



## A Novel Sensor Based on Polyoxometalates Modified Electrode

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(Received: 10 November 2011;

Accepted: 10 September 2012)

AJC-12129

A novel  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /poly(ferrocenylsilane) (PFS)/phthalocyanatocobalt(II) (Co(II)TAPc) modified gold (Au) electrode was fabricated by stepwise self-assembly of Co(II)TAPc, PFS and Keggin-type  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$  on gold electrode. The properties and electrochemical behaviours of the modified electrode had been investigated by atomic force microscopy and electrochemical methods. Atomic force microscopy results showed that the Au electrode surface had been successfully covered by the three materials which formed three-dimensional (3D) porous film. The electrochemical results showed that the 3D porous film modified gold electrode combined the properties of  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ , PFS and Co(II)TAPc and exhibited good electrocatalytic ability to a series of chemicals, including  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}$ ,  $\text{SO}_3^{2-}$ , uric acid and ascorbic acid. The resulted  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode could be used in a large range of pH (0-8) and exhibited extremely fast amperometric response, low detection limit, high selectivity and wide linear range to these analyses.

**Key Words:** Electrochemistry, Phthalocyanatocobalt, Polyoxometalates, Sensor.

### INTRODUCTION

Polyoxometalates (POMs) are well-defined, discrete transition metal oxide clusters and possess diverse properties that have attracted much attention in materials, biology and catalysis<sup>1-4</sup>. Transition metal substituted polyoxometalates, owing to the transition metals encapsulated in the molecule, the structure of the whole compound changed with the transition metal and they exhibited some special properties<sup>5</sup>, have been extensively employed to modify electrode<sup>6</sup>. The electrode modified with the polyoxometalates has exhibited good electrocatalytic properties towards a series of chemicals<sup>7-11</sup> such as  $\text{NO}_2^-$ ,  $\text{BrO}_3^-$  and  $\text{IO}_3^-$ .

Attaching redox-active polyoxometalates onto electrodes can simplify their electrochemical studies and facilitate their applications in many fields. Some materials have been exploited to attach polyoxometalates on a electrode surface, such as conductive polymer<sup>12</sup>, cysteine<sup>13</sup>, cystamine<sup>14</sup>, poly(ferrocenylsilane) (PFS)<sup>15</sup> etc. The polyoxometalates immobilized on electrode surface by using these materials exhibited unique property and good electrocatalytic properties toward some chemicals. For example, the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  assembled on cysteamine modified gold electrode by poly(ferrocenylsilane) showed good electrocatalytic activity towards several chemicals<sup>15</sup>. The  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$  immobilized on a cystamine modified gold electrode surface by electrodeposition showed good electrocatalytic ability toward<sup>14</sup>  $\text{NO}_2^-$ .

Transition metal nickel substituted polyoxometalates, Keggin-type  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ , has been used to modify electrode due to its intrinsic structure. The electrode modified with  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$  displays two reduction peaks and one oxidation peak and can be existed in a large pH range<sup>14</sup>. The poly(ferrocenylsilane) is an electroactive polyelectrolyte with positive charge, containing organometallic units in the backbone, belongs to the class of stimulus-responsive materials<sup>16</sup>. The electrochemical studies show that the poly(ferrocenylsilane) modified electrode exhibits two pairs of redox peaks<sup>17,18</sup>. The first oxidation wave is attributed to oxidation of ferrocene centers at alternating positions along the chain and the second wave results from the oxidation of the remaining ferrocene centers. After the ferrocene centers are oxidized, the poly(ferrocenylsilane) films can be partially swollen and counterions can diffuse into the films to facilitate the electron transfer in the next step. Therefore, the ferrocene groups in poly(ferrocenylsilane) can enhance the chain mobility, the electron transfer and the active species diffusion. The poly(ferrocenylsilane) has been used to immobilize polyoxometalate on electrode surface and the resulted electrode shows a good electrocatalytic ability toward several chemicals<sup>15</sup>. Phthalocyanatocobalt(II) (Co(II)TAPc) can self-assemble on gold surface and form well-ordered monolayer<sup>19</sup>. The Co(II)TAPc monolayer shows two pairs of reversible redox peaks and has good catalytic activity towards the reduction of  $\text{O}_2$ .

