

# Fabrication of a Metalloporphyrin–Polyoxometalate Hybrid Film by a Layer-by-Layer Method and Its Catalysis for Hydrogen Evolution and Dioxygen Reduction

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[Tetrakis (*N*-methylpyridyl) porphyrinato] cobalt (CoTMPyP) and 1:12 silicotungstic acid (SiW<sub>12</sub>) were alternately deposited on a 4-aminobenzoic acid (4-ABA)-modified glassy carbon electrode through a layer-by-layer method. The resulting organic–inorganic hybrid films were characterized by cyclic voltammetry (CV) and UV/vis absorption spectroscopy. We proved that the prepared multilayer films are uniform and stable. SiW<sub>12</sub>-containing multilayer films (SiW<sub>12</sub> as the outermost layer) exhibit remarkable electrocatalytic activity for the hydrogen evolution reaction (HER). The kinetic constants for HER were comparatively investigated at different layers of SiW<sub>12</sub>/CoTMPyP multilayer film-modified electrodes by hydrogen evolution voltammetry. In addition, rotating disk electrode (RDE) and rotating ring–disk electrode (RRDE) voltammetric methods confirm that SiW<sub>12</sub>/CoTMPyP (CoTMPyP as the outermost layer) multilayer films catalyze almost a two-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> in pH 1–6 buffer solutions. Furthermore, P<sub>2</sub>W<sub>18</sub>/CoTMPyP films were also assembled, and their catalytic activity for HER is very different from that of SiW<sub>12</sub>/CoTMPyP multilayer films.

## 1. Introduction

Heteropolyacids are among the most stable and the best defined systems because they possess a rigid anionic primary structure and contain a central heteroatom, which is usually nonelectroactive and has a stabilizing effect on the structure.<sup>1</sup> More than 15 years ago, it was<sup>2–9</sup> reported that heteropoly and isopoly oxometalates, deposited on an electrode surface, showed a strikingly high activity toward the hydrogen evolution reaction (HER) in acid media. An evaluation of the kinetic parameters of the HER was also reported. But this method of deposition showed that no useful derivatization of the electrode surface for the HER was obtained unless the potential of the working electrode was at least as negative as a proton-dependent wave, and it was also time-consuming.

In recent years, heteropoly anion-modified electrodes have attracted more and more interest because of their good stability and electroactivity. In general, there are three main methods for modifying this kind of species on electrode surfaces: electrochemical deposition,<sup>10</sup> adsorption,<sup>11,12</sup> and immobilization of heteropolyanions as dopants in a conducting polymer matrix.<sup>13–16</sup> The layer-by-layer (LBL) assembly, initially developed for pairs of oppositely charged polyelectrolytes,<sup>17</sup> has recently been applied to the preparation of inorganic materials such as metalloporphyrin<sup>18</sup> and nanoparticle thin films.<sup>19</sup> Metalloporphyrin is an attractive redox catalyst or mediator in many electrochemical reactions for the reduction of substrates such as O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>. In the present study, polyoxometalate-containing multilayer films were fabricated on a 4-aminobenzoic acid (4-ABA) derivatization glassy carbon (GC) electrode by the LBL method, with metalloporphyrins as counterions. Through derivatization of 4-ABA on a GC electrode,<sup>20,21</sup> the 4-ABA/GC electrode surface was negatively charged at suitable

pH conditions (pH > 3.1). Then, CoTMPyP cations and SiW<sub>12</sub> anions were deposited alternately on the 4-ABA/GC electrode surface by electrostatic interaction. The as-prepared multilayer films were characterized by cyclic voltammetry (CV) and UV/vis absorption spectroscopy (UV). The multilayer films (SiW<sub>12</sub> as the outermost layer) had good uniformity and stability and showed remarkable electrocatalytic activity for the HER in acid media. The dynamic constants of HER were estimated by hydrogen evolution voltammograms. In addition, rotating disk electrode (RDE) and rotating ring–disk electrode (RRDE) experiments confirm that the SiW<sub>12</sub>/CoTMPyP (CoTMPyP as the outermost layer) hybrid films can catalyze the reduction of dioxygen to H<sub>2</sub>O<sub>2</sub> at all pH values studied. In addition, P<sub>2</sub>W<sub>18</sub>/CoTMPyP multilayer films were also assembled, and their catalytic activity for HER was investigated.

