Nanostructure Pt Electrode Obtained via Self-assembly of Nanoparticles on Conductive Oxide-coated Glass Substrate

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Self-assembly of platinum nanoparticles were applied to fabrication of counter electrode for dye-sensitized solar cells on conductive oxide-coated glass substrate. The present Pt electrode exhibits high exchange current density of 220 mA/cm^2, which is comparable to those prepared by electrodeposition, magnetron sputtering or thermal decomposition of platinum chloride. After analysis by transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), it was found that the catalyst was structurally characterized as nanosized platinum metal clusters and was continuously arranged on electrode surface. The present nanostructure electrode had high electrocatalytic activity for the reduction of iodine in organic solution.

Keywords   platinum, nanostructure, electrochemical activity, iodide/triiodide redox couple

Introduction

Dye-sensitized nanocrystalline solar cells utilize the iodide/triiodide redox couple as the mediator that shuttles the charge between the photoelectrode and the counter electrode.[1] The transparent conductive oxide-coated glass substrates are presently used as cathodes in solar cells, which are extremely poor catalysts for iodine reduction;[2,3] therefore they have to be modified, mainly by means of electrodeposition,[4] thermal decomposition,[5] and magnetron sputtering.[6] Comparing the charge-transfer resistances, it turned out that the nanostructure Pt electrode had higher catalytic reactivity than the bulk structure Pt electrode. This result can be explained by the structure with the high effective surface. And it is undoubtedly linked to the character of Pt structure on the substrate.

The platinum colloidal particles can be modified by the addition of dodecanethiol (thiol) leading to self-assembled monolayers (SAMs) and become ordered to form closest packed arrays in solution.[7-9] There have been a great deal of research efforts devoted to the development of new methodologies for the construction of particle-ordered assemblies,[10-14] involving surface exchange reactions with thiols and bifunctional ligands to bridge the particles onto the substrate surfaces. Understandably, the main technological challenge is the lack of efficient methods to fabricate microscopic ordered structures.

In this paper, we report the way to synthesize narrow dispersion Pt nanoparticles by hydrothermal method for the first time. The nanoparticles were capped with thiols, and then applied to fabrication of Pt electrode for dye-sensitized solar cells on conductive oxide-coated glass substrate.

Experimental

The Pt nanoparticles were prepared by alcohol-reduction hydrothermal method. 0.4 mL of 1.0 mol/L acrylic acid solution (sodium acrylate, Aldrich, 97%) was added to 250 mL of an aged aqueous solution of 6×10^{-4} mol/L K_2PtCl_6 (Aldrich, 99.99%). 40 mL of ethanol was added to 40 mL of the above mentioned solution. Argon gas was bubbled in the solution for 15 min. Afterwards, the reduction of platinum ions was carried out by heating the solution at 180 ℃ for 10 h in a autoclave. Then reaction mixture was evaporated in order to eliminate methanol formed. 0.2 mL of thiol (purchased from Acros) was added to the remained reaction mixture, in which Pt nanoparticles have been formed. After vigorous stirring for 30 min, Pt nanoparticles were transferred from the aqueous phase to the organic phase.

The morphology of the sample was studied by transmission electron microscopy (TEM), which was carried out on a JSM-35CF microscope with an accelerating voltage of 200 kV. Atomic force microscopy (AFM) was measured on Seiko SPL-3800N scanning probe microscope. X-ray photoelectron spectroscopic (XPS) investigations were performed using ESCALAB 220i-XL spectrometer with standard Al Kα radiation.

The organic phase containing Pt nanoparticles was spreaded onto the top of a conducting glass plate (FTO, F-doped SnO_2 coated glass (10 Ω/square) purchased from Pilkington-Flabeg, Germany) which offered uniformity of coating. The coated electrodes were heated in air, with temperature gradually increased to 380 ℃, and keep this temperature for 15 min.

Platinum loadings were determined by dissolution of the electrodes in aqua regia, and platinum content was measured by atomic emission spectroscopy (AES). Electrochemical impedance spectroscopy was employed on symmetric thin-layer cells, similar to the ones described elsewhere.[5,6] The active area of the electrode is 0.25 cm^2. The cell is filled with following electrolyte: 0.5 mol/L KI and 0.05 mol/L I_2 in propylene carbonate (PC)：ethylene carbonate (EC)＝8：2 solvents. All measurements were carried out at a temperature of 25 ℃. Electrochemical measurements were performed with the Solartron 1255B impedance spectrum analyzer.

