Nanosize Copper Encapsulated Carbon Thin Films on a Dye-Sensitized Solar Cell Cathode

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Deposition of the nanosize copper encapsulated carbon (Cu@C) thin film onto the cathode has been studied to enhance efficiency of the dye-sensitized solar cell (DSSC). The X-ray diffraction (XRD) patterns of the Cu@C are suggestive of existence of metallic copper (Cu) nanoparticles in the thin film. The UV-visible spectrum of the Cu@C coated on indium-doped tin oxide (ITO) shows a red shift (probably due to the longitudinal resonance) as the size of Cu in the Cu@C increases. Moreover, the images observed by field-emission scanning electron microscopy (FE-SEM) indicate that the Cu@C nanoparticles are well dispersed on ITO. By extended X-ray absorption fine structure (EXAFS) spectroscopy, a decrease of the coordination number (CN) of Cu–Cu with decreasing sizes of Cu in the Cu@C is observed. Interestingly, an enhanced efficiency of the DSSC with the Cu@C nanoparticles coated ITO cathode by 50% is found if compared with the relatively expensive Pt electrode. As the size of Cu in the Cu@C on ITO decreases (e.g., 20 → 7 nm), the efficiency of the DSSC can be increased by 80% approximately.

Keywords: Copper, Carbon, DSSC, Nanoparticles.

1. INTRODUCTION

Metal particles in the nano-scale are of increasing interest in multidisciplinary fields due to their unique optical, electric, and catalytic properties.¹ Nanosize metals have many promising applications such as biological labeling, catalysis, and trace of tumors.²–⁵ It is rather challenging to fabricate metal nanoparticles with narrow size distribution and well dispersed via the traditional methods such as thermal and chemical reduction, metal evaporation and irradiation.⁶ Metal nanoparticles encapsulated within inert shells have high stabilization and well dispersion properties comparing to the bare ones, and create compatibility between the core metals and ambient environment.²–⁹ In the separate experiments, a simple and cheap method to synthesize Cu nanoparticles encapsulated within carbon has been developed.¹⁰

Dye-sensitized solar cell (DSSC) are considered as potential photovoltaic devices.¹¹,¹² To have a higher efficiency new photoanode, cathode, dye, and electrolyte of the DSSC have been studied.¹³ In particular, deposition of nanoparticles or nanorods on the cathode to have a better efficiency of DSSC has been investigated.¹⁴ In the present work, a novel cathode of the DSSC has been studied to substitute the relatively expensive Pt electrode.

2. EXPERIMENTAL DETAILS

Starch (Riedel-de Haën) and copper nitrates (Fluka) at the carbon (starch)-to-copper atomic ratios of 14, 7.0 or 4.7 were dissolved in distilled water. The solution was well stirred at 353 K and deposited onto ITO (SnO₂:In, RITEK) by spin coating at a rotation rate of 2,000 rpm. After dried at 343 and 373 K for totally 2 h, the starch-Cu²⁺ complex was carbonized under high purity nitrogen (99.99%) at 573–673 K for 2 h to yield the Cu@C core–shell nanoparticle thin films.

The Pt cathode was prepared by deposition of H₂PtCl⁶·6H₂O (Alfa Aesar) onto ITO by spin coating at 1,500 rpm and dried at 323 K for 15 min. The cathode was calcined at 658 K for 10 min and used as the standard DSSC electrode.

Chemical Structure of the Cu@C samples was characterized by X-ray diffraction spectroscopy (XRD, Bruker D8 Advanced) scanned from 10 to 80° (2θ) with a scan rate of 3°/min. Absorption (400–800 nm) of the nanosize...
Cu@C nanoparticles coated on ITO was determined on a UV-visible spectrometer (Varian, Cary 100). Morphologies of the Cu@C thin films were studied by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7000) and transmission electron microscopy (TEM, Philips CM-200). The EXAFS spectra of copper in the nanosize Cu@C nanoparticles were collected on the Wiggler BL17C beamline at the Taiwan Synchrotron Radiation Research Center (SRRC). The EXAFS data were analyzed using the UWX-AFS 3.0 and FEFF 8.0 simulation programs.15

In the previous study, it was found that the sizes of Cu in the Cu@C core–shell materials were 7, 14, and 20 nm.10 It is also worthy to note that the thickness of the carbon shell that can prevent the core Cu from being aggregated and oxidized was about 3 nm.10

The photoanode of the DSSC was coated with a nanosize TiO2 (P25) paste by the doctor blade method on the transparent conductivity glass FTO (fluorine-doped tin oxide) (SnO2:F, Solaronix SA), dried at 323 K for 15 min, and calcined at 723 K for 30 min. Furthermore, the nanosize TiO2 coated photoanode was immersed in the ethanol solution containing 0.3 mM of N3 dye (cis-di(thiocyanate) bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II), ruthenium 535, Solaronix SA) for 16–20 h to adsorb N3 to the maximum extent. The photoanode and cathode (counter electrode) were assembled like a sandwich via a 60 µm spacer of hot-melt thermal foil (Solaronix SA) and an electrolyte (0.1 M LiI (Aldrich), 0.05 M I2 (Riedel-de Haën), 0.6 M DMPII (Solaronix SA), and 0.5 M 4-tert-butyl-pyridine (Aldrich) in acetonitrile (Mallinckrodt)) introduced between electrodes and sealed with AB epoxy.