## 2. Experimental Section

**2.1. Reagents.** 4-Aminobenzoic acid (4-ABA) was purchased from Aldrich. Absolute ethanol was dried over 3-Å molecular sieves before use. A solution of 4-ABA was freshly prepared for each modification. Lithium perchlorate was dried at about 90 °C in a vacuum oven before use. H<sub>4</sub>SiW<sub>12</sub> (SiW<sub>12</sub>) was purchased from Beijing Xinhua Chemical Co., China. α-K<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·14H<sub>2</sub>O (P<sub>2</sub>W<sub>18</sub>)<sup>22</sup> and CoTMPyP(ClO<sub>4</sub>)<sub>5</sub><sup>23</sup> were synthesized according to the literature. Other reagents were of analytical reagent grade and were used as received. Buffer solutions were prepared from 0.1 M NaAc + HAc (pH 3–6) and 0.1 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH < 3). Water was purified using a Millipore Milli-Q purification system in all experiments. Unless otherwise stated, all of the solutions were degassed thoroughly with pure nitrogen and kept under a positive pressure of this gas during experimentation.

**2.2. UV/Visible Absorption Spectroscopy.** UV/vis absorption spectra were recorded using a Cary 500 Scan UV/vis/NIR

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spectrophotometer (Varian Co.) on a transparent indium tin oxide (ITO) glass substrate, which was previously sonicated in acetone for 5 min, followed by rinsing with water, ultrasonic agitation in concentrated NaOH in 1:1 V/V water/ethanol, rinsing further with water, immersion in  $\text{CHCl}_3$  for 10 min, and drying according to the literature.<sup>24</sup> The immobilization of  $\text{SiW}_{12}/\text{CoTMPyP}$  multilayer films on the ITO substrate was the same as above.

**2.2. Electrochemical Measurements.** Cyclic voltammetry and hydrogen evolution voltammograms were performed with a CHI 660 electrochemical workstation in a conventional three-electrode electrochemical cell using glassy carbon (GC 2000, 4-mm diameter, Tokai Corp., Japan) as the working electrode, twisted platinum wire as the auxiliary electrode, and  $\text{Ag}/\text{AgCl}$  as the reference electrode. The GC electrode was successively polished with 1.0- and 0.3- $\mu\text{m}$   $\alpha\text{-Al}_2\text{O}_3$  powders and sonicated in water for about 5 min after each polishing step. Finally, the electrodes were sonicated in  $\text{H}_2\text{O}$  and in ethanol, washed with ethanol, and dried in a high-purity nitrogen stream immediately before use.

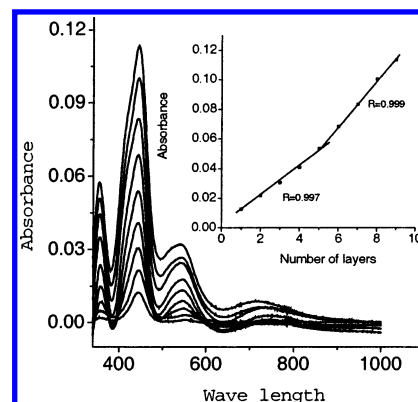
An EG&G PARC model 636 rotating ring–disk electrode system and an EG&G PARC model 366 bipotentiostat were used for rotating disk and rotating ring–disk voltammetric experiments. A rotating GC disk–platinum ring electrode was used as a working electrode. The collection efficiency ( $N$ ) of the ring electrode obtained by reducing ferricyanide at a disk electrode was 0.1385.