Results and discussion

The Pt clusters and colloids were prepared by chemical reduction of metal salts as described in the experimental section. The stable and dark brown solution was observed, and corresponding absorption spectrum showed the formation of platinum colloid. Aging the metal nanocluster solution often leads to reduction of particles polydispersity.[7] Effective sample aging at room temperature usually takes weeks or months. In the case of present hydrothermal method, it can be demonstrated that thermal annealing could reduce the time, annealing is an effective route to the production of monodispersed Pt nanoclusters. The particle size distribution is fairly narrow as explored by TEM in Figure 1A.

When thiol is added to Pt nanoparticle hydrosol, particles were readily transferred to a nonpolar medium. The TEM image in Figure 1B reveals that thiol-passivated particles form nanocrystalline arrays with regular spacing between the particles. The Pt particles with the mean diameter of *ca.* 7 nm form a close-packed structure. The particles showed the following characteristics: small average diameters, narrow size distributions, similar shapes, as well as alkyl stabilizing agents. In each case, the capping agent played a key role in influencing the ordered packing to be compatible with conductive oxide-coated glass surface.

On the FTO surface, substantially large islands of rough surface domain can be observed by large scale AFM image. Thiol capped Pt nanoparticles spreaded on this substrate surface and then sintered. Figure 2 is the atomic force micrograph of Pt particles attached to the FTO island surface showing an almost continuous layer of Pt particles with an average diameter of *ca.* 15 nm. In contrast to the value estimated from the TEM image, the diameter of the present particles was enlarged by sintering. It should be noted that we have not observed
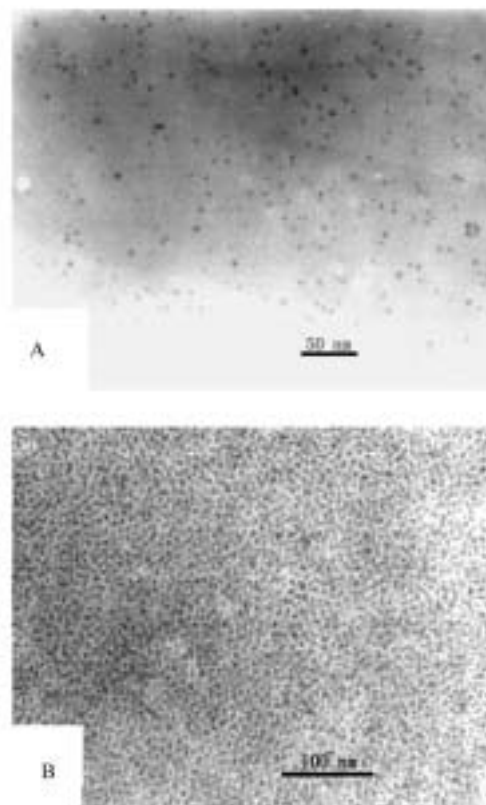
Figure 1 (A) TEM image of Pt nanoparticles before the addition of dodecanethiol. (B) TEM image of the self-assembled array of Pt nanoparticles.
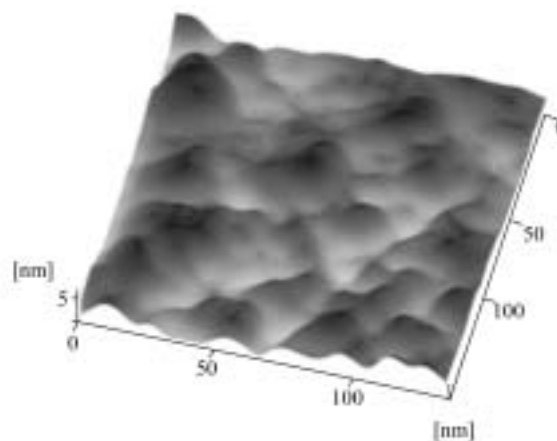

Figure 2 The AFM image acquired at the island area of FTO substrate.

above nanostructure image on FTO surface in a blank experiment.