The I–V characteristics of the DSSC were measured on a 300 W xenon lamp solar simulator coupled with an AM 1.5 Globe filter (Oriel). The DSSC samples were illuminated with an 100 mWcm\(^{-2}\) simulated sunlight in the dark room.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of copper in the Cu@C nanoparticles on the ITO. The peaks at 43.3° (Cu(111)) and 50.4° (Cu(200)) indicate that the existence of Cu in the Cu@C coated on ITO. Note that the XRD intensity of the nanosize Cu is relatively less than its bulky state.

Generally, metal nanoparticles such as Cu have surface plasmon resonance (SPR) at the wavelength range of UV-visible and absorb incident light at a specific wavelength (e.g., Cu at 580 nm).16 The UV-visible spectra of Cu (sizes of 7, 14, and 20 nm) in the Cu@C nanoparticles coated on ITO are shown in Figure 2. The broadened absorption feature at 607 nm for the Cu@C (Cu size = 7 nm) indicates the transverse SPR of the Cu nanoparticles.14 Interestingly, red shifts of absorption to 614 and 621 nm for the Cu having sizes of 14 and 20 nm, respectively are also observed (probably due to the longitudinal resonance). In the absence of the nanosize core Cu (by leaching out of Cu from the Cu@C nanoparticles with 1 N HNO3) as expected, the absorption features at 607–621 nm are not found. The less difference between the solid and dotted line of 7 nm compared to 14 or 20 nm Cu in the Cu@C nanoparticles (see Fig. 2) may be attributed to the relatively low concentration of larger nanoparticles.

It is well-known that fractions of surface atoms are always negligible in the bulk state. On the contrary, contribution of surface atoms is of increasing importance as the size of particles is decreased to the nano scale (<100 nm). Surface atoms have generally less coordination atoms, weak bounding, and less constrain. The ratio of surface to total atoms increases with the particle size decreases. The average CN of nanoparticles also decreases along with the particle size. By EXAFS, speciation of Cu in the Cu@C nanoparticles can be observed (see Table I). The CN of the nanosize Cu decreases as the size of Cu decreases.

Figure 3 shows a high dispersion and uniform distribution of Cu@C (Cu sizes = 7–20 nm) on ITO. The Cu@C nanoparticles coated ITO can be used as cathode of the DSSC to replace the relatively expensive Pt electrode. The efficiency, short circuit density (J\(_{sc}\)), open circuit voltage (V\(_{oc}\)), and fill factor (FF) of the DSSC assembled with the cathode coated with Cu@C nanoparticles have been determined (shown in Table II). As the size of Cu in the Cu@C on ITO decreases (e.g., 20 → 7 nm), the efficiency of the
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Fig. 2. UV-visible spectra of Cu having sizes of (a) 7, (b) 14, and (c) 20 nm in the Cu@C nanoparticles coated on ITO. The dotted line denotes the spectrum of the hollow carbon spheres thin film.

Table I. Speciation of copper in the Cu@C nanoparticles coated on ITO.

<table>
<thead>
<tr>
<th>Cu size (nm)</th>
<th>Shell</th>
<th>R (Å)</th>
<th>CN</th>
<th>σ²(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Cu–Cu</td>
<td>2.53</td>
<td>7.9</td>
<td>0.0082</td>
</tr>
<tr>
<td>14</td>
<td>Cu–Cu</td>
<td>2.53</td>
<td>9.8</td>
<td>0.0087</td>
</tr>
<tr>
<td>20</td>
<td>Cu–Cu</td>
<td>2.53</td>
<td>9.9</td>
<td>0.0088</td>
</tr>
<tr>
<td>&gt;63,000</td>
<td>Cu–Cu</td>
<td>2.53</td>
<td>13</td>
<td>0.0082</td>
</tr>
</tbody>
</table>

R: Bond distance; CN: Coordination number; σ²: Debye-Waller factor.

DSSC can be increased by 80% approximately. The high surface area Cu@C on the cathode enhances adsorption of the dye and subsequently promotes electron transport to electrolyte. In Table II, the DSSC has the Jsc values of 6–8 mAcm⁻². Most interestingly, the efficiency of the DSSC assembled with the smaller (7 nm) Cu in the Cu@C coated cathode is much greater than that of the conventional Pt coated cathode by about 50%.

4. CONCLUSIONS

The well dispersed Cu@C nanoparticles coated on the cathode for the DSSC have a much greater efficiency (increasing 50%) if compared with the relatively expensive Pt coated cathode. The Cu@C with the Cu size of 7 nm on the cathode possesses an enhanced efficiency by at least 80% if compared with the larger Cu size (e.g., 20 nm). This work also demonstrates a promising application of the Cu@C nanoparticles used in the cathode of a DSSC.

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References and Notes

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