**2.3. Modification Procedure.** The GC electrode was first derivatized with 4-ABA according to the published procedures,<sup>20,21</sup> and the subsequent  $\text{SiW}_{12}/\text{CoTMPyP}$  multilayer films were constructed as follows: The 4-ABA-derivatized GC electrode was placed in 1 mM  $\text{CoTMPyP}$  + 0.1 M acetate buffer (pH 3.8), and then cyclic potential scanning was started between  $-0.4$  and  $0.4$  V at a scan rate of 100 mV/s for 100 cycles. After rinsing with water, the modified electrode with the  $\text{CoTMPyP}$  layer was transferred to a 2 mM  $\text{SiW}_{12}$  + 0.1 M  $\text{H}_2\text{SO}_4$  solution, and cyclic potential scanning was conducted between  $-0.3$  and  $0.3$  V. In this way, a  $\text{SiW}_{12}$  layer was deposited on the surface of the  $\text{CoTMPyP}/4\text{-ABA}/\text{GC}$  electrode, and the charge state of the electrode surface was reversed to be negative again. The  $\text{CoTMPyP}$  multilayers could be formed when the electrode was placed alternately in  $\text{CoTMPyP}$  and  $\text{SiW}_{12}$  solutions in a cyclic fashion. The multilayer films with different thicknesses were readily obtained by choosing different cycles of the layer-by-layer modification method.  $\text{P}_2\text{W}_{18}/\text{CoTMPyP}$  multilayer films were also fabricated through the same procedure.

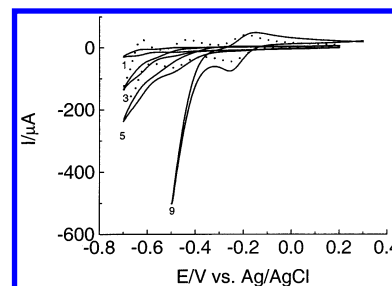
### 3. Results and Discussion

#### 3.1. UV/Visible Absorption Spectroscopy for Layer Growth.

The porphyrin has characteristic absorption in the UV/vis region, and UV/vis spectroscopy was employed to follow the deposition process of the multilayer films. The films were prepared by the alternate deposition of positively charged  $\text{CoTMPyP}$  and negatively charged  $\text{SiW}_{12}$  on the ITO electrode by the LBL method. Assuming that the absorption intensity is proportional to the concentration of metalloporphyrin molecules, the buildup of a multilayer film can be estimated from UV/vis absorption spectroscopy. Figure 1 shows the UV/vis absorption spectra of the  $\text{SiW}_{12}/\text{CoTMPyP}$  films with different layer numbers as  $\text{CoTMPyP}$  existed in the outermost layer. It is clear that the multilayer absorption of the  $\text{SiW}_{12}/\text{CoTMPyP}$  assemblies is reproducible with sequential deposition. The absorbance at 445 nm, which corresponds to the porphyrin Soret band, is observed to increase linearly with the number of bilayers up to five bilayers, as shown in the inset of Figure 1. But a departure from



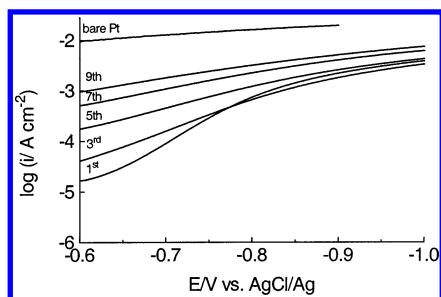
**Figure 1.** UV/vis absorption spectra of  $\text{SiW}_{12}/\text{CoTMPyP}$  multilayer films ( $\text{CoTMPyP}$  as the outermost layer) with different numbers of layers: from bottom to top, 1–9 layers. The inset shows the absorbance at 445 nm vs the number of layers.



