



Ultrasonic-assisted synthesis of Pd–Pt/carbon nanotubes nanocomposites for enhanced electro-oxidation of ethanol and methanol in alkaline medium



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ABSTRACT

Herein, a facile ultrasonic-assisted strategy was proposed to fabricate the Pd–Pt alloy/multi-walled carbon nanotubes (Pd–Pt/CNTs) nanocomposites. A good number of Pd–Pt alloy nanoparticles with an average of 3.4 ± 0.5 nm were supported on sidewalls of CNTs with uniform distribution. The composition of the Pd–Pt/CNTs nanocomposites could also be easily controlled, which provided a possible approach for the preparation of other architectures with anticipated properties. The Pd–Pt/CNTs nanocomposites were extensively studied by electron microscopy, induced coupled plasma atomic emission spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy, and applied for the ethanol and methanol electro-oxidation reaction in alkaline medium. The electrochemical results indicated that the nanocomposites had better electrocatalytic activities and stabilities, showing promising applications for fuel cells.

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1. Introduction

Owing to their high efficiencies and low pollutions, fuel cells are considered to be a kind of potential energy sources for vehicles and portable electronic devices [1–3]. Direct ethanol and methanol fuel cells have been extensively investigated due to their high power density, low operation temperatures, and ease of handling, etc. [4,5]. Pt is generally the most active electrocatalyst for fuel cells. However, practical applications of Pt are severely hindered because of high cost, and easy poisoning by intermediate products [6,7]. In hence, to enhance the electrocatalytic properties accordingly, binary electrocatalysts including Pt–Au and Pt–Ag, have been developed with the increase of d-band vacancy in Pt and more favorable Pt–Pt inter-atomic distance [8–12]. Among which, Pd not only is less expensive than Pt, but also has high catalytic activity. Enormous

efforts were directed for the preparation of Pd-based alloy nanoparticles (NPs) for fuel cell. It has been proven that Pd–Pt alloy NPs express excellent electrocatalytic performance with long-term stabilities [13–15]. However, it still remains challenges to overcome to promote their use in commercial applications.

On the other hand, it is of great significance to explore effective catalyst supports with high conductivity, large surface area and low cost, to maximize the electrocatalytic properties of catalysts. Moreover, the supporting materials can prevent NPs aggregate, and reduce the usage of noble metals to some content. Carbon nanotubes (CNTs) have received significant attentions due to their unique chemical and physical properties [16–18]. They have been widely investigated in the fields of electronics, biomedicines and sensors [19–22] for their fast electron transfer, large active surface area, and high stability. Specifically, large efforts have also been made to assemble various nanomaterials on the surface of CNTs. Nanocomposites consisting of CNTs and metal NPs continue to attract considerable interests because they could effectively improve the properties and functionalities on the molecular level, achieving a wider range of applications [23,24]. Although many works have been reported to construct the corresponding nanocomposites, showing promising electrocatalytic activities for fuel cells, the approaches reported previously have some

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limitations, such as time-consuming, capping ligands used, and/or high operating temperatures [25–27]. Therefore, it is highly desirable to open simple and economic methods for the synthesis of alloy NPs/CNTs nanocomposites with high quality and study their electrochemical performance.

Ultrasonic-assisted strategy is known as a unique synthesis method in materials chemistry. Ultrasonic irradiation provides unusual physical and chemical effects which derive from acoustic cavitation. Liquid treated with ultrasound can lead to the formation, growth, and collapse of a bubble, and localized hot spots will generate with extremely high pressures and temperatures, and rapid heating and cooling rates [28–31]. Moreover, the advantages of sonochemistry have also been actively applied in many other fields [32,33].

To the best of our knowledge, utilizing ultrasonic irradiation to directly deposit Pd–Pt alloy NPs on CNTs for the electro-oxidation of ethanol and methanol in alkaline medium have not been reported. In this work, we reported a simple one-step ultrasonic-assist route to fabricate well-dispersed Pd–Pt alloy NPs on sidewalls of CNTs. The composition of Pd and Pt in the nanocomposites could be tuned for catalytic reactions. Electrochemical experiments further demonstrated that the Pd–Pt/CNTs nanocomposites exhibited enhanced electrocatalytic activities and stabilities towards ethanol and methanol oxidation.

2. Experimental section

2.1. Materials

Carboxylic acid functionalized CNTs (C-CNTs, 10–30 nm in diameter, 95%) were purchased from Nanostructured & Amorphous Materials Inc, USA. Sodium tetrachloropalladate (Na_2PdCl_4) and potassium tetrachloroplatinate(II) (K_2PtCl_4) were obtained from Strem Chemicals Inc. Methanol (CH_3OH , 99.9%), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, absolute), nafion (Dupont, 5 wt%) and sodium borohydride (NaBH_4), were bought from Sigma–Aldrich. E-TEK Pd/C and E-TEK Pt/C (20%) catalysts were purchased from Alfa Aesar. Millipore water was used throughout the work. All the chemicals were used as received without further purification.

