Sensors and Actuators B 183 (2013) 34–39

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Preparation of platinum/carbon nanotube in aqueous solution by femtosecond laser for non-enzymatic glucose determination

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ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form 26 March 2013
Accepted 26 March 2013
Available online 3 April 2013

Keywords:
Multiwalled carbon nanotubes
Platinum nanoparticles
Femtosecond laser
Glucose

ABSTRACT

Multiwalled carbon nanotubes (MWCNTs) supported platinum (Pt) nanoparticles were fabricated in aqueous solution without reducing agents by femtosecond laser. The surface morphological, compositional, and structural characterizations of the prepared Pt/MWCNT were examined using scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. The results showed that the Pt nanoparticles with about 5–10 nm in diameter were well dispersed on the surface of MWCNTs. Cyclic voltammetry was employed to investigate the electrocatalytic activity toward the electrooxidation of glucose in alkaline solution at the Pt/MWCNT. The Pt/MWCNT modified glassy carbon electrode displayed high electrocatalytic ability for the direct electrochemical oxidation of glucose in alkaline solution. At an applied potential of −0.25 V vs. Ag/AgCl 3 M KCl, the Pt/MWCNT modified electrode exhibited a sensitivity of 0.106 A M^{-1} cm^{-2} with a linear range up to 2.4 mM. This proposed glucose sensor also showed good abilities of anti-interference to acetaminophen, uric acid, fructose, and ascorbic acid.

1. Introduction

The determination of glucose is very important in blood sugar monitoring, food industry, and bio-processing. For the construction of enzymatic electrochemical glucose biosensors mainly glucose oxidase is used [1]. Glucose oxidase catalyzes the oxidation of glucose to gluconolactone; however, a drawback of this approach is that the activity of enzyme can be easily affected by solution pH value, temperature, and humidity. Recently, the development in the field of non-enzymatic glucose sensors has opened a new range of possibility for the fabrication of forth generation biosensors. Much effort has been made in using Pt [2,3], Au [4,5], Ni [6,7], and Cu [8,9] electrodes in an attempt to directly oxidize glucose in the sample. In particular, the use of platinum (Pt) nanoparticles seems very useful for glucose oxidation. Metal nanoparticles have large surface-to-volume ratio, strong adsorption ability, high catalytic efficiency, and high surface reaction activity. Several methods such as solution-phase reduction [10], electrochemical deposition [11], and thermal reduction [12] have been developed to prepare Pt nanoparticles. Sensor technology has more general applications including those in respiratory medicine [13,14].

Recent studies suggested that carbon nanotubes (CNTs) can be regard as a supporting material for catalyst because of its high chemical stability, large surface area, unique electronic properties, and relatively high mechanical strength. The applications of CNTs as catalyst support have been explored, for instance, as biosensors [15,16] and as dye sensitized solar cells [17]. The shape and high surface area of CNTs introduce beneficial effects in terms of branched electrical conductivity coupled to increased electrode surface area. Much research has been developed to the fabrication of Pt/CNTs. The strategies of preparation of Pt/CNTs can be roughly classified as solution-phase reduction [18,19] and electrochemical deposition [20,21]. For the solution-phase reduction, reducing agents such as sodium borohydride and ethylene glycol were introduced into a solution containing Pt precursor.

Recently, femtosecond laser has attracted much attention to fabricate nanostructured materials because the laser pulse duration is shorter than the electron cooling time and heat diffusion into target materials can be minimized [22]. Metal surfaces under liquid water environments have been converted with controlled femtosecond laser into nanoparticles and nano-materials [23]. Here we report a green procedure for the fabrication of Pt/multiwalled CNT (Pt/MWCNT) in aqueous solution by femtosecond laser. The synthesis of Pt nanoparticles on MWCNT is achieved without the addition of any poisonous reducing agent. Pt nanoparticles with about 5–10 nm in diameter are well dispersed on the surface of MWCNTs. The advantages of this method are simple, reproducible, and

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http://dx.doi.org/10.1016/j.snb.2013.03.115

easy handling as compared to other preparations such as solution-phase reduction and electrochemical deposition. The performance with respect to sensitivity and linear range and anti-interference capability of the prepared glucose biosensor are presented and discussed. The improvement of the electrocatalytic ability toward the direct electrochemical oxidation of glucose is observed in comparison with other methods.

2. Experimental

2.1. Reagents

Potassium hexachloroplatinate (IV) (K_2PtCl_6) was obtained from Showa. MWCNTs were used as-received with an outer diameter in the range 40–90 nm and a length of up to several micrometers (Mitsui & Co., Ltd, Japan). D-(+)-glucose, acetaminophen (AP), uric acid (UA), fructose (Fru), and ascorbic acid (AA) were purchased from Sigma–Aldrich. All solutions were prepared with demineralized and filtered water of resistivity of not less than 18 MΩ cm which was taken from a Milli-Q water purification system (Milli-Q, USA).

2.2. Apparatus

Scanning electron microscopy (SEM) images were performed using an Ultra Plus (Zeiss, Germany). Ultraviolet (UV)–visible absorption spectra were obtained with a Lambda 25 UV-VIS spectrophotometer (Perkin Elmer, USA). Transmission electron microscopy (TEM) images were recorded on a JEM-2010 (JEOL, Japan). X-ray diffraction (XRD) patterns were recorded using a D8 Discover X-ray diffractometer with Cu Kα radiation (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) measurements were obtained on a Phi 5000 VersaProbe Scanning ESCA Microprobe using Al Kα radiation (Ulvac-Phi, Japan). Electrochemical measurements were performed with an Autolab PGSTAT30 Electrochemical Analyzer (Eco Chemie, Netherlands). A conventional three-electrode system was carried out with a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode.