**Figure 2.** Cyclic voltammograms of  $\text{SiW}_{12}/\text{CoTMPyP}$  ( $\text{SiW}_{12}$  as the outermost layer) multilayer films deposited on a 4-ABA/GC electrode with different numbers of layers. From top to bottom: 1, 3, 5, and 9 layers. The dotted line is a cyclic voltammogram pattern at a glassy carbon electrode with 2 mM  $\text{SiW}_{12}$  in a 0.1 M  $\text{H}_2\text{SO}_4$  solution. Electrolyte: a 0.1 M  $\text{N}_2$ -saturated 0.1 M  $\text{H}_2\text{SO}_4$  solution. Scan rate: 100 mV/s.

linearity is observed after five bilayers, which indicates that as the assembly grows over five bilayers there is more and more  $\text{CoTMPyP}$  in each layer than in the preceding layer. When this graph is made up of five to nine bilayers, the line is also very good. This is very different from the  $\text{CoTMPyP}/\text{P}_2\text{W}_{18}$  multilayer system, in which as the assembly grows over six bilayers and there is less  $\text{CoTMPyP}$  in each layer than in the preceding layer.<sup>25</sup> This difference may be due to the different structures of  $\text{SiW}_{12}$  (Keggin) and  $\text{P}_2\text{W}_{18}$  (Dawson).<sup>26</sup> These results confirm that  $\text{SiW}_{12}/\text{CoTMPyP}$  multilayer films have been constructed uniformly and homogeneously. The linear increase in the intensity of the absorption bands as a function of the number of successive coatings is consistent with a well-behaved LBL assembly process as described previously.<sup>27</sup> The Soret absorption peaks of metalloporphyrin in the multilayer films show a red shift of ca. 10 nm as compared to that in solution, which results from the formation of aggregates of chromophores within the layers. In addition, when the outermost layer is  $\text{SiW}_{12}$  at the same layer number, the absorption peaks of metalloporphyrin show little change. This is also different from that of the multilayer film of  $\text{P}_2\text{W}_{18}/\text{CoTMPyP}$ .<sup>25</sup>

**3.2. Cyclic Voltammetry of  $\text{CoTMPyP}$  and  $\text{SiW}_{12}$  Multilayers on a 4-ABA-Modified GC Electrode.** LBL assembly based on the electrostatic attraction between polycations and polyanions was used to build up multilayer films. Following the attachment of 4-ABA to the GC electrode, the derivatized 4-ABA/GC electrode surface with  $\text{COOH}$  groups was alternately placed in  $\text{CoTMPyP}$  and  $\text{SiW}_{12}$  solutions, and then potentials were scanned in a suitable potential range. After each modification, CV was used to characterize the increase in the quantity of modifiers loaded on the multilayer films. Figure 2 shows



**Figure 3.** Tafel plots for the HER in a 0.1 M H<sub>2</sub>SO<sub>4</sub> solution with N<sub>2</sub> saturation. The electrode is glassy carbon modified with 1, 3, 5, 7, and 9 SiW<sub>12</sub>/CoTMPyP layers (SiW<sub>12</sub> as the outmost layer) and a bare Pt electrode. The rotation rate is 3500 rpm.

the cyclic voltammograms of the as-prepared multilayer films (SiW<sub>12</sub> as the outermost layer) with different numbers of SiW<sub>12</sub> layers (curves from top to bottom corresponding to  $n = 1, 3, 5$ , and 9, respectively) in a 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. In this potential region, we could not observe all three redox couples, which correspond to two one-electron processes and one two-electron process, respectively<sup>28</sup> because of hydrogen evolution.<sup>29</sup> With the number of SiW<sub>12</sub> layers increasing, HER starts at progressively more positive potentials. This suggests that SiW<sub>12</sub> is deposited onto the multilayer coating in an LBL fashion. The growth of the thin film could be “seen” by the steady deepening of the surface color.

