Facile synthesis of SnO$_2$-Pt/carbon nanotubes nanocatalyst with high electrocatalytic performance for methanol oxidation

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A green, low-cost and facile strategy for synthesis of SnO$_2$-Pt/carbon nanotubes nanocomposites with SnO$_2$-around-Pt structure by in situ spontaneous reduction of PtCl$_6^{2-}$ with Sn$^{2+}$ on the CNT surface is reported. The morphology and structure of the prepared SnO$_2$-Pt/CNTs nanocatalyst are characterized by scanning electron microscopy, transmission electron microscopy and X-ray diffraction. In addition, energy dispersive X-ray spectroscopy and inductively coupled plasma-atom emission spectroscopy results prove the presence of Pt and SnO$_2$ nanoparticles on CNTs surface with the molar ratio of Pt:SnO$_2$ in SnO$_2$-Pt/CNTs as 0.48. In comparison with the commercial Pt/C, SnO$_2$-Pt/CNTs nanocatalyst exhibits higher electrocatalytic mass activity and better long-term cycle stability for methanol oxidation.

Keywords: Carbon nanotubes, Nanocatalysts, Electrooxidation, Methanol, Tin dioxide, Platinum

Since the first report about carbon nanotubes (CNTs) presented by Iijima in 1991, CNTs have been extensively studied over the past decades because of their potential applications in many fields$^{1-5}$. Due to their high surface area, good electronic conductivity and excellent chemical and electrochemical stability, CNTs are widely used as the support material for noble metal nanoparticles(NPs) to give metal NPs/CNTs, which have many potential applications in chemo/biosensors, heterogeneous catalysis and fuel cells.$^{2,5}$ Numerous studies have indicated that Pt/CNTs are one of the most active electrocatalysts for methanol oxidation.$^{4}$ However, the formation of CO-like intermediates poison the Pt catalyst leading to the gradual decrease of their electrocatalytic activity$^{4-7}$. The presence of transition metal oxide (such as tungsten trioxide$^{4}$, ceria$^{5}$, ruthenium dioxide$^{6}$, and tin dioxide$^{7}$) has been shown to improve the CO-tolerance of Pt. Among these, tin dioxide (SnO$_2$) which is cheap and easily available not only efficiently enhances the resistance of Pt to CO poisoning but also prevents Pt nanoparticles aggregation, leading to a high electrocatalytic performance of SnO$_2$-Pt/CNTs towards methanol electrooxidation.$^{7}$

Several strategies have been developed for preparation of Pt/SnO$_2$@CNTs.$^{7-10}$ In these typical approaches, generally SnO$_2$ nanoparticles were first deposited on the acid-pretreated CNTs to form SnO$_2$@CNTs, and then Pt nanoparticles were deposited on the SnO$_2$@CNTs surface.$^{7,10}$ However, some of the Pt nanoparticles deposited on the SnO$_2$ surface were not used in the electrocatalytic oxidation of methanol due to the semiconductivity of SnO$_2$, leading to low utilization of Pt nanoparticles in the electrocatalysis. On the other hand, acid-oxidation pretreatment of CNTs inevitably causes some structural damage of CNTs and results in the loss of their electronic conductivity and corrosion resistance. Moreover, the excessive reductants or solvents normally used in the preparation of Pt/SnO$_2$@CNTs, such as EG and PVP, are usually discarded as waste solution$^{7,10}$. The preparation process is complicated, not environmental friendly and uneconomical. Therefore, it is worthwhile to develop a simple, environment friendly and cost effective method to synthesize SnO$_2$-Pt/CNTs electrocatalyst with high electrocatalytic performance.

Herein, we report a facile approach for the synthesis of SnO$_2$-around-Pt nanocatalyst on CNT surface by in situ spontaneous reduction of PtCl$_6^{2-}$ with Sn$^{2+}$, as illustrated in Fig. 1. The CNTs were first functionalized with 1-aminopyrene (1-AP) via $\pi-\pi$ stacking to obtain positively charged 1-AP-CNTs in acidic condition.$^{11}$ PtCl$_6^{2-}$ was then
self-assembled on the CNT surface by electrostatic force, followed by Sn^{2+} ions uniformly adhering to the CNT surface by electrostatic action between PtCl_6^{2-} and Sn^{2+}. Due to the galvanic cell effect between PtCl_6^{2-} and Sn^{2+}, the redox reaction between PtCl_6^{2-} and Sn^{2+} will spontaneously occur in situ on the CNT surface with the SnO_2-around-Pt nanocatalyst directly deposited on the CNT surface. The possible reaction mechanism may be described as follows:

\[
PtCl_6^{2-} + 2Sn^{2+} + 4H_2O \rightarrow Pt + 2SnO_2 + 8H^+ + 6Cl^- \quad (1)
\]

Compared with Pt/SnO_2@CNTs obtained by the earlier reported method\textsuperscript{7-10}, the entire synthesis process of SnO_2-Pt/CNTs nanocatalyst is effective and simple. The SnO_2-Pt/CNTs prepared by the present method has high utilization of Pt nanoparticles due to the direct contact between Pt nanoparticles and CNTs, and good CO-tolerance ability due to the Pt nanoparticles surrounded by SnO_2 which acts as the second catalyst similar to Ru in an earlier report\textsuperscript{11}, resulting in high electrocatalytic performance for methanol oxidation.

Materials and Methods

Pristine multi-walled carbon nanotubes (CNTs) (length 1-2 µm, diameter 20-60 nm) were purchased from Shenzhen Nanotech Port Co. Ltd., China. 1-Aminopyrene (1-AP, 99%) was purchased from Alfa Aesar., USA. Other chemicals obtained from XiLong Corp, China, were of analytical grade and used as received.

Preparation of SnO_2-Pt/CNTs nanocatalyst

The entire procedure for synthesis of SnO_2-Pt/CNTs nanocatalyst is shown in Fig. 1. Non-covalent functionalization of CNTs (1-AP-CNTs) was firstly carried out according to the literature\textsuperscript{11}. The obtained 1-AP-CNTs (20 mg) was dispersed in 25 mL of doubly distilled water, and then mixed with 2.159 mL of H_2PtCl_6 (19.3 mM) under ultrasonic stirring. Next, 5 mL of HCl (38 wt.%) and 18.75 mg of SnCl_2·2H_2O were successively added to the mixture. After being agitated for 30 min, the pH of the solution was adjusted to 8 with 0.1 M NaOH. The entire experiment was carried out in nitrogen atmosphere. The obtained product (SnO_2-Pt/CNTs) was repeatedly centrifuged, washed with doubly distilled water and then vacuum-dried at 0.085 MPa and 70 °C for 24 h.

Characterization of SnO_2-Pt/CNTs nanocatalyst

The morphology and elemental composition of SnO_2-Pt/CNTs nanocatalyst were investigated by scanning electron microscopy (SEM, JSM-5600 LV) and transmission electron microscopy (TEM, JEM-3010) along with energy dispersive X-ray spectroscopy (EDS, OXFORD-INCA). The structural analysis of SnO_2-Pt/CNTs was obtained by X-ray diffraction (XRD, D/MAX-RA) with Cu-Kα radiation (λ = 0.15406 nm) at 50 kV and 100 mA in the 20 range of 15°- 85°. Furthermore, the amounts of Pt and Sn in SnO_2-Pt/CNTs nanocatalyst were determined by inductively coupled plasma-atom emission spectroscopy (ICP-AES, IRIS-1000).

Electrochemical properties of electrocatalysts

All electrochemical measurements were performed on a CHI660B electrochemical workstation (Shanghai Chenhua Instrument Factory, China) with a conventional three-electrode system. A saturated calomel electrode (SCE) and a Pt wire were used as the reference and counter electrode, respectively (Fig. 2). The glassy carbon (GC, 5 mm diameter) electrode was polished to mirror-like plane with 0.5 and 0.05 µm alumina slurries successively and washed ultrasonically in doubly distilled water prior to use. The catalyst ink was prepared by dispersing the catalyst (2 mg) in water (1 mL) by sonication. When a dark homogeneous dispersion was formed, 20 µL of the ink was dropped onto the GC electrode using a microsyringe. After air drying, the electrode was coated with 5 µL of 0.05 wt.% Nafion ethanol solution. The electrochemical surface area (ESA) and the electrochemical performance of the electrocatalyst were evaluated by cyclic voltammetry and chronoamperometry. For comparison, the commercial catalyst Pt/C (E-ETK 20 wt.% ) was also investigated. All experiments were carried out at ambient temperature. All the potentials here are with respect to SCE.
Results and Discussion
Characterization of SnO$_2$-Pt/CNTs nanocatalyst

The morphology and microstructure of SnO$_2$-Pt/CNTs nanocatalyst were investigated by FESEM and TEM, respectively. The FESEM image (Fig. 2a) shows that CNTs are homogeneously covered by SnO$_2$ and Pt nanoparticles layer with dense morphology, which will facilitate electron transport during the electrochemical reactions. Moreover, TEM image (Fig. 2b) also shows that Pt and SnO$_2$ nanoparticles are deposited on the entire surface of the CNTs. From the high-resolution TEM image (Fig. 2c), it is noted that Pt nanoparticles are deposited on the CNT surface and surrounded by SnO$_2$ nanoparticles, as expected from Fig. 1. The HRTEM image also indicates that the diameter of SnO$_2$ nanoparticles (or Pt nanoparticles) is ~ 5.4 nm (or 4.0 nm), and the interplanar spacing of the lattice of SnO$_2$ nanoparticles (or Pt nanoparticles) is 0.322 nm (or 0.225 nm), consistent with that of the (110) lattice spacing of SnO$_2$ (or the (111) plane of Pt).

The polycrystalline structure of nanoparticles was also confirmed by XRD of SnO$_2$-Pt/CNTs (Fig. 3a). The characteristic diffraction peaks and their intensities are consistent with the face-centered cubic platinum and tetragonal SnO$_2$ crystal structure (Pt: JCPDS PDF#04-0802; SnO$_2$: JCPDS PDF#41-1445). The results further indicate the presence of segregated Pt and SnO$_2$ phases on the CNT surface. The average crystallite sizes of Pt and SnO$_2$ NPs on SnO$_2$-Pt/CNTs nanocatalyst were estimated from the line broadening of the Pt (220) and SnO$_2$ (110) peaks using Debye-Scherrer's equation: $d = 0.9 \lambda / \beta \cos \theta$, where $d$ is the average diameter, $\lambda$ the wavelength of X-ray radiation (0.15406 nm), $\theta$ is the position of the diffraction peak, and $\beta$ is the full-width at half-maximum in radians. The calculated average crystallite sizes of Pt and SnO$_2$
NPs were found to be ~ 3.9 nm and 5.2 nm, respectively, which are consistent with the results from HRTEM image. EDS analysis of SnO$_2$-Pt/CNTs nanocatalyst further confirms that both Pt and SnO$_2$ NPs are successfully deposited on CNTs surface (Fig. 3b). ICP-AES measurement shows the molar ratio of Pt:SnO$_2$ to be 1:2.1, indicating that the reaction between PtCl$_6^{2-}$ and Sn$^{2+}$ is as shown in Eq. (1).

It is well known that the electrochemical active surface area (ESA) is one of the important parameters for electrocatalysts. Figure 4a shows the cyclic voltammograms of the SnO$_2$-Pt/CNTs and Pt/C (E-TEK) electrocatalysts in argon-saturated 0.5 $M$ H$_2$SO$_4$ solutions. The ESAs were calculated using the hydrogen adsorption-desorption peak area after correcting for the double layer charging current from the cyclic voltammograms from the following equation, $\text{ESA} = Q_{\text{H}}/(0.21 \times [\text{Pt}])$, where $Q_{\text{H}}$ (mC cm$^{-2}$) represents the mean value between the amounts of charge exchanged during the electroadsorption ($Q_1$) and desorption ($Q_2$) of H$_2$ on Pt sites, [Pt] is the Pt loading (mg cm$^{-2}$) on the electrode and 0.21 (mC cm$^{-2}$) represents the charge required to oxidize a monolayer of H$_2$ on bright Pt. The electrochemical surface area value of SnO$_2$-Pt/CNTs electrocatalyst was found to be 523.2 cm$^2$ mg$^{-1}$, higher than 287.3 cm$^2$ mg$^{-1}$ of Pt/C (E-TEK). This may be due to the interaction between Pt and SnO$_2$ nanoparticles and the excellent electrical conductivity of CNTs$^8$. The positive effect of SnO$_2$ nanoparticles on the ESA of Pt nanoparticles is attributed to the OH removal on Pt by SnO$_2$, as reported in the literature$^8$. i.e., the lateral repulsion towards the OH or other oxygen species on the SnO$_2$ surface prevents the generation of oxygen species on the adjacent Pt and makes it a clean metallic surface for electrocatalysis$^8$. It may be noted that SnO$_2$-Pt/CNTs has higher ESA value than Pt/SnO$_2$@CNTs (481.3 cm$^2$ mg$^{-1}$) as reported by Zhang et al.$^{10}$, suggesting that the direct contact between Pt nanoparticles and CNTs in SnO$_2$-Pt/CNTs is beneficial to the utilization of Pt. The results suggest that the SnO$_2$-Pt/CNTs electrocatalyst has good electrocatalytic properties for methanol oxidation.

The CV profiles for methanol electro-oxidation on the SnO$_2$-Pt/CNTs and Pt/C (E-TEK) modified electrode are shown in Fig. 4b. Compared with Pt/C, the significant enhancement of the peak currents and the obvious negative shift of the peak potential can be observed on SnO$_2$-Pt/CNTs. The forward peak current on SnO$_2$-Pt/CNTs is 327.6 mA mg$^{-1}$, being 2.25 and 1.11 times higher than that on Pt/C (145.9 mA mg$^{-1}$) and Pt/SnO$_2$@CNT (134 mA mg$^{-1}$) reported previously$^{10}$. On the other hand, the forward peak potential on SnO$_2$-Pt/CNTs shifts more than 70 mV in the negative direction as compared to that on Pt/C. These results show that the SnO$_2$-Pt/CNTs catalyst possesses good electrocatalytic mass activity for methanol oxidation.

The potential dependent steady state current obtained on SnO$_2$-Pt/CNTs and Pt/C (E-TEK) in the potential range of 0.4–0.8 V, recorded at 120 s from the $i$-$t$ curve results, (Fig. 5) indicates that the methanol oxidation on SnO$_2$-Pt/CNTs is much higher.
For practical applications, both the electrochemical activity and the long term stability of the catalysts are important. Hence, the electrochemical stability of the SnO$_2$-Pt/CNTs electrocatalyst was investigated by chronoamperometric (CA) technique and long term cyclic voltammery, respectively. The SnO$_2$-Pt/CNTs catalyst exhibits significantly better stability towards methanol electro-oxidation than Pt/C (E-TEK). The oxidation current of methanol on SnO$_2$-Pt/CNTs is easier than that on Pt/C (E-TEK). It further reveals that methanol oxidation on SnO$_2$-Pt/CNTs is easier than on the Pt/C (E-TEK). Furthermore, Fig. 5 also displays that the ratio of the current density on the SnO$_2$-Pt/CNTs catalyst versus that acquired on the Pt/C (E-TEK) catalyst varies between 1.45 and 4.07 in all applied potentials. As discussed in cyclic voltammetric experiments, larger the electrochemical surface area (ESA) value and better the CO-tolerance ability of the SnO$_2$-Pt/CNTs catalyst, higher is the electrocatalytic activity of the SnO$_2$-Pt/CNTs catalyst possesses for methanol oxidation.

For practical applications, both the electrochemical activity and the long term stability of the catalysts are important. Hence, the electrochemical stability of the SnO$_2$-Pt/CNTs electrocatalyst was investigated by chronoamperometric (CA) technique and long term cyclic voltammery, respectively. The SnO$_2$-Pt/CNTs catalyst exhibits significantly better stability towards methanol electro-oxidation than Pt/C (E-TEK). The oxidation current of methanol on SnO$_2$-Pt/CNTs is 26.73 mA mg$^{-1}$ and 6.64 times higher than that on Pt/C (4.03 mA mg$^{-1}$) after 1 h, implying that SnO$_2$-Pt/CNTs has excellent electrocatalytic stability towards methanol oxidation. Investigations on long term cycle stabilities of SnO$_2$-Pt/CNTs and Pt/C catalysts for methanol oxidation by CV show that for both SnO$_2$-Pt/CNTs and Pt/C catalysts, the value of $I_{pl}/I_{pr}$ decreases gradually with the successive scan. The forward peak current for SnO$_2$-Pt/CNTs at 1000 cycle was ~ 83% of that at the first cycle. However, ~ 42% loss after 1000 cycles was observed on the Pt/C catalyst. This further confirms that SnO$_2$-Pt/CNTs catalyst has better electrochemical stability than the Pt/C (E-TEK) catalyst, as observed in the CA results. The reasons may be interpreted by the well-known bifunctional mechanism similar to PtRu catalysts$^{11}$, i.e., the existence of SnO$_2$ around Pt nanoparticles can not only effectively prevent the aggregation of Pt NPs but can also conveniently produce oxygen-containing species (OH$_{ads}$) and improve the CO-tolerance of Pt nanoparticles during the electrocatalytic oxidation of methanol$^7$, resulting in a high electrocatalytic mass activity and long term stability of SnO$_2$-Pt/CNTs catalyst.

In the present study, SnO$_2$-Pt/CNTs nanocatalyst has been synthesized via in situ spontaneous reduction of PtCl$_6^{2-}$ with Sn$_2^{2+}$ on CNTs. The obtained SnO$_2$-Pt/CNTs electrocatalyst shows a higher electrocatalytic mass activity and long term stability towards methanol oxidation than the commercial Pt/C (E-TEK) and the Pt/SnO$_2$@CNTs catalysts reported previously.

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References