The chemical composition of the outermost sample layers was studied by XPS, paying attention to the Pt state and to the Pt particle surface contaminants (Figure 3). The $Pt4f_{7/2}$ component was always centered at binding energy of approximate 71.3 eV, a value in good agreement with that reported for Pt(0).[15] The XPS spectral peaks were all dominated by platinum signals, and the weak carbon signal was related to air exposure. It is suggested that sintering temperature at 380 ℃ can lead

258 *Chin. J. Chem.*, 2004, Vol. 22, No. 3

WANG *et al.*

to the loss of the capping agent and obtaining purified nanostructure Pt electrode. Therefore, the catalyst on electrode surface was structurally characterized as nanosized platinum metal clusters. In addition, the platinum loading was determined by AES, and it gives a value of 5 $\mu g/cm^2$ under this experimental condition.
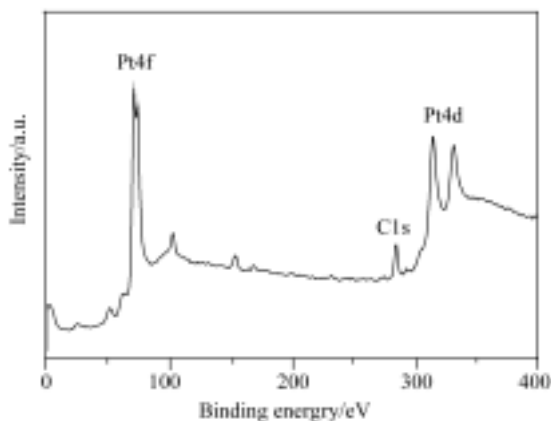
Figure 3 XPS of a Pt film obtained on quartz substrate after sintering at 380 ℃.

The result of our impedance experiment (Figure 4) showed the typical feature for a electrochemical system. The impedance spectrum is controlled by mass transport at lower frequency and by charge transfer at higher frequency. The charge-transfer resistance, R_{ct}, value of the electrode can be taken as the half of the real part of the electrochemical impedance.[16] The charge-transfer resistance value is 0.05 $\Omega \cdot cm^2$ under the present experimental condition, which can be interpreted as a loss of merely 1.0 mV on counter electrode at 20 mA/cm^2 during solar cell operation. This charge-transfer resistance value also corresponds to an exchange current density J_0 = 220 mA/cm^2 on the basis of the formula $R_{ct} = RT/nFJ_0$, where $n = 2$ for reaction $I_3^- + 2e = 3I^-$. For the thermal decomposition and magnetron sputtering electrodes, we also measured the exchange current densities to be 55 mA/cm^2 and 11 mA/cm^2, respectively. The catalyst has been structurally characterized as nanosized Pt metal clusters for thermal decomposition electrode.[5] From the above results, we could see that nanostructure electrodes have a higher electrochemical activity than that of bulk electrode. The low charge-transfer resistance for nanostructure Pt layer may be explained by the high effective surface or may be due to the different multistep reaction mechanism with iodide and iodine.[5] Moreover, the electrode via self-assembly of nanoparticles has a higher electrochemical activity than that of platinum chloride electrode by thermal decomposition. This effect may be due to the different Pt nanoparticle coverage on the conductive oxide-coated glass substrate. From Figure 2, the nanostructure Pt electrode via self-assembly of nanoparticles can give nearly continuous distribution on conductive oxide-coated glass substrate.
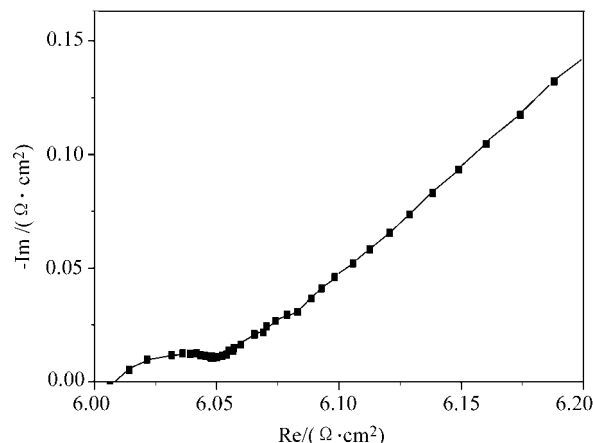
Figure 4 Typical Nyquist plot of the impedance taken at zero bias potential and 10 mV amplitude. The electrolyte is 0.5 mol/L KI, 0.05 mol/L I_2 in PC：EC＝8：2, area＝0.25 cm^2.

Conclusion

Self-assembly of Pt nanoparticles was applied to fabrication of nanostructure Pt thin films on conductive oxide-coated glass substrate. The catalyst was structurally characterized as nanosized platinum metal clusters and continuously arranged on electrode surface. The nanostructure Pt electrode has high electrocatalytic activity for the reduction of iodine in organic solution.

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