Research Article

Metal-Free Counter Electrode for Efficient Dye-Sensitized Solar Cells through High Surface Area and Large Porous Carbon

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Highly efficient, large mesoporous carbon is fabricated as a metal-free counter electrode for dye-sensitized solar cells. The mesoporous carbon shows very high energy conversion efficiency of 7.1% compared with activated carbon. The mesoporous carbon is prepared and characterized by nitrogen adsorption, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The nitrogen adsorption data reveals that the material possesses BET specific surface area ca.1300 m^2/g and pore diameter 4.4 nm. Hexagonal rod-like morphology and ordered pore structure of mesoporous carbon are confirmed by electron microscopy data. The better performance of this carbon material is greatly benefited from its ordered interconnected mesoporous structure and high surface area.

1. Introduction

Global energy demand is likely to increase with the expansion of economy, even though great efforts are made to increase the energy utilization efficiency. In recent years, fuel cells and solar cells have contributed remarkably for the development of renewable energy technologies. Photovoltaic cells such as dye-sensitized solar cells (DSCs) have attracted much attention as an alternative energy source for future requirements [1], which composed of porous nanostructured oxide film with adsorbed dye molecules as a dye-sensitized anode, an electrolyte containing iodide/triiodide redox couple, and a platinized fluorine-doped tin oxide (FTO) glass as the counter electrode [2–4]. DSCs have advantages over traditional Si-solar cells due to low cost, easy fabrication, and high energy conversion efficiency [5, 6]. For additional improvement in energy efficiency and commercialization of DSCs [7, 8], further cost reduction is necessary. Therefore, efforts have been made to lower the production cost of DSCs

by using flexible ITO-coated polyester film, metal foil [9], and organic dyes or metalorganic complex dyes [10]. In DSCs the platinum counter electrode is very crucial towards catalytic reduction of tri-iodine. But the platinum is an expensive metal and takes large portion of fabrication cost of DSCs, which retards commercialization of the process. To reduce to the cost of DSCs process various carbon materials such as carbon black [11], activated carbon [12], carbon nanotubes, porous carbon [13], and graphite [14] have been investigated as counter electrode. However, energy conversion efficiency of reported carbon counter electrode of DSCs is still low. Therefore, further enhancement of efficiency is necessary. Among the other carbon materials, mesoporous carbon materials have received much attention due to their large internal surface area and pore volume, tunable and narrow pore diameter [15, 16]. Templated synthesis method of mesoporous carbon, which is also known as "nanocasting" has been extensively used due to the obtained material possesses uniform and interconnected

pores. This synthetic technique involves impregnation of silica templates with an appropriate carbon source, carbonization of carbon precursor, and subsequent removal of silica. The resulