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Intense pulsed light induced platinum–gold alloy formation on carbon nanotubes for non-enzymatic glucose detection

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ABSTRACT

We demonstrated a novel method for the formation of alloy nano-islands on carbon nanotube (CNT). The two metal layers (Pt, Au) were sputtered on CNTs and the intense pulsed light (IPL) was irradiated on the metal layers. The absorbed light provides enough energy for the diffusion mixing between Pt and Au, forming Pt–Au alloy phase. While the alloy is being formed by the IPL irradiation, the metal layers are broken into nano-islands on CNT due to the surface energy minimization between the metal layers and CNT. The surface characterizations of the Pt–Au/CNT were performed with X-ray diffraction, scanning electron microscope, and energy-dispersive X-ray spectroscopy. Different compositions of alloy nanoparticles were obtained by adjusting the deposition thicknesses of Pt and Au on CNT. $Pt_{50}Au_{50}$/CNT electrode showed the highest glucose oxidation current peak among Pt, $Pt_{70}Au_{30}$, $Pt_{50}Au_{50}$, $Pt_{30}Au_{70}$, and Au/CNT electrodes while the electroactive surface areas of them are kept to be similar (average surface area = 7.00 cm^2, coefficient of variation = 0.06). The amperometric response of $Pt_{50}Au_{50}$/CNT electrode to the glucose concentrations showed a wide linear range up to 24.44 mM with a high detection sensitivity of 10.71 $\mu A\,mM^{-1}\,cm^{-2}$. Reproducibility and long-term stability of the Pt–Au/CNT electrode were also proven in the experiments.

1. Introduction

Continuous glucose monitoring (CGM) has been proven its advantage on diabetes control, which monitors the change of real-time glucose level by diet, exercise, and medical treatment (Deiss et al., 2006; Klonoff, 2005; Mastrototaro et al., 2008). However, most of the CGM devices in market are based on enzymatic sensors and suffer instability of enzymes in long-term use (Girardin et al., 2009; Wilkins et al., 1995). Therefore, non-enzymatic catalysts have been investigated to address this problem (Cui et al., 2007; Jin and Chen, 2007; Kurniawan et al., 2006; Park et al., 2003; Rong et al., 2007; Song et al., 2005). Among the non-enzymatic glucose sensors, platinum (Pt) has been the most popular materials due to its high catalytic activity toward glucose oxidation (Park et al., 2003; Song et al., 2005). However, pure Pt electrodes are also degraded over time due to the surface poisoning by the adsorbed intermediates, mainly CO (Jin and Chen, 2007). To overcome the drawback, bimetallic alloys, such as Pt–Au (Habrioux et al., 2009; Jin and Chen, 2007) and Pt–Pb (Cui et al., 2007), were developed as the poisoning-resistive catalysts. In the biometallic alloys, the secondary element functions to oxidize the adsorbed CO or to suppress the adsorption of CO (Markovic and Ross, 2002), and therefore the higher electrocatalytic activity is achieved with improved stability (Cui et al., 2007; Habrioux et al., 2009; Jin and Chen, 2007; Xu et al., 2008). Among many candidates of secondary elements for the CGM application, Au is particularly attractive because it oxidizes both the adsorbed CO intermediate and glucose (Habrioux et al., 2009; Jin and Chen, 2007).

In addition to the stability of catalyst to the degradation, the surface-to-volume ratio of catalyst supporting matrix is another critical factor to increase the electrochemical reaction. For this reason, carbon nanotubes (CNTs), which have high electrical conductivity, mechanical strength, chemical resistance, and large specific surface areas (400–900 m^2/g and 200–400 m^2/g for single-wall, and multi-wall CNT, respectively) (Serp et al., 2003), have attracted increasing attention in their applications as the catalyst matrix (Li et al., 2002; Wang et al., 2004; Lee et al., 2006; Zhao et al., 2007).

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The Pt alloy nanoparticles on CNTs have been mainly obtained through chemical based methods including electrodeposition (Cui et al., 2007; He et al., 2004), chemical reduction (Xu et al., 2006), and pyrolysis (Yao et al., 2006). Here, we report a novel method for Pt–Au nano-islands formation on CNTs using the intense pulsed light (IPL). In our previous work, the formation of Pt nano-islands was demonstrated by using the IPL-induced dewetting phenomena on CNT (Ryu et al., 2010). In the present paper, the IPL-induced surface diffusion is applied to form Pt–Au alloy on CNTs. While the alloy is formed, the metallic layer is broken into nano-islands due to the surface energy minimization on CNTs as discussed in the literature (Ryu et al., 2010). Using this surface energy driven dewetting process, we can graft metallic nanoparticles on CNT without oxidizing the sidewall of CNTs for the nucleation of the metal nanoparticle growth, which accompanies with the degradation of mechanical and electrical properties of CNT (Grag and Sinnott, 1998; Zhang et al., 2004, 2008). One of the most significant advantages of this IPL-assisted manufacturing is its easy and accurate control of the alloy composition by adjusting the thicknesses of Pt and Au layers. Moreover, the process time of alloy formation is extremely short (2 ms) and the whole process is performed under the ambient room temperature condition.

2. Experiment

2.1. Materials

In this study, CNT mat was used instead of the conventional CNT powder for the convenience of sputtering of metal layers. The CNT mat is a sheet of multi-wall CNTs (MWCNTs). The length and diameter of the MWCNTs are about 1–3 mm and 40–100 nm, respectively. A roll of CNT mat (3′ × 6′, 12 μm of thickness) was provided by NanoComp Technologies, Inc. D-(+)-Glucose was purchased from Sigma. Phosphate buffered saline (PBS, pH 7.4) and KCl were bought from Fisher Scientific. Ag/AgCl reference electrode and 0.5 mm platinum wire counter electrode were purchased from CH Instruments.

2.2. Alloy formation by IPL irradiation

IPL was originally used for the dermatological treatment. In this paper, IPL system was used for the photothermal diffusion to form the alloy nano-islands. The detail features of IPL are described in our previous study (Ryu et al., 2010). The IPL system can control the intensity and pulse duration of a xenon flash lamp (Perkin-Elmer, QXA) with simmer triggering pulse controller, and capacitors. The lamp holder has an aluminum reflector. The wavelength of the light from the xenon flash lamp covers the range from 160 nm to 2.5 μm. The intensity and pulse duration of the lamp can be controlled between 20 J/cm^2 and 50 J/cm^2, and 2 ms and 10 ms, respectively. In the present work, they are fixed to at 50 J/cm^2 and 2 ms.

The metal layer dewetting by IPL irradiation is analogous with the thermal dewetting phenomena. The main force of the film breaking is the instability driven by surface energy minimization at the interface between the metal film and substrate (Jiran and Thompson, 1992). Fig. 1 gives the illustration of the metal layer dewetting and alloy formation on CNT by IPL irradiation.

The surface energy of platinum and gold are 1.746 J/m^2 and 1.138 J/m^2 with the temperature coefficients of −0.31 mJ/(m^2 K) and −0.18 mJ/(m^2 K) in the liquid metal phase (Lu and Jiang, 2005), which are much higher than that of the CNT, 0.0826 J/m^2 (Hong et al., 2006). Therefore the heated metal layers on the CNT are prone to reduce the interface and expose more CNT surface (Duxstad et al., 1997). In addition to the dewetting of metal layers on CNT, the IPL irradiation also provides enough energy for atomic diffusion between Pt and Au layers, resulting in Pt–Au alloy phase. The crystal phase analysis was performed using X-ray diffraction (XRD, Phillips, Cu Kα radiation). The structure and surface composition of Pt–Au alloy were characterized by a scanning electron microscope (SEM, JEOL JSM 6700F), and energy-dispersive X-ray spectroscopy (EDX, EDAX Genesis 2000).

2.3. Sensor electrode preparation

1 cm × 1 cm of CNT mat was placed on a glass substrate and heated at 350 °C under the airflow condition for 1 h to remove amorphous carbon. Pt and Au layers were deposited using a DC sputterer (Hummer 6.2, Anatech Ltd.) at a constant current of 15 mA. Au was sputtered on the top of Pt layer because Au can transfer the photothermal heat more efficiently; the thermal conductivities of Au and Pt are 3.17 W/cm K and 0.716 W/cm K, respectively (Incropera and DeWitt, 2001). In this study, five different atomic ratios (Pt, $Pt_{70}Au_{30}$, $Pt_{50}Au_{50}$, $Pt_{30}Au_{70}$ and Au) were

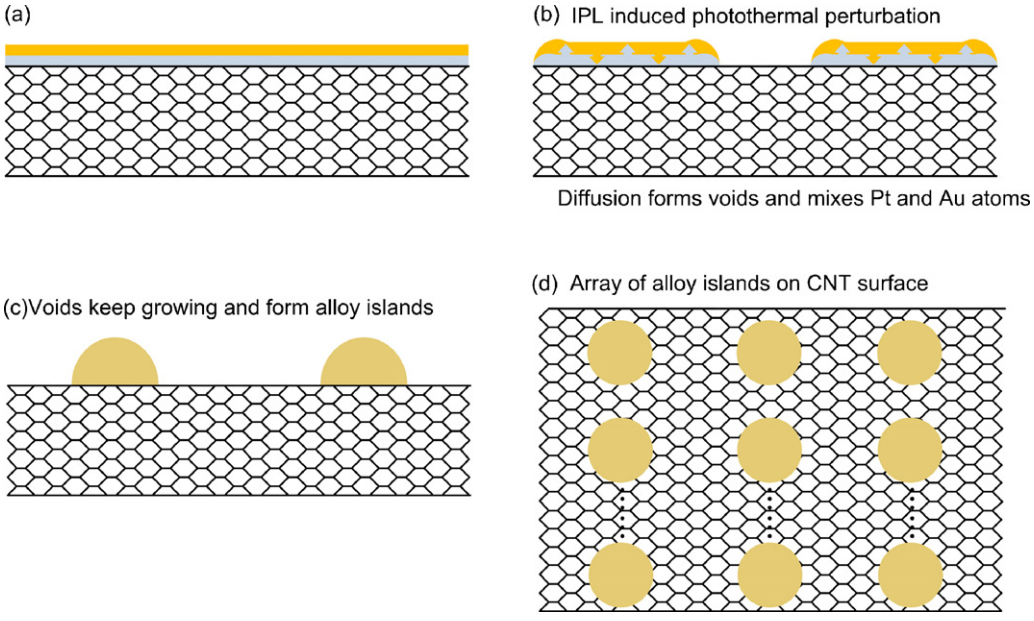

Fig. 1. Schematics of alloy formation and dewetting process induced by IPL: (a) Pt (bottom) and Au (top) layers on CNT, (b) void and alloy formation by the diffusion induced by IPL, (c) voids keep growing and form alloy islands on CNT, and (d) two-dimensional schematics of alloy nano-islands on CNT.