2.3. Preparation of Pt/MWCNT in aqueous solution by femtosecond laser

The acid functionalized MWCNTs was achieved by treatment of MWCNTs with sulfuric acid/nitric acid (3:1, v/v) mixture [24]. The 10 mg of acid functionalized MWCNTs was dispersed in 1 mL deionized water by ultrasonication for 10 min to obtain a uniform acid functionalized MWCNTs solution. A total of 4 mL of 1 mg mL^{-1} MWCNTs and 1 mM $PtCl_6^{2-}$ aqueous solution was kept in a 10 mm × 10 mm × 45 mm quartz vessel. The high intensity femtosecond laser pulses generated by a regenerative amplified mode-locked Ti:Sapphire laser (SPIT FIRE, Spectra-Physics) with central wavelength at ~800 nm, pulse duration of ~120 fs, repetition rate of 1 kHz, and laser intensity 1.5×10^{15} W cm^{-2} were introduced into the vessel perpendicular to its surface and tightly focused in the solution using an aspheric lens with a focal length of 8 mm and a numerical aperture of 0.5 (Thorlabs C240TME-B). After the irradiation, the product was centrifuged, rinsed, and characterized by UV–visible spectroscopy, SEM, TEM, XPS, and XRD.

2.4. Preparation of Pt/MWCNT modified glassy carbon electrodes

Before the surface modification, the 3 mm bare glassy carbon electrode was polished with 0.3 and 0.05 μm alumina slurries and washed with deionized water several times. The 1 mL of 1 mg mL^{-1} Pt/MWCNT was added in 1 mL of 0.5 wt% Nafion™ aqueous solution with the aid of ultrasonic agitation for 10 min. The Pt/MWCNT modified glassy carbon electrodes were prepared by casting 8 μL aliquot of this suspension on glassy carbon electrodes and the solvent was allowed to evaporate at room temperature in the air.

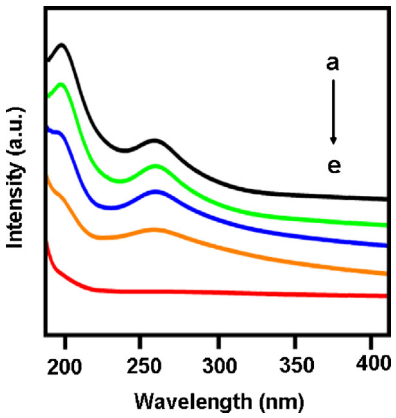

Fig. 1. UV–visible spectra of $PtCl_6^{2-}$ and MWCNTs in aqueous solution with femtosecond laser irradiation time of (a) 0, (b) 1, (c) 5, (d) 10, and (e) 20 min.

3. Results and discussion

3.1. Preparation of Pt/MWCNT in aqueous solution by femtosecond laser

For the preparation of Pt/MWCNT, a mixture of K_2PtCl_6 and MWCNTs in aqueous solution was subjected to a femtosecond laser irradiation with different times. The reduction process of $PtCl_6^{2-}$ in aqueous solution by femtosecond laser was monitored by UV–visible absorption spectroscopy. The UV–visible spectra of $PtCl_6^{2-}$ and MWCNTs in aqueous solution before and after the irradiation of femtosecond laser with different times are shown in Fig. 1. Along with the reduction process of $PtCl_6^{2-}$ by femtosecond laser, the absorption peaks at 201 and 260 nm, characteristic of $PtCl_6^{2-}$ in aqueous solution [25], decreased gradually with the increase of femtosecond laser irradiation time (1–10 min) and disappeared completely after 20 min. The disappearance of the characteristic peaks of $PtCl_6^{2-}$ at 201 and 260 nm with the increase of femtosecond laser irradiation time is evident of the reduction of $PtCl_6^{2-}$ in aqueous solution.

3.2. Pt/MWCNT characterization by SEM and TEM

The morphologies of the formation of Pt nanoparticles-decorated MWCNTs by femtosecond laser were investigated by SEM and TEM. The SEM images of MWCNTs before and after irradiation of femtosecond laser in an aqueous solution containing MWCNTs and $PtCl_6^{2-}$ are shown in Fig. 2a and b, respectively. It can be observed from Fig. 2b that the Pt nanoparticles dispersed on the MWCNTs. This suggested that the MWCNTs are suitable to support the Pt catalyst during the reduction process of $PtCl_6^{2-}$ by femtosecond laser in aqueous solution. The TEM images of MWCNTs before and after irradiation of femtosecond laser in an aqueous solution containing MWCNTs and $PtCl_6^{2-}$ are shown in Fig. 3a and b, respectively, which give further information about the structure. It is clearly seen from Fig. 3b that the Pt nanoparticles with a diameter of about 5–10 nm dispersed individually on the MWCNTs and some nanoparticles aggregated to form large Pt particle. No dissociated Pt nanoparticles seen out of the MWCNT, indicating Pt nanoparticles are extensively assembled on the MWCNT. It is possible to control the Pt nanoparticles size and size distribution with the femtosecond laser irradiation time, the femtosecond laser energy,