2.2. Fabrication of Pd–Pt/CNTs nanocomposites

Ethylenediamine was first used to functionalize C-CNTs [34]: N-[(dimethylamino)-1H-1,2,3-triazolo[4,5,6]-pyridine-1-ylmethyl]ene]-N-methylmethanamonium hexafluorophosphate N-oxide (HATU), was used for the amide formation on the surface of CNTs with catalytic amount. The solutions were centrifuged for 10 min, washed with water three times, and then dried under vacuum overnight (ethylenediamine functionalized CNTs). In a typical ultrasonic-assisted synthesis of the PdPt/CNTs (the mole ratio of Pd/Pt was 1/1), a Fisher Scientific made mechanical ultrasonic cleaner bath FS60H (USA) was employed for continuous sonication. Briefly, 20 mg of ethylenediamine modified CNTs in 20 mL of ethanol was first sonicated for 1 h to get the uniform CNTs dispersion in a 50 mL beaker. The mixture of 200 μL Na_2PdCl_4 (0.1 M) and 200 μL (0.1 M) K_2PtCl_4 was then added into the resulting CNTs dispersion. 20 mg of NaBH_4 was also added into the mixed CNTs-solution as the reducer. After that the above system was sonicated and reacted for another 20 min to form the nanocomposite. The black solution was centrifuged for 10 min at 5000 rpm, and the precipitate was purified and washed with water three times and then dried overnight. The whole procedure was simple. The other samples from the Na_2PdCl_4 and K_2PtCl_4 solution with Pd/Pt mole ratios of 0/1, 1/3, 3/1 and 1/0 were also prepared, referred as Pt/CNTs, PdPt₃/CNTs, Pd₃Pt/CNTs and Pd/CNTs, respectively.

2.3. Characterization

The morphology and structure of the obtained nanocomposites were recorded by JEM-1200EXII transmission electron microscope (TEM) with a field emission source and the accelerating voltage was 120 kV. High-resolution TEM (HRTEM) images were taken using a JEOL 2010 microscope at an accelerating voltage of 200 kV. The composition was investigated using energy dispersive X-ray spectrometer (EDS) technique. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, J-A1100) was also used to analyze the actual metal loading including the weight and atomic percentages of the samples. X-ray photoelectron spectrometric (XPS, ESCALAB MK II) experiments were performed with Al K α X-ray radiation for excitation. Fourier transform infrared spectroscopy (FT-IR) analyses were carried out on a Nicolet 6700 FT-IR spectrometer using KBr pressed disks. The X-ray diffraction (XRD) patterns of the samples were measured on a Shimadzu XD-3A X-ray diffractometer using Cu K α as the radiation source ($\lambda = 1.54056 \text{ \AA}$).

2.4. Electrochemical measurement

Electrochemical tests were performed using a standard three-electrode cell on a CHI model 660C electrochemical analyzer (CH Instruments, Inc., USA). A platinum wire was used as the counter electrode, a saturated calomel electrode (SCE) was the reference, and a glassy carbon electrode (GCE, diameter of 3.0 mm) worked as the working electrode for the electro-oxidation of ethanol and methanol. Before testing, the GCE was polished with Al_2O_3 powders (Aldrich, 0.05 μm), rinsed with water, and dried with a high-purify nitrogen steam. To prepare the catalyst-coated GCE, 5.0 mg of the catalyst was dispersed in 5.0 mL of a mixture of water, ethanol and Nafion with a ratio of 1/3.85/0.15, followed by sonication to form a homogenous ink. Finally the resultant suspension (10 μL , 1.0 mg mL^{-1}) was drop-casted onto the pretreated GCE, and the modified electrode was dried thoroughly in air prior to use. Electrochemical impedance spectroscopy (EIS) experiments were measured in a mixture of 0.10 M KNO_3 containing 2.0 mM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (1:1) by an Autolab electrochemical analyzer. The alternating current voltage amplitude was 5.0 mV with a frequency range of 0.01 Hz–100 kHz. The measurement was carried out with a direct current potential of 0.2 V (vs. SCE).

3. Results and discussions

3.1. Characterization of the Pd–Pt/CNTs

Fig. 1 summarizes the synthetic routes for the Pd–Pt/CNTs nanocomposites. Herein, we followed an ultrasonic-assisted, surfactant free approach for depositing alloy NPs on CNTs. The structure, morphology, and composition of the products were further systematically studied. According to the FT-IR results (shown in Fig. 2), C-CNTs showed characteristic absorption peaks of C=O, aromatic C=C and carboxy C–O groups (curve a). After the reaction with ethylenediamine (curve b), a new broad band at 1571 cm^{-1} was observed corresponding to the vibration of N–H group. The increase of the peak intensity at 1484 cm^{-1} was associated with a stretching of the new C–N bond. The results showed the successful chemical reduction and surface modification of CNTs.

Fig. 3 shows representative TEM and HRTEM images of the samples. As shown in Fig. 3A, the tubular appearance and layered structure of ethylenediamine functionalized CNTs was clearly observed (Fig. 3A), meaning good state of the wall structure of CNTs, which was helpful for electrochemical applications. After sonication, alloy NPs homogeneously dispersed on sidewalls of

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