA-0.15. Furthermore, the MFA-0.5 (CoFe-LDH/Mn-TPPS)₆ electrode exhibits remarkable electrocatalytic activity toward the oxidation of glucose with a wide linear response range, low detection limit, high sensitivity, and selectivity as well as resistance to poison in a chloride ion solution. Therefore, the novel strategy in this work can be effectively used for the fabrication of glucose nonenzyme sensor and other electronic devices with prospective applications in electroanalysis and sensing.

ASSOCIATED CONTENT

S Supporting Information. Characterization of the CoFe-LDH, AFM images for the MFA-0.5 (CoFe-LDH/Mn-TPPS)_n UTFs with different bilayer number, CVs of the MFA (CoFe-LDH/TPPS)_n UTFs (*n* = 2–8) assembled with different magnetic density, CVs of the MFA-0.5 (CoFe-LDH/Mn-TPPS)₆-modified ITO electrode in different concentration of NaOH solution, CVs of the electrode in 0.1 M NaOH with and without NaCl, scheme for the electrochemical oxidation of glucose on the CoFe-LDH/Mn-TPPS-modified electrode, a table for glucose sensing performance, and the stability measurement for the CoFe-LDH/Mn-TPPS electrode. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) (a) Yuen, J. M.; Shah, N. C.; Walsh, J. T., Jr.; Glucksberg, M. R.; Van Duyne, R. P. *Anal. Chem.* **2010**, *82*, 8382. (b) Shafer-Peltier, K. E.; Haynes, C. L.; Glucksberg, M. R.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2003**, *125*, 588.
- (2) (a) Movia, D.; Canto, E. D.; Giordani, S. *J. Phys. Chem. C* **2010**, *114*, 18407. (b) Marvin, J. S.; Hellinga, H. W. *J. Am. Chem. Soc.* **1998**, *120*, 7. (c) Suri, J. T.; Cordes, D. B.; Cappuccio, F. E.; Wessling, R. A.; Singaram, B. *Angew. Chem., Int. Ed.* **2003**, *42*, 5857.
- (3) (a) Kremeskoetter, J.; Wilson, R.; Schiffrin, D. J.; Luff, B. J.; Wilkinson, J. S. *Meas. Sci. Technol.* **1995**, *6*, 1325. (b) Bertonecello, P.; Forster, R. J. *Biosens. Bioelectron.* **2009**, *24*, 3191.
- (4) (a) Wang, J. *Chem. Rev.* **2008**, *108*, 814. (b) Xian, Y.; Hu, Y.; Liu, F.; Xian, Y.; Feng, L.; Jin, L. *Biosens. Bioelectron.* **2007**, *22*, 2827. (c) Wang, Z.; Liu, S.; Wu, P.; Cai, C. X. *Anal. Chem.* **2009**, *81*, 1638.
- (5) (a) Zeng, G. H.; Xing, Y. B.; Gao, J.; Wang, Z. Q.; Zhang, X. *Langmuir* **2010**, *26*, 15022. (b) Luo, D. B.; Wu, L. Z.; Zhi, J. F. *ACS Nano* **2009**, *3*, 4009. (c) Shoji, E.; Freund, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 3383. (d) Lin, Y. H.; Lu, F.; Tu, Y.; Ren, Z. F. *Nano Lett.* **2004**, *4*, 191. (e) Zhang, D.; Zhang, K.; Yao, Y. L.; Xia, X. H.; Chen, H. Y. *Langmuir* **2004**, *20*, 7303.
- (6) Du, P.; Zhou, B.; Cai, C. X. *J. Electroanal. Chem.* **2008**, *614*, 149.
- (7) Beden, B.; Largeaud, F.; Kokoh, K. B.; Lamy, C. *Electrochim. Acta* **1996**, *41*, 701.
- (8) (a) Hsiao, M. W.; Adzic, R. R.; Yeager, E. B. *J. Electrochem. Soc.* **1996**, *143*, 759. (b) Jena, B. K.; Raj, C. R. *Chem.—Eur. J.* **2006**, *12*, 2702.
- (9) (a) Holt-Hindle, P.; Nigro, S.; Asmussen, M.; Chen, A. *Electrochem. Commun.* **2008**, *10*, 1438. (b) Cui, H. F.; Ye, J. S.; Zhang, W. D.; Li, C. M.; Luong, J. H. T.; Sheu, F. S. *Anal. Chim. Acta* **2007**, *594*, 175. (c) Bai, Y.; Sun, Y.; Sun, C. *Biosens. Bioelectron.* **2008**, *24*, 579.
- (10) (a) Shi, G. Y.; Sun, Z. Y.; Liu, M. C.; Zhang, L.; Liu, Y.; Qu, Y. H.; Jin, L. T. *Anal. Chem.* **2007**, *79*, 3581.
- (11) Santos, W. J. R.; Sousa, A. L.; Luzb, R. C. S.; Damos, F. S.; Kubota, L. T.; Tanaka, A. A.; Tanaka, S. M. C. N. *Talanta* **2006**, *70*, 588.
- (12) Keefe, M. H.; Slone, R. V.; Hupp, J. T.; Czaplewski, K. F.; Snurr, R. Q.; Stern, C. L. *Langmuir* **2000**, *16*, 3964.
- (13) Collinson, M. M.; Howells, A. R. *Anal. Chem.* **2000**, *72*, 702.
- (14) (a) Yin, F.; Shin, H.-K.; Kwon, Y.-S. *Biosens. Bioelectron.* **2005**, *21*, 21. (b) Ravaine, S.; Lafuente, C.; Mingotaud, C. *Langmuir* **1998**, *14*, 6347.
- (15) (a) Tang, Z. Y.; Wang, Y.; Podsiadlo, P.; Kotov, N. A. *Adv. Mater.* **2006**, *18*, 3203. (b) Shao, M. F.; Han, J. B.; Shi, W. Y.; Wei, M.; Duan, X. *Electrochem. Commun.* **2010**, *12*, 1077. (c) Wang, Y. D.; Joshi, P. P.; Hobbs, K. L.; Johnson, M. B.; Schmidtke, D. W. *Langmuir* **2006**, *22*, 9776.
- (16) (a) Lalatonne, Y.; Richardi, J.; Pileni, M. P. *Nat. Mater.* **2004**, *3*, 121. (b) Suda, M.; Einaga, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 1754. (c) Gupta, S.; Zhang, Q.; Emrick, T.; Russell, T. P. *Nano Lett.* **2006**, *6*, 2066. (d) Park, J.; Jun, Y.; Choi, J.; Cheon, J. *Chem. Commun.* **2007**, *43*, 5001.
- (17) (a) Fogg, A. M.; Green, V. M.; Harvey, H. G.; O'Hare, D. *Adv. Mater.* **1999**, *11*, 1466. (b) Xu, Z. P.; Braterman, P. S. *J. Phys. Chem. C* **2007**, *111*, 4021. (c) Costantino, U.; Coletti, N.; Nocchetti, M. *Langmuir* **1999**, *15*, 4454. (d) O'Leary, S.; O'Hare, D.; Seeley, G. *Chem. Commun.* **2002**, *38*, 1506. (e) Xu, Z. P.; Stevenson, G. S.; Lu, C. Q.; Lu, G. Q.; Bartlett, P. F.; Gray, P. P. *J. Am. Chem. Soc.* **2006**, *128*, 36.
- (18) (a) Scavetta, E.; Berrettoni, M.; Giorgetti, M.; Tonelli, D. *Electrochim. Acta* **2002**, *47*, 2451. (b) Darder, M.; Lopez-Blanco, M.; Aranda, P.; Leroux, F.; Ruiz-Hitzky, E. *Chem. Mater.* **2005**, *17*, 1969.