The dotted line in Figure 2 represents the cyclic voltammetric curve of 2 mM SiW<sub>12</sub> at a freshly polished glassy carbon electrode in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution, and three well-defined redox couples appear. In comparison to the CV of nine SiW<sub>12</sub>/9 CoTMPyP multilayer films to the dotted line, only one voltammetric pattern appears, along with abundant hydrogen evolution. Obviously, this also indicates that SiW<sub>12</sub>, which was assembled on a GC electrode, has remarkable catalytic activity for HER. In addition, the current for HER increases drastically with the number of layers increasing from five to nine because as the assembly grows over five bilayers there is more and more CoTMPyP in each layer than in preceding layer. Consequently, this leads to SiW<sub>12</sub> increasing more than in the former five layers, so the capability of catalytic activity toward the HER of modified electrodes is enhanced.

**3.3. Kinetic Analysis of HER on the SiW<sub>12</sub>/CoTMPyP Multilayer Film-Modified Electrodes.** It is known that a freshly polished GC electrode, whether SiW<sub>12</sub> is present in the solution, does not change the potential at which HER is observed.<sup>30</sup> But when SiW<sub>12</sub> is assembled on the glassy carbon electrode, it has remarkable catalytic activity for HER. Figure 3 shows Tafel plots for the HER on SiW<sub>12</sub>/CoTMPyP multilayer films with different numbers of layers. The multilayer films exhibit the expected shifts in overpotential with an increasing number of layers. The data of Figure 3 may be considered more quantitatively by examining several kinetic parameters. Table 1 summarizes the main results pertaining to different numbers of SiW<sub>12</sub>/CoTMPyP multilayers on modified electrodes. The Tafel slopes refer to the plots of  $\ln i$  vs overpotential ( $\eta$ ) for HER in 0.1 M H<sub>2</sub>SO<sub>4</sub>, and the exchange current density was determined by extrapolating to zero potential. These calculations were made by using the equation

$$\eta = \frac{RT}{\alpha n F} \ln i_0 - \frac{RT}{\alpha n F} \ln i$$

which is valid in the high-overpotential<sup>31</sup> approximation regime. From Table 1, we can see that except for “experimental” fluctuations the results seem to be perfectly smooth and show

**TABLE 1: Tafel Parameters for the HER on Glassy Carbon Electrodes Modified with Different Numbers of Layers of SiW<sub>12</sub>/CoTMPyP<sup>a</sup> and Bare Pt Electrode<sup>b</sup>**

SiW <sub>12</sub> layer number	$-\log(i_0/\text{A cm}^{-2})$	slope $V$	$\alpha$
1	9.81	0.102	0.583
3	7.23	0.161	0.365
5	6.91	0.171	0.346
7	5.07	0.185	0.319
9	4.08	0.237	0.250
bare Pt electrode	3.30	0.422	0.141

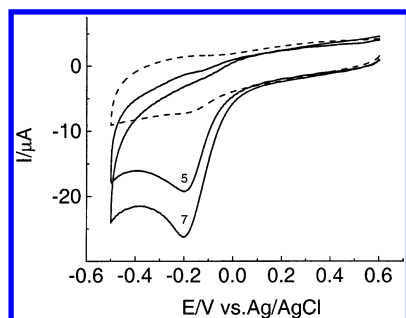
<sup>a</sup> SiW<sub>12</sub> is the outmost layer. <sup>b</sup> The test solution contains 0.1 M H<sub>2</sub>SO<sub>4</sub>.

expected trends. With the number of SiW<sub>12</sub> layers increasing, the exchange current density increases. This means that the catalytic activity of SiW<sub>12</sub> is enhanced. Only the  $\alpha$  value is much smaller than 0.5 except for in the first layer. Here,  $\alpha$  is the cathodic transfer coefficient as defined for multistep  $n$ -electron-transfer processes, with possible chemical steps included. It is well known that at the same  $\eta$  the exchange current density is much larger and the  $\alpha$  value is much smaller.<sup>32</sup> The results of the experiments also conform to this. All of the experiments were done at the rotating disk electrode with a high rotating rate, eliminating the effect of mass transfer on the current. So the process in which multilayer films containing SiW<sub>12</sub> catalyze HER is a kinetically controlled process.<sup>33</sup>

Similarly, the P<sub>2</sub>W<sub>18</sub>/CoTMPyP multilayer films can also grow uniformly by the LBL method on 4-ABA/GCE, and its catalytic activity for the reduction of O<sub>2</sub> has been studied in detail previously.<sup>25</sup> But its catalytic activity for HER is very different from that of SiW<sub>12</sub>/CoTMPyP films. HER occurs only at about  $-0.6$  V, and with the number of layers of multilayer films increasing, the overpotential for HER shows almost no change. This can be further confirmed by the polarization curves (see Supporting Information). However, the SiW<sub>12</sub>/CoTMPyP multilayer film electrode can catalyze the HER at different potentials (two positions as shown in Figure 2) with the SiW<sub>12</sub> quantity increasing. This may result from the different structures of SiW<sub>12</sub> (Keggin) and P<sub>2</sub>W<sub>18</sub> (Dawson).<sup>26</sup>

Furthermore, after assembly with 9SiW<sub>12</sub>/9CoTMPyP (SiW<sub>12</sub> as the outermost layer), the electrode retains its catalytic properties without any particular care. For instance, such an electrode modified with 9SiW<sub>12</sub>/9CoTMPyP (SiW<sub>12</sub> as the outermost layer) multilayer films, kept in the atmosphere of the laboratory or in water for more than 3 months and then tested in a 0.1 M H<sub>2</sub>SO<sub>4</sub> solution, shows the same activity regarding the hydrogen evolution reaction. The modified glassy carbon electrode that we selected for duration tests has been working continuously under an imposed current density of 1 A cm<sup>-2</sup> in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution for more than 100 h without any sign of decay. Under these galvanostatic conditions, the measured electrode potential is always in the range of  $-0.400$  to  $-0.500$  V versus Ag/AgCl. No potential drift toward more negative values is observed. Through the use of a number of purposely nonpurified solutions of HCl, H<sub>2</sub>SO<sub>4</sub>, and HClO<sub>4</sub>, it has been ascertained that the catalyst is insensitive to impurities that are usually deleterious to platinum and palladium catalysts.<sup>3</sup> In addition, the experiment concerning HER on a bare Pt electrode was also studied as shown in Figure 3, and the specific values for Pt were also added to Table 1. The values for platinum are in good agreement with the literature.<sup>32</sup> Although at the same current density, the overpotential of the modified electrode is lower than that of platinum. These properties make such catalysts very good candidates for use in extremely diverse conditions.



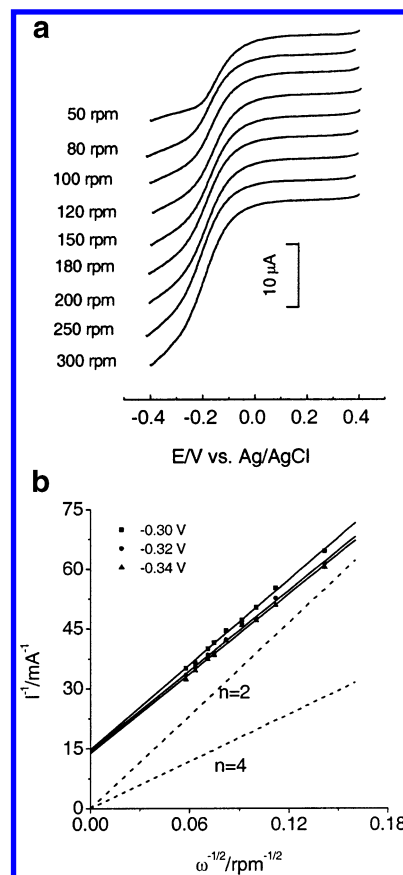


**Figure 4.** Cyclic voltammograms of  $O_2$  reduction at the 4-ABA/GC electrode assembled with  $SiW_{12}/CoTMPyP$  (CoTMPyP as the outermost layer) with different numbers of layers (air-saturated). The dotted line corresponds to the voltammogram on the  $5SiW_{12}/5CoTMPyP/4-ABA/GC$  electrode in  $N_2$ -saturated solution. Electrolyte: pH 3.77 acetate buffer. Scan rate: 100 mV/s.

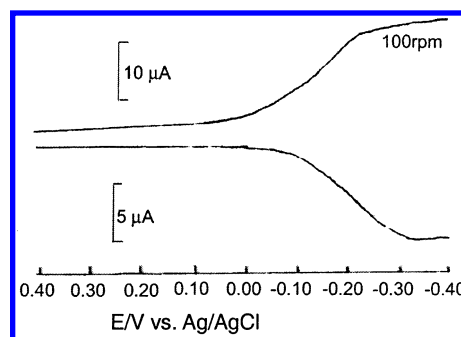
**3.4. Electrocatalytic Reduction of  $O_2$  on  $SiW_{12}/CoTMPyP$  Multilayer Films.** It is well known that metalloporphyrins can reduce dioxygen to  $H_2O$  or  $H_2O_2$ . Cyclic voltammograms of the multilayer films of  $CoTMPyP/SiW_{12}$  assembled on a GC electrode in 0.1 M  $H_2SO_4-Na_2SO_4$  solution with and without dioxygen are shown in Figure 4. The dotted line corresponds to the  $5SiW_{12}/5CoTMPyP$  (CoTMPyP as the outermost layer) multilayer film electrode. A very small redox peak at about  $-0.18$  V corresponds to a Co-centered redox reaction.<sup>34</sup> In the presence of dioxygen, a marked catalytic reduction current appears at the  $SiW_{12}/CoTMPyP$  multilayer film (CoTMPyP as the outermost layer), and the peak current of  $O_2$  reduction is increased with the increase in the number of layers. This also indicates that the catalyst is deposited in the multilayer films in an LBL fashion. The peak potential of  $O_2$  reduction at the GC electrode assembled with the multilayer films of  $SiW_{12}/CoTMPyP$  is located at  $-0.18$  V, which shifts positively by 500 mV when compared to that at the bare GC electrode ( $-0.65$  V).<sup>25</sup> This result indicates that the multilayer film of  $SiW_{12}/CoTMPyP$  with CoTMPyP as the outermost layer possesses catalytic activity for the reduction of dioxygen.

To establish the stoichiometry of the catalytic reduction of dioxygen, the multilayer film electrodes were further investigated by RDE and RRDE experiments. Depicted in Figure 5a are current–potential curves of dioxygen reduction at the rotating GC disk electrode modified with  $9SiW_{12}/9CoTMPyP$  multilayer films (CoTMPyP as the outermost layer) for each electrode rotation rate. Note that relatively constant, potential-independent plateau currents are present in Figure 5a at lower rotation rates. However, at the higher rotation rates, the current exhibits a potential dependence over an extensive range of potentials.<sup>35</sup> The corresponding Koutecky–Levich plot is shown in Figure 5b, from which the number of electrons transferred for the  $O_2$  reduction can be determined.<sup>36</sup> From the slope of the Koutecky–Levich plot, the  $n$  value was evaluated to be 2.3 for the  $9SiW_{12}/9CoTMPyP$  multilayer electrode. The slope was quite similar to that of the dashed line calculated for the two-electron reduction of  $O_2$  by a diffusion-controlled process. When CoTMPyP simply adsorbs on a GC electrode, it can catalyze the reduction of oxygen by two electrons, but the simple film is not very stable.<sup>37</sup>

A rotating glassy carbon disk–platinum ring electrode was employed to determine the quantity of  $H_2O_2$  that results from the reduction of  $O_2$  at an electrode assembled with  $SiW_{12}/CoTMPyP$  multilayer films. The glassy carbon disk was assembled with the catalyst, and the platinum ring was maintained at 1.0 V to oxidize the  $H_2O_2$  generated by the reduction of  $O_2$  at the disk. The result is shown in Figure 6.



**Figure 5.** (a) Current–potential curves of  $O_2$  reduction at an RDE assembled with  $9SiW_{12}/9CoTMPyP$  (CoTMPyP as the outermost layer) multilayer films with different rotation rates in an air-saturated 0.1 M  $Na_2SO_4-H_2SO_4$  solution (pH 3.0). Scan rate: 20 mV/s. (b) Koutecky–Levich plot for the plateau currents of the step in a. The solid line is from the experimental data, and the dashed lines are from the calculated data considering the reduction of  $O_2$  by two and four electrons, respectively.



**Figure 6.** Rotating ring–disk electrode voltammograms of a  $9SiW_{12}/9CoTMPyP$  film (CoTMPyP as the outermost layer) modified glassy carbon electrode (disk scan rate 20 mV/s,  $\omega = 100$  rpm) in an air-saturated 0.1 M  $Na_2SO_4-H_2SO_4$  solution (pH 3.0). The potential of the platinum ring electrode was set to 1.0 V to oxidize  $H_2O_2$  completely to  $O_2$ .

When the glassy carbon disk was assembled with  $9SiW_{12}/9CoTMPyP$  (CoTMPyP as the outermost layer), the reduction of  $O_2$  proceeded essentially without  $H_2O_2$ , and the observed ratio of ring to disk currents was 0.1275 compared with a collection efficiency of 0.1385 measured with the  $[Fe(CN)_6]^{3-/2-}$  redox couple. From the ratio of the ring–disk current, the electron-transfer number ( $n$ ) of 2.2 is calculated according to the equation  $n = 4 - \{2(I_R/I_D)N\}$ .<sup>38</sup> The value is almost identical to that acquired from the Koutecky–Levich curve (vide supra). This result indicates that the reduction product of dioxygen at

the disk electrode coated with a 9SiW<sub>12</sub>/9CoTMPyP multilayer film contains a high concentration of H<sub>2</sub>O<sub>2</sub>, so the SiW<sub>12</sub>/CoTMPyP multilayer film electrodes may be recommended as promising O<sub>2</sub> sensors. The Dowson-type heteropolyanion P<sub>2</sub>W<sub>18</sub> was also used as an oppositely charged ion to fabricate the P<sub>2</sub>W<sub>18</sub>/CoTMPyP multilayer films, and the P<sub>2</sub>W<sub>18</sub>/CoTMPyP multilayer film electrodes can realize the four-electron reduction of O<sub>2</sub> in higher pH buffer solutions. The electron transfer number and kinetic rate constants for the catalytic reduction of dioxygen in different pH solutions in both systems were comparatively studied by RDE experiments. The results from the Koutecky-Levich plots have been discussed in detail.<sup>25</sup>

#### 4. Conclusions

This article demonstrates the successful preparation of hybrid multilayer films consisting of CoTMPyP and SiW<sub>12</sub> deposited LBL by electrostatic interaction on a 4-ABA-derivatized GC electrode surface. The resulting homogeneous, ordered metalloporphyrin hybrid film improves the stability and reproducibility of the SiW<sub>12</sub>-modified electrodes reported previously.<sup>39</sup> In addition, the electrostatically assembled films are easy to build up and allow for fine thickness control. The SiW<sub>12</sub>-containing multilayer films exhibit remarkable electrocatalytic activity for the HER at much more positive potentials in acid media. P<sub>2</sub>W<sub>18</sub>/CoTMPyP multilayer films were also assembled, and their catalytic activity for HER is very different from that of SiW<sub>12</sub>/CoTMPyP multilayer films. The method we used is very simple and allows for easy preparation. Our findings suggest that the LBL method is superior when it is used to modulate compositionally the hybrid films of metalloporphyrins and polyoxometalates with arbitrary thickness and rationally tailored catalytic properties. The assembled films of SiW<sub>12</sub>/CoTMPyP hybrid films are promising as an electrode material for HER in acid media. In addition, the multilayer films can also be used as promising dissolved-oxygen sensors.

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**Supporting Information Available:** Cyclic voltammograms and polarization curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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