In this work, a novel  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}/\text{PFS}/\text{Co}(\text{II})\text{TAPc}/\text{Au}$  electrode is fabricated by stepwise assembly of  $\text{Co}(\text{II})\text{TAPc}$ , PFS and  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$  on gold electrode. The modified gold electrode combined the properties of  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ , PFS and  $\text{Co}(\text{II})\text{TAPc}$ . Compared to these previous reported electrode modified with polyoxometalates<sup>20-24</sup>, the resulted electrode made here showed good electrocatalytic ability towards a series of chemicals and could be used in the neutral condition. The electrochemical and electrocatalytic properties of the modified electrode were also investigated.

### EXPERIMENTAL

$\text{H}_6[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]$  was prepared according to the published procedure<sup>25</sup>. Phthalocyanatocobalt(II) ( $\text{Co}(\text{II})\text{TAPc}$ ) was synthesized on the basis of the reported procedure<sup>26</sup>. Poly(ferrocenylsilane) (PFS) was purchased from Sigma-Aldrich (St. Louis, USA). Other chemicals were purchased from Beijing Chemical Reagent Factory (Beijing, China). All reagents and solvents were of analytical grade and used without further purification. Phosphate buffer solutions (PBS, pH 7.0) were prepared from  $0.2 \text{ mol L}^{-1} \text{ NaH}_2\text{PO}_4$  and  $0.2 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_4$ . The aqueous solutions were prepared with thrice-distilled water and the solutions were deoxygenated by saturated  $\text{N}_2$  before experiments.

**Preparation of  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}/\text{PFS}/\text{Co}(\text{II})\text{TAPc}/\text{Au}$  electrode:** Gold electrode was polished with 1.0, 0.3 and  $0.05 \mu\text{m} \text{ Al}_2\text{O}_3$  powders before experiments and then ultrasonicated with copious amount of thrice-distilled water and absolute ethanol for 2 min. This pretreated electrode was immersed in a  $100 \mu\text{mol L}^{-1}$  benzene solution of  $\text{Co}(\text{II})\text{TAPc}$  for 4 h, followed by rinsing with thrice-distilled water in an ultrasonic bath for 1 min to remove the unbound  $\text{Co}(\text{II})\text{TAPc}$  from the Au electrode. Then the  $\text{Co}(\text{II})\text{TAPc}$  modified Au electrode was dipped into  $0.5 \text{ mol L}^{-1} \text{ NaCl}$  solution containing  $1.0 \text{ mmol L}^{-1} \text{ PFS}$  for 1 h. Subsequently, the  $\text{PFS}/\text{Co}(\text{II})\text{TAPc}/\text{Au}$  electrode was immersed in PBS (pH 7.0) containing  $2.0 \text{ mmol L}^{-1} [\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$  for 4 h. Through the above mentioned process, the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}/\text{PFS}/\text{Co}(\text{II})\text{TAPc}/\text{Au}$  electrode was obtained.

Electrochemical experiments were performed with a CHI660C electrochemical workstation (USA) in a conventional three-electrode (the three electrode purchased from CHI (USA)) electrochemical cell, using  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}/\text{PFS}/\text{Co}(\text{II})\text{TAPc}/\text{Au}$  electrode as working electrode, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. Magnetic stirrer (IKA RH basic 1) was used to stir the solution. Atomic force microscopy (AFM) measurements were carried out with an AJ-III (Shanghai Aijian Nanotechnology) in tapping mode. Standard silicon cantilevers (spring constant,  $0.6\text{-}6 \text{ N/m}$ ) were used under its resonance frequency (typically,  $60\text{-}150 \text{ kHz}$ ) at room temperature under ambient condition.

### RESULTS AND DISCUSSION

**Atomic force microscopic images:** The surface morphology of the bare Au electrode and the Au electrode modified with  $\text{Co}(\text{II})\text{TAPc}$ ,  $\text{PFS}/\text{Co}(\text{II})\text{TAPc}$  and  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}/\text{PFS}/\text{Co}(\text{II})\text{TAPc}$  were shown in Fig. 1. There were some Au

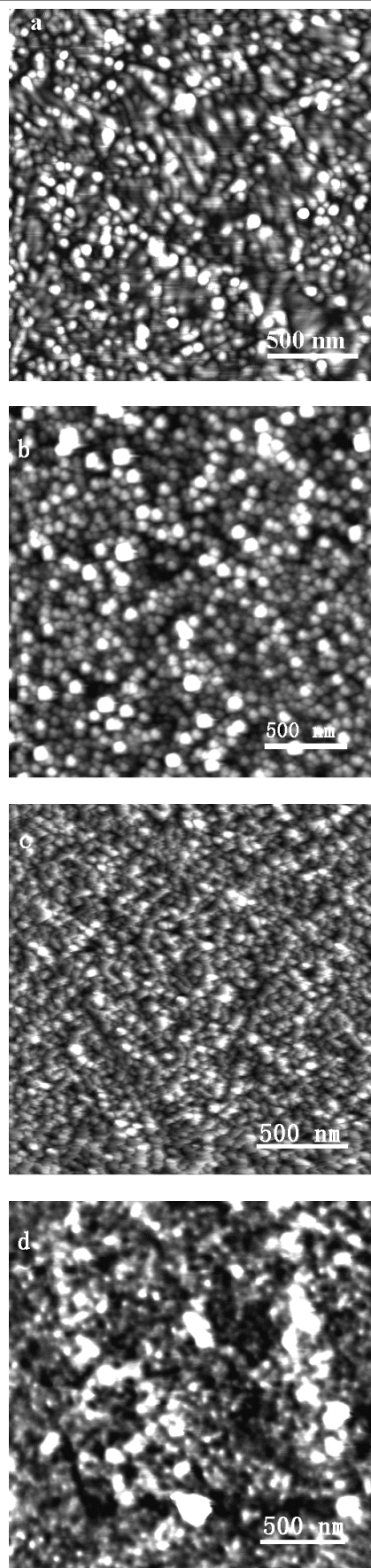


Fig. 1. Atomic force microscopic images of differently modified Au substrates: bare Au substrate (a),  $\text{Co}(\text{II})\text{TAPc}/\text{Au}$  substrate (b),  $\text{PFS}/\text{Co}(\text{II})\text{TAPc}/\text{Au}$  substrate (c) and  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}/\text{PFS}/\text{Co}(\text{II})\text{TAPc}/\text{Au}$  substrate (d). The z ranges were 20 nm

nanoparticles on the bare gold substrate as shown in Fig. 1a. The root mean square (RMS) roughness of the surface was *ca.* 1.32 nm. After the Co(II)TAPc adsorbed onto the gold substrate, many nanoparticles appeared and some nanoparticles became large (Fig. 1b) as compared with bare gold substrate (Fig. 1a). Some nanoparticles were ascribed to the aggregates of Co(II)TAPc and the other came from the Au nanoparticles with Co(II)TAPc. The RMS roughness of the surface was about 2.22 nm, which was larger than the RMS of bare gold film. When the PFS adsorbed to the Co(II)TAPc/Au surface, the surface became smoother (Fig. 1c) and the RMS decreased to 2.15 nm, suggesting that the PFS assembled on the Co(II)TAPc/Au surface. After the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$  adsorbed on the PFS/Co(II)TAPc/Au substrate, a three-dimensional (3D) porous film was formed (Fig. 1d) and many convex dots also appeared on the surface of  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au substrate. Its RMS increased to 2.82 nm. The large surface roughness might result from the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$  particles and clearly indicated that the formation of  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode.

**Electrochemical properties of  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode:** The electrochemical properties of the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode were investigated in  $\text{N}_2$ -saturated PBS (pH 7.0) in the potential range of -0.85~0.7 V. The typical cyclic voltammograms (CVs) were shown by curve a in Fig. 2. Three double redox peaks were exhibited, which were agreement with previous research<sup>14</sup>. The three anodic peaks (I, II and III) occurred at 325, -227 and -694 mV and the corresponding cathodic peaks (I', II' and III') appeared at 295, -236 and -724 mV, respectively. The peak potential separations were 30 (I-I'), 9 (II-II') and 30 mV (III-III'), respectively. The second redox peaks were very small and even if disappeared. It is noticeable that after the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode was repetitively scanned for 100 cycles in  $\text{N}_2$ -saturated PBS (pH 7.0) in the range of -0.85V~0.7 V at 50  $\text{mV s}^{-1}$ , the peak current only decreased by 5.2 % and the peak potential was almost unchanged (curve b in Fig. 2). These results suggested the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode was very stable in the neutral condition.

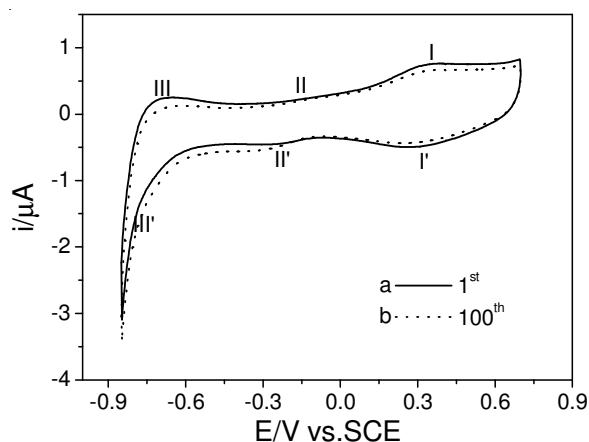


Fig. 2. Cyclic voltammograms of  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode in 0.2 mol  $\text{L}^{-1}$  PBS (pH 7.0) with first (a) and 100th scan (b). Scan rate: 50  $\text{mV s}^{-1}$

Fig. 3 showed the cyclic voltammograms of the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode scanned at different scan rates in the range of -0.85 V ~ 0.7 V in 0.2 mol  $\text{L}^{-1}$  PBS (pH 7.0). The peak currents of the three redox couples increased linearly with the scan rates increasing (the inset). And the peak-to-peak separation was almost unchanged, indicating that electron transfer reaction involved with a surface confined process. The electron transfer rate  $k_s$  is estimated to be 2.52  $\text{s}^{-1}$  according to  $k_s = \alpha n F v / RT$ <sup>27</sup>, where  $\alpha$  is the cathodic electron transfer coefficient,  $n$  is the electron transfer number,  $R$  is the gas constant ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature in Kelvin ( $T = 298 \text{ K}$ ) and  $F$  is the Faraday constant.

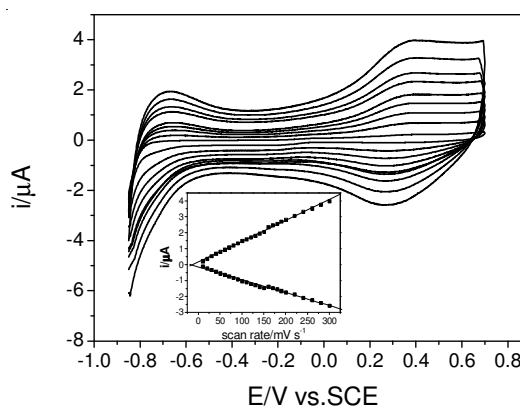


Fig. 3. Cyclic voltammograms of the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode in 0.2 mol  $\text{L}^{-1}$  PBS (pH 7.0) at different scan rates (from inner to outer: 10, 40, 70, 100, 130, 160, 190, 240, 300  $\text{mV s}^{-1}$ ). Inset: the plot of the first redox peak current versus the scan rates

In general, the reduction of  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$  was accompanied by protonation and the construction of the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode was also based on the electrostatic interaction. Thus, the pH of the solution might possibly play a crucial role in the electrochemical behaviours and stability of the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode. As shown in Fig. 4, the peak currents decreased rapidly with the increase of pH in the range of 0.0-2.0 (*ca.* 25 %) and subsequently was maintained, suggesting the  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode was stable in neutral solution and could be used in a large range of pH (0-8.0).

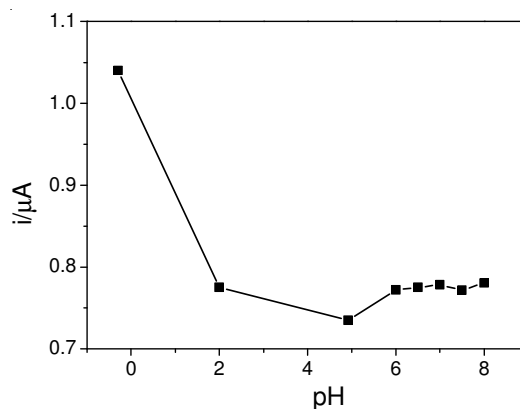


Fig. 4. Plots of peak current for  $[\text{SiNi}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{6-}$ /PFS/Co(II)TAPc/Au electrode versus pH of electrolyte solution (PBS)

**Electrocatalytic activity of [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode:** The [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode showed a good electrocatalytic activity toward the oxidation of ascorbic acid. As shown in Fig. 5b, an obviously catalytic current appeared in 0.2 mol L<sup>-1</sup> PBS (pH 7.0) in the presence of 1.3 mM ascorbic acid as compared with Co(II)TAPc/Au electrode, PFS/Au electrode, PFS/Co(II)TAPc/Au electrode, [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/Au electrode (data not shown) and the [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode in the absence of ascorbic acid (Fig. 5a). With the ascorbic acid concentration increasing, the anodic peak (I) current increased apparently while corresponding cathodic current decreased markedly. Other peak currents changed slightly, which suggested that ascorbic acid was mainly catalyzed by the first redox process. The plots of steady-state current *versus* substrate concentration showed that the catalytic current was linear to the ascorbic acid concentration in the range of 1.0-160 μmol L<sup>-1</sup> ( $r = 0.9990$ ,  $n = 8$ ) and 3.25-12.57 mmol L<sup>-1</sup> ( $r = 0.9998$ ,  $n = 20$ ) (inset b). The reduction current increased rapidly to achieve 95 % of the steady-state current within 2 s. The important parameters were summarized in Table-1.

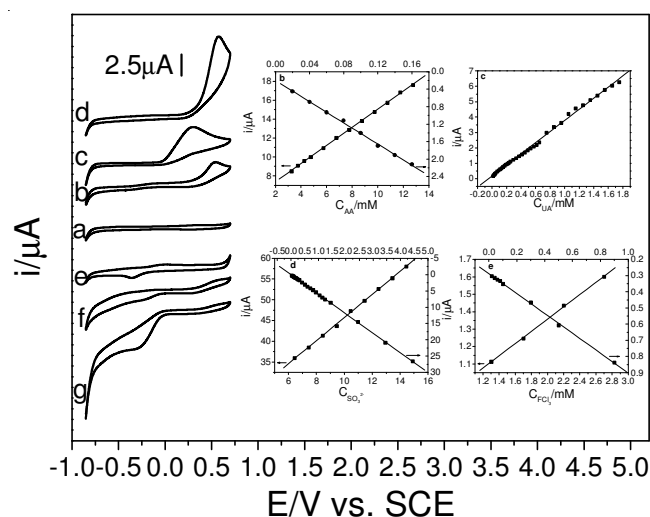


Fig. 5. CVs of the [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode in 0.2 mol L<sup>-1</sup> PBS (pH 7.0) in the absence (a) and presence of 1.3 mmol L<sup>-1</sup> ascorbic acid (b), 0.5 mmol L<sup>-1</sup> uric acid (c), 2.0 mmol L<sup>-1</sup> NaSO<sub>3</sub> (d), 4.0 mmol L<sup>-1</sup> FeCl<sub>3</sub> (e), 1.0 mmol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (f) and saturated O<sub>2</sub> (g). Inset: the plots of steady-state current *versus* substrate concentration. Scan rate: 50 mV s<sup>-1</sup>

TABLE-1  
PARAMETERS OF CHRONOAMPEROMETRIC  
RESPONSE TO DIFFERENT SPECIES FOR  
[SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/GOLD ELECTRODE  
(RECORDED IN 0.2 mol L<sup>-1</sup> PBS, pH = 7.0)

Species	Linear range (mmol L <sup>-1</sup> )	Detection limit (μmol L <sup>-1</sup> )	Correlation coefficient	n
AA	0.001-0.16	0.30	0.9990	8
	3.25-12.57		0.9998	20
UA	0.001-1.75	0.20	0.9985	20
	5.44-14.44		0.9996	9
SO <sub>3</sub> <sup>2-</sup>	0.002-4.44	0.24	0.9999	23
	5.44-14.44		0.9996	9
Fe <sup>3+</sup>	0.002-0.9	0.45	0.9996	8
	1.30-2.71		0.9996	4

AA = Ascorbic acid, UA = Uric acid

The [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode also had good catalytic ability toward the oxidation of uric acid (Fig. 5c). The [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/Au electrode, PFS/Au electrode and Co(II)TAPc/Au electrode showed poor catalytic effects toward the electrocatalytic oxidation of uric acid (data not shown). While, the [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode showed a better catalytic ability as compared with above modified electrodes. With the increase of uric acid concentration in the electrolyte solution, the anodic peak current (I) increased obviously and other peak was almost unchanged. This result indicated that the first redox processes catalyzed the oxidation of uric acid. The catalytic current was linear to the uric acid concentration in the range of 1.0 μmol L<sup>-1</sup>-1.75 mmol L<sup>-1</sup> ( $r = 0.9985$ ,  $n = 20$ ) (inset c) and the detection limit was 0.2 μmol L<sup>-1</sup> (Table-1).

In addition, the [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode also showed good catalytic ability toward SO<sub>3</sub><sup>2-</sup>, Fe<sup>3+</sup>, H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> as shown in Fig. 5d-g. The electrocatalytic oxidation of SO<sub>3</sub><sup>2-</sup> was shown in Fig. 5d. A dramatic increase of anodic peak currents appeared at potential around 0.5 V after 2.0 mmol L<sup>-1</sup> SO<sub>3</sub><sup>2-</sup> was added into the 0.2 mol L<sup>-1</sup> PBS (pH 7.0). Meanwhile, the related cathodic peak current was not observed. The amplitude of the SO<sub>3</sub><sup>2-</sup> oxidation current was proportional to the concentration of SO<sub>3</sub><sup>2-</sup> in the range of 2 μmol L<sup>-1</sup>-4.44 mmol L<sup>-1</sup> ( $r = 0.9999$ ,  $n = 23$ ) and 5.44-14.44 mmol L<sup>-1</sup> ( $r = 0.9996$ ,  $n = 9$ ) (inset d). The detection limit was 0.24 μmol L<sup>-1</sup> (Table-1). According to previous studies<sup>15</sup>, the possible reason was that poly(ferrocenylsilane) has an effect on the oxidation of SO<sub>3</sub><sup>2-</sup>. Fig. 5e showed the electrocatalytic reduction of Fe<sup>3+</sup>. The second redox process was a key factor on the reduction of Fe<sup>3+</sup> here. It is worth to note a new redox pair at potential of 0.4-0.5 V appeared after the oxidation by Fe<sup>3+</sup>. It may be interpreted that the hybrid film has somewhat redox responsive permeability. When Fe<sup>3+</sup> ions were added to electrolyte solution, they can be diffused to the inner layer. The hybrid film would be swollen along the ferrocene main chain and the redox peak of poly(ferrocenylsilane) appeared. This behaviour has potential application on the molecular release. The catalytic current was linear to the Fe<sup>3+</sup> concentration in the range of 2 μmol L<sup>-1</sup>-0.9 mmol L<sup>-1</sup> ( $r = 0.9996$ ,  $n = 8$ ) (inset e) and the detection limit was 0.24 μmol L<sup>-1</sup> (Table-1). The electrocatalytic reduction of H<sub>2</sub>O<sub>2</sub> was related to the third redox pair. Fig. 5f showed the CVs of reduction of H<sub>2</sub>O<sub>2</sub>. Upon addition of H<sub>2</sub>O<sub>2</sub> into the 0.2 mol L<sup>-1</sup> PBS (pH 7.0), the catalytic current increased obviously. The phenomena indicated that the third redox pair played an important role toward the reduction of H<sub>2</sub>O<sub>2</sub>. The [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode has the ability to the reduction of O<sub>2</sub> gas. Fig. 5g showed the cyclic voltammograms in 0.2 mol L<sup>-1</sup> PBS (pH 7.0) in the presence of O<sub>2</sub>. The second and the third redox couples increased greatly and other peak currents remained almost unchanged. This feature could be explained that the second redox couples played an important role in the process of reduction of O<sub>2</sub> gas. Thus, the electrocatalytic behaviour was ascribed to the Co(II)TAPc, for the capability to the reduction of O<sub>2</sub> gas.