- (c) Han, J. B.; Xu, X. Y.; Rao, X. Y.; Wei, M.; Evans, D. G.; Duan, X. *J. Mater. Chem.* **2011**, *21*, 2126.
- (19) (a) Li, F.; Liu, J. J.; Evans, D. G.; Duan, X. *Chem. Mater.* **2004**, *16*, 1597. (b) Han, Y. F.; Liu, Z. H.; Yang, Z. P.; Wang, Z. L.; Tang, X. H.; Wang, T.; Fan, L. H.; Ooi, K. *Chem. Mater.* **2008**, *20*, 360.
- (20) Shao, M. F.; Wei, M.; Evans, D. G.; Duan, X. *Chem. Commun.* **2011**, *47*, 3171.
- (21) (a) Adachi-Pagano, M.; Forano, C.; Besse, J. P. *Chem. Commun.* **2000**, *36*, 91. (b) Gardner, E.; Huntoon, K.; Pinnavaia, T. *Adv. Mater.* **2001**, *13*, 1263. (c) Gursky, J.; Blough, S.; Luna, C.; Gomez, C.; Luevano, A.; Gardner, E. *J. Am. Chem. Soc.* **2006**, *128*, 8376.
- (22) Laurent, D.; Schlenoff, J. B. *Langmuir* **1997**, *13*, 1552.
- (23) (a) Park, S.; Boo, H.; Chung, T. D. *Anal. Chim. Acta* **2006**, *556*, 46. (b) Beden, B.; Largeaud, F.; Kokoh, K. B.; Lamy, C. *Electrochim. Acta* **1996**, *41*, 701.
- (24) (a) Safavi, A.; Maleki, N.; Farjami, E. *Biosens. Bioelectron.* **2009**, *24*, 1655. (b) Zhao, C.; Shao, C.; Li, M.; Jiao, K. *Talanta* **2007**, *71*, 1769.
- (25) (a) Qiu, R.; Zhang, X. L.; Qiao, R.; Li, Y.; Kim, Y.; Kang, Y. S. *Chem. Mater.* **2007**, *19*, 4174. (b) Cui, H. F.; Ye, J. S.; Zhang, W. D.; Li, C. M.; Luong, J. H. T.; Sheu, F. S. *Anal. Chim. Acta* **2007**, *594*, 175.
- (26) (a) Li, Y.; Song, Y. Y.; Yang, C.; Xia, X. H. *Electrochem. Commun.* **2007**, *9*, 981. (b) Shen, Q.; Jiang, L.; Zhang, H.; Min, Q.; Hou, W.; Zhu, J. J. *J. Phys. Chem. C* **2008**, *112*, 16385.
- (27) (a) Bao, S. J.; Li, C. M.; Zang, J. F.; Cui, X. Q.; Qiao, Y.; Guo, J. *Adv. Funct. Mater.* **2008**, *18*, 591. (b) Li, Y.; Song, Y. Y.; Yang, C.; Xia, X. H. *Electrochem. Commun.* **2007**, *9*, 981.
- (28) Sun, Y.; Buck, H.; Mallouk, T. E. *Anal. Chem.* **2001**, *73*, 1599.
- (29) (a) Shen, Q.; Jiang, L.; Zhang, H.; Min, Q.; Hou, W.; Zhu, J. J. *J. Phys. Chem. C* **2008**, *112*, 16385. (b) Myung, Y.; Jang, D. M.; Cho, Y. J.; Kim, H. S.; Park, J.; Kim, J. U.; Choi, Y.; Lee, C. J. *J. Phys. Chem. C* **2009**, *113*, 1251. (c) Li, Y.; Song, Y. Y.; Yang, C.; Xia, X. H. *Electrochem. Commun.* **2007**, *9*, 981.