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A novel hybrid based on carbon nanotubes and heteropolyanions as effective catalyst for hydrogen evolution

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Abstract

Heteropolyanions of tungstophosphoric acid (PWA) have been successfully hybridized with carbon nanotubes (CNTs) by a severe mechanical milling. The obtained hybrid is electroactive for hydrogen evolution (HE) at potentials as positive as -0.16 V vs. Ag/AgCl in 0.2 M $HClO_4$ aqueous solution and its electrocatalysis is up to the level of Pt/CNTs (20 wt% Pt) for HE, indicating a vigorous alternative to Pt group metals. The HE mechanism of the hybrid was also studied and it was found that the tungsten oxycarbides are the electroactive components for HE.
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1. Introduction

The interest in electrochemical hydrogen evolution (HE) catalysts is currently increasing due to that molecular hydrogen is being considered as an energy carrier [1]. Unlike hydrocarbon fuels used today, hydrogen produces only water during oxidation, for instance in fuel cells. For hydrogen to be a real alternative to hydrocarbons, it must be produced in large scaled fashions. One possibility is electrochemical evolution with electric current to split water, which requires an efficient electrocatalyst. This requires that the HE process preferably bases on materials that are cheap and abundant. Currently the HE processes are catalyzed most effectively with expensive noble metals (such as Pt) that are not only high in cost but also limited in resources [2]. Therefore it is urgent to find alternatives to the noble metals, such as Pt, for HE [3–5].

In recent years, carbon nanotubes (CNTs) and heteropolyanions (HPA) have attracted more and more attention from various chemical fields [6–27]. The particularities of

high surface area, hollow geometry, high electronic conductivity and special mechanical properties exhibit that CNTs can greatly promote electron transfer reactions [6–8]. HPA based on oxometallate compounds have been used for several years. For example, for some metallic electrodes [16–21] and semiconducting electrodes [22–27], the overvoltage of HE can be significantly and persistently reduced by a treatment with HPA.

In the present work an effective electrocatalyst for HE was prepared based on CNTs and PWA (Keggin-type, PW_{12}) by a severe mechanical milling. It was found that the tungsten carbides or tungsten oxycarbides are the electroactive components for HE.

2. Experimental

Carbon nanotubes (CNTs) were purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China). 12-Tungstophosphic acids (PWA, Keggin-type: PW_{12}), sulfuric acid, perchloric acid ($HClO_4$) and ammonium tungstate ((NH_4)$_2WO_4$) were from Beijing Xinhua Chemical Co., China. The CNTs/PWA hybrid was prepared based on the following process: firstly the commercial CNTs were

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refluxed in 2.6 M nitric acid for 16 h and then the mixture was washed with deionized water several times to remove residual acid and then the pretreated CNTs were obtained, secondly both pretreated CNTs (100 mg) and different PWA (50 mg, 100 mg, 150 mg, 200 mg and 300 mg, respectively) were weighed into a stainless steel capsule containing a milling ball (Specks Co., 3500 cycles per min). Then the capsule was vigorously shaken for 4 h at room temperature. The reaction mixture was then washed with water and ethanol to get neutral state, finally dried under vacuum at 60 °C overnight to obtain the CNTs/PWA hybrid. The CNTs/PWA mixture was prepared by dipping the GC/CNTs electrode into saturated PWA aqueous solution for 30 min to adsorb intact PWA molecules and then rinsed with pure water for three times before testing. Pt/CNTs (20 wt% Pt) catalyst was prepared as the following: the acid-treated CNTs were sonicated in a bit of concentrated sodium dodecylbenzene sulfonate solution for 10 h, then the H_2PtCl_6 solution (3.08 mg Pt/mL) was added with stirring for 24 h and strong alkali NaOH was added to adjust the pH value to 9. Two hours later the reducing reagent of $NaBH_4$ water solution (0.2 g/mL) was dropped to reduce the metallic precursors in 3 h. Then the mixture was filtrated and washed with ethanol and water repeatedly to remove impurities. The XC-72 carbon black (CB)/PWA and XC-72 CB/tungstic acid hybrids were prepared with the same mechanical milling procedure as shown above. The heat-treated CNTs/$(NH_4)_2WO_4$ hybrid was prepared as following: 100 mg CNTs and 200 mg $(NH_4)_2WO_4$ were weighed into a beaker containing 100 mL water. After being sonicated for 30 min the obtained mixture was dried under air. Then the dried mixture was calcined under Ar atmosphere at 500 °C for 5 h.

XPS analyzes were recorded by a Phi Quantum 2000 XPS system (Physical Electronics Inc.). The samples were characterized by FT-IR spectroscopy (Bio-Rad FTS) with KBr pellets. An EG&G model 273 potentiostat/galvanostat and a conventional three-electrode test cell were used for electrochemical measurements. The working electrode was a thin layer of Nafion impregnated catalyst cast on a glassy carbon disk electrode (∅5 mm, Tokai carbon from Japan) held in a Teflon cylinder. The solid loading in catalyst layer was 0.15 mg/cm^2. The electrode was then dried at 60 °C for 1 h. A Pt foil electrode and an Ag/AgCl (KCl saturated) were used as the counter and reference electrodes, respectively. All electrolyte solutions were deaerated by high purity argon for 15 min prior to any measurement.

3. Results and discussion

The electrocatalytic properties of CNTs/PWA hybrids for HE were studied as shown in Fig. 1. Compared with glassy carbon (GC) electrode (Fig. 1A(a)), the HE current for GC/CNTs electrode commenced slowly at the onset potential of −0.4 V as shown in Fig. 1A(b). This indicates CNTs as electrode material could promote electron transfer in reaction, [6–8] but the electrocatalysis for HE is very
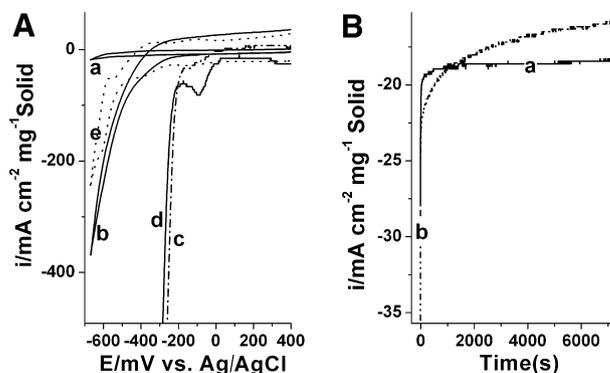

Fig. 1. (A) Cyclic voltammograms for GC electrode (a), GC/CNTs (b) and GC/CNTs/PWA (intact structure, e), linear sweep voltammograms for CNTs/PWA hybrid (c) and Pt/CNTs (d), electrolyte: 0.2 M HClO$_4$ aqueous solution. Scan rate: 100 mV/s. (B) Current–time plot when poised at −0.3 V vs. Ag/AgCl in 0.2 M HClO$_4$ aqueous solution of CNTs/PWA hybrid (a) and Pt/CNTs (b).

weak. While after typically hybridized with PWA (200 mg), an obvious HE current appeared at a more positive onset potential of −0.16 V as shown in Fig. 1A(c), which is even higher than that (−0.2 V) of Pt/CNTs (20 wt% Pt) catalyst (Fig. 1A(d)) for HE. The onset potential of −0.16 V is also higher than that of −0.4 V for HE reported by Dong et al. obtained from metalloporphyrin-heteropolyanion hybrid film [9] and slightly higher than that of −0.20 V for HE on α_2-$P_2W_{17}MoO_{62}K_6$-modified GC electrode [17]. The higher onset potential for HE probably could be attributed to the utilization of CNTs, which can greatly promote the electron transfer in HE process [6–8].

Further tests of HE rates under potentiostatic conditions were conducted at −0.3 V vs. Ag/AgCl to avoid complications from the adsorption effects [4] (Fig. 1B). Although the initial current on CNTs/PWA hybrid (Fig. 1B(a)) is lower than that on Pt/CNTs (Fig. 1B(b)), after the shorter decline time the steady current is slightly higher than that on Pt/CNTs. These results indicated that these CNTs/PWA hybrids could be a vigorous alternative to Pt group metals for HE. It was further found that the electroactivity for HE of these hybrids increased with the increase of the initial PWA/CNTs weight ratio and then when the weight of PWA is higher than 200 mg, the electroactivity is almost constant. The reason obviously is due to the saturation of PWA immobilized on CNTs at higher PWA/CNTs weight ratio. So in the following the CNTs/PWA hybrid with optimal composition (initial weight ratio of CNTs/PWA = 100 mg/200 mg) was used to perform the following all experiments.

Fig. 2 shows the IR spectra of pure PWA and CNTs/PWA hybrid. Three of the characteristic peaks (at 891 cm^{-1} (W–O$_b$–W), 982 cm^{-1} (W=O$_d$) and 1080 cm^{-1} (P–O$_a$)) in CNTs/PWA hybrid show a blue shift while the fourth characteristic peak near 798 cm^{-1} (W–O$_c$–W) shifts a little in red compared with intact PWA. A new peak also appears near 1028 cm^{-1} after hybridized with CNTs, which obviously should be attributed to the special interaction between CNTs and PWA. The relative contents of the
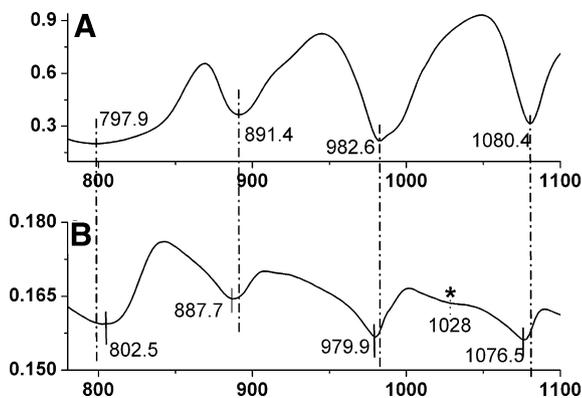
Fig. 2. IR spectra for pure PWA (A) and CNTs/PWA hybrid (B) after severe mechanical milling.

characteristic covalent bonds were also obtained approximately from peak areas. It was found that the contents of $W–O_b–W$, $W=O_d$ and $P–O_a$ decreased from 10.3%, 22.5% and 17.2% in the intact PWA to 10.2%, 14.1% and 6.7% after hybridized with CNTs, respectively, indicating the interruption of covalent bonds of $W–O_b–W$, $W=O_d$ and $P–O_a$ in the rigid structure. The energy dispersive X-ray spectra (EDX) shows the atomic ratio of W/P is 12 for intact Keggin PWA while the ratio of W/P for CNTs/PWA hybrid is about 9, further confirming some covalent bonds in the rigid $P–O_a–W$ primary structure of heteropolyanions had been interrupted.

The XPS spectra (Figs. 3A and C) of C 1s in pure CNTs and CNTs in CNTs/PWA hybrid showed great difference. The large peak located at 290 eV (Fig. 3C) indicated a great deal of C–W covalent bonds had been formed in the hybrid after the severe mechanical milling [28,29]. Figs. 3B and D show the XPS spectra of the W 4f region in pure PWA and CNTs/PWA samples. The spectra were fitted with two dif-

ferent doublets of W 4f with $4f_{7/2}$ located at 35.3 and 40.0 eV representing the tungsten oxides (+6) and superoxides (>+6), respectively [12,13]. As for the intact PWA almost all the valences of tungsten are equal to +6 (Fig. 3B) while after hybridized with CNTs by severe mechanical milling, the percentage of tungsten superoxides increased greatly. Combining the above IR spectra it could be deduced that some of the WO_6 octahedral units had been broken off from the central of PO_4 and some covalent bonds between P and O in the $W–O_a–P$ rigid structure had been interrupted and then produced some fragments of tungsten superoxides. Combining the XPS spectra of C 1s, it could be further deduced that the tungsten oxycarbides had been formed from the destruction of PWA. Figs. 4A and C show the XPS spectra of P_{2p} in intact PWA and CNTs/PWA hybrid, respectively. The slight enhanced signal of P_{2p} at 134.2 eV on hybrid indicates a slight enrichment of surface with phosphorus as a result of the interruption of $P–O_a$ in the rigid structure of PW_{12} [12]. Figs. 4C and D show the XPS spectra of O 1s in pure PWA and CNTs/PWA hybrid, respectively. The spectrum of intact PWA shows two strong peaks at 531.2 eV (labeled A, assigned to W–O–W) and 532.6 eV (labeled B, assigned to $W–O_a–P$) [12,13]. After hybridized with CNTs, peak B decreased greatly, further confirming the interruption of $P–O_a$. The new peaks of C and D should be attributed to oxo-groups on CNTs or water species on the sample surface [14,15]. Based on the above results, it could be concluded firmly that the intact structure of PW_{12} had been wrecked and the tungsten oxycarbides had been formed on carbon after the severe mechanical milling.

Just as that shown on the above, the conditions in the mechanical milling were so severe that the intact heteropolyoxotungstates were destroyed and transformed into completely different tungsten carbides or oxycarbides. As
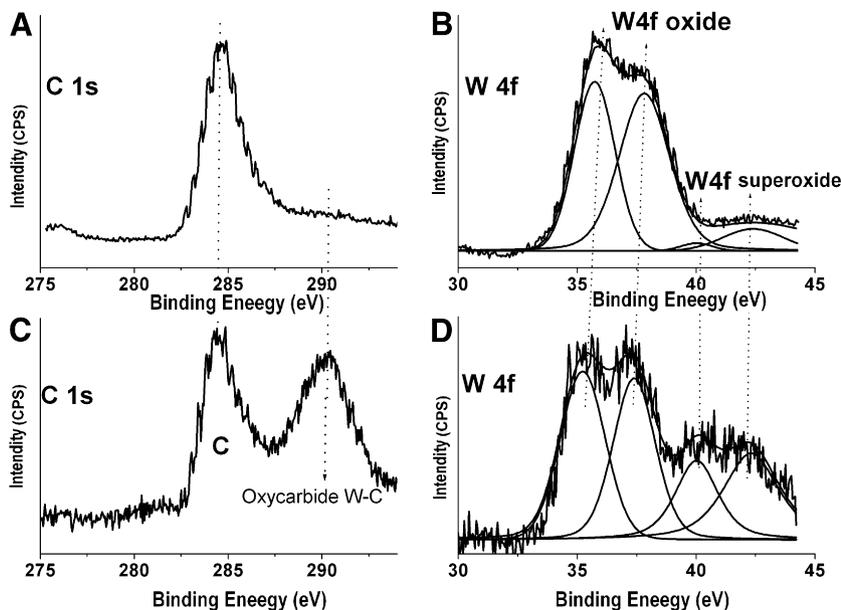

Fig. 3. XPS spectra for C 1s in pure CNTs (A) and CNTs/PWA hybrid (C) and W 4f in pure PWA (B) and CNTs/PWA hybrid (D).
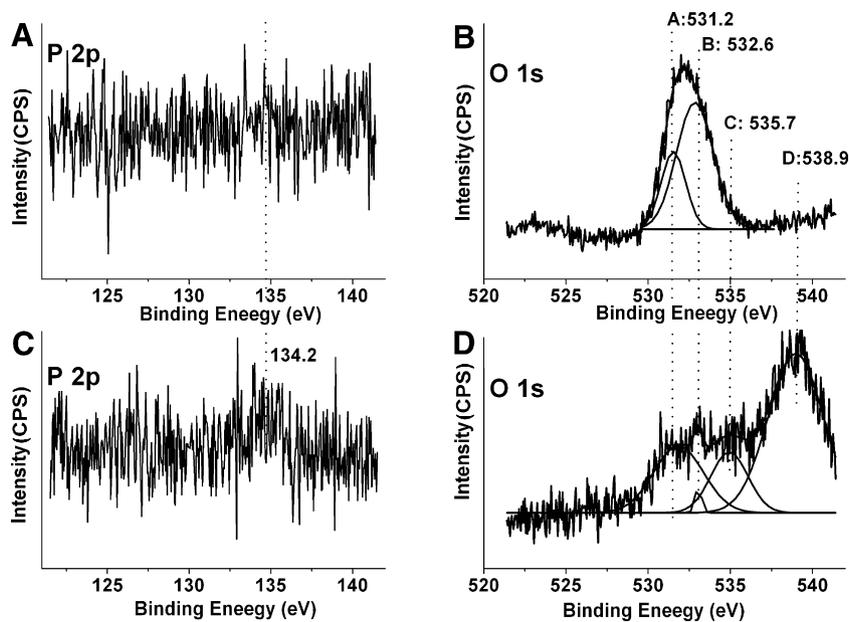
Fig. 4. XPS spectra for P 2p and O 1s in intact PWA (A,B) and CNTs/PWA hybrid (C,D).

shown in Fig. 1A(e), the intact PWA physically adsorbed on CNTs shows no catalysis for HE. This fact implies the tungsten carbides or oxycarbides rather than the intact units are the effective components for HE.

In order to further validate the above conclusion, a new hybrid was prepared by hybridization of CNTs with $(NH_4)_2WO_4$ solution followed by calcinations at 500 °C under Ar atmosphere for 5 h. As shown in Fig. 5A, the intact tungstate shows a very weak catalysis for HE on

CNTs (curve a), while after hybridized with CNTs at high temperature, a relatively large HE current appears (curve c). While the pure tungsten oxide (WO_3) simply supported by CNTs, as shown in curve b, only shows a very small HE current. The XPS spectra show the W–C covalent bonds were also formed in the heat-treated CNTs/$(NH_4)_2WO_4$ hybrid but do not appear in the simple mixtures of CNTs/PWA, CNTs/$(NH_4)_2WO_4$ or CNTs/tungsten oxide. Similar conclusions were also obtained on the other two
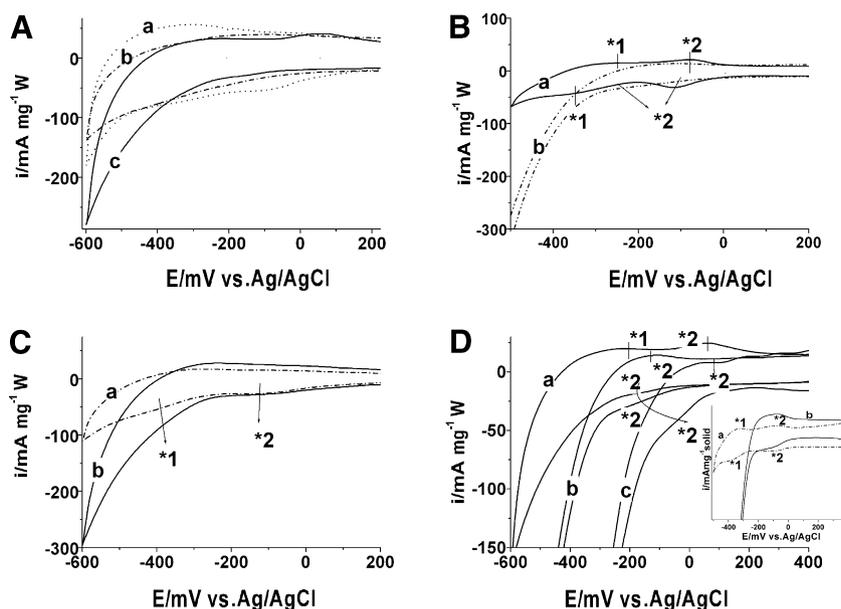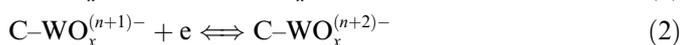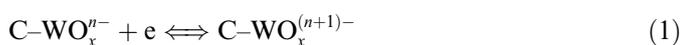

Fig. 5. (A) Cyclic voltammograms (CVs) of CNTs/$(NH_4)_2WO_4$ mixture (curve a), CNTs/heat-treated $(NH_4)_2WO_4$ mixture (curve b) and the heat-treated CNTs/$(NH_4)_2WO_4$ hybrid (curve c) in 0.2 M $HClO_4$ aqueous solution. (B) CVs of intact PWA supported by XC-72 CB (curve a) and the XC-72 CB/PWA hybrid after the severe mechanical milling (curve b) in 0.2 M $HClO_4$ aqueous solution. (C) CVs of (curve a) the mixture of XC-72 CB/tungstic acid and the hybrid of XC-72 CB/tungstic acid obtained after a severe mechanical milling. (D) CVs of the heat-treated CNTs/$(NH_4)_2WO_4$ hybrid (curve a), XC-72 CB/ PWA hybrid (curve b) and CNTs/PWA hybrid (curve c) after the severe mechanical milling in 0.2 M $HClO_4$ aqueous solution. The inset is the CV comparison between intact PWA (curve a) and CNTs/PWA hybrid (curve b) in 0.2 M $HClO_4$ aqueous solution. Scan rate: 100 mV/s.

kinds hybrids of XC-72 CB/PWA and XC-72 CB/tungstic acid prepared with the same severe mechanical milling (Figs. 5B and C). All these facts further validate the tungsten oxycarbides are the electroactive components for HE. In fact Etcheberry et al. [27] had reported that tungsten oxide rather than the intact Keggin structure ($SiW_{12}O_{40}^{4-}$) was the effective component for HE.

Fig. 5D shows the comparison among the heat-treated CNTs/$(NH_4)_2WO_4$ (curve a), XC-72 CB/PWA (after severe mechanical milling, curve b) and CNTs/PWA (after severe mechanical milling, curve c) hybrids. The inset shows a comparison between intact PWA and the CNT/PWA hybrid. Compared with the intact PWA a similarity among these hybrids could be found: the large HE currents covered all the *1 peaks. Based on this fact, the HE mechanism for the above hybrids could be described as following with the immobilized tungsten oxycarbides denoted as C–WO_x^{n-} ($3 \leqslant x < 6$) [9,16–27,11]:

$$C\text{–}WO_x^{n-} + e \Longleftrightarrow C\text{–}WO_x^{(n+1)-} \qquad (1)$$

$$C\text{–}WO_x^{(n+1)-} + e \Longleftrightarrow C\text{–}WO_x^{(n+2)-} \qquad (2)$$

$$2H^+ + 2C\text{–}WO_x^{(n+2)-} \rightarrow C\text{–}WO_x^{(n+1)-} + H_2 \qquad (3)$$

On the other hand as shown in Fig. 5D, with the same W loadings the CNTs/PWA hybrid (curve c) shows the highest catalysis for HE and the heat-treated CNTs/$(NH_4)_2WO_4$ hybrid (curve a) only shows a relatively weak catalysis for HE. This difference probably could be attributed to the different effective amounts of tungsten oxycarbides immobilized on carbon. Their C 1s XPS spectra show there is a higher C–W content in the CNTs/PWA hybrid.

4. Conclusions

In summary the CNTs/PWA hybrid was prepared as a vigorous electrocatalysts for HE, which is much cheaper and more abundant than noble metal catalysts. Its activity and stability are all up to the level of Pt/CNTs (20 wt% Pt) catalysts. Spectra and electrochemical results show that the tungstate oxycarbides formed on carbon materials by W–C covalent bonds are the main electroactive components for HE.

Acknowledgements

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