**Interference study:** Since the modified electrode showed good electrocatalytic activity toward a series of chemicals including O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, Fe<sup>3+</sup>, SO<sub>3</sub><sup>2-</sup>, uric acid, ascorbic acid and it

TABLE-2  
EFFECTS OF INTERFERENCES ON THE CATALYTIC CURRENT OF [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au ELECTRODE TO FOLLOWING SPECIES (RECORDED IN 0.2 mol L<sup>-1</sup> PBS, pH 7.0, SCAN RATE 50 mV s<sup>-1</sup>)

Responding substrates concentration: 1.0 (mmol L <sup>-1</sup> )	Interferences substrates (mmol L <sup>-1</sup> )																	
	AA			UA			H <sub>2</sub> O <sub>2</sub>			Na <sub>2</sub> SO <sub>4</sub>			Fe <sup>3+</sup>			SO <sub>3</sub> <sup>2-</sup>		
	1	5	10	1	5	10	1	5	10	1	20	100	1	5	10	1	5	10
AA	-	-	-	o <sup>a</sup>	• <sup>b</sup>	-	o	o	•	o	o	•	o	•	-	•	-	-
UA	•	-	-	-	-	-	o	o	•	o	o	•	o	•	-	o	•	-
Fe <sup>3+</sup>	o	o	o	•	-	-	o	o	•	o	o	o	-	-	-	•	-	-
SO <sub>3</sub> <sup>2-</sup>	•	-	-	-	•	-	o	o	•	o	o	o	•	-	-	-	-	-

<sup>a</sup>No interference (variance of catalytic current ≤ 6 %); <sup>b</sup>interference (variance of catalytic current > 6 %); AA = ascorbic acid; UA = uric acid

might have potential applications as sensor to detect these analyses, the interference study is inevitable. Common chemicals such as K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in 20-fold concentration did not show interference to these analyses. While, one analyse in 1-fold concentration, others in 5-fold concentration displayed serious interference. The results were shown in Table-2, indicated the sensor has good selectivity.

**Reproducibility and stability of the [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode:** 0.5 mmol L<sup>-1</sup> ascorbic acid was determined repeatedly at the identical surface of [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode successive 10 times and the relative standard deviation (RSD) was 4.2 %. The precision at renewed surface of [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au was also investigated and the RSD of 7.8 % (n = 6). It indicated that the modeled electrode has a good reproducibility.

## Conclusion

The [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>/PFS/Co(II)TAPc/Au electrode has been successfully fabricated by stepwise assembly of Co(II)TAPc, PFS and Keggin-type [SiNi(H<sub>2</sub>O)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup> on Au electrode. The resulted electrode could be used in a large range of pH (0-8.0) and showed good electrocatalytic ability toward a series of chemicals. The modified electrode has good stability and selectivity. It might have potential application as sensor to detect these analyses in the field of electrocatalysis.

## ACKNOWLEDGEMENTS

This work was financially supported by National Natural Science Foundation of China (20905032, 21065005, 21174058), Natural Science Foundation of Jiangxi Province (2008GZH0028), Foundation of Jiangxi Educational Committee (GJJ10389), the State Key Laboratory of Electroanalytical Chemistry (2008003), Young Scientist of Jiangxi Province (20112BCB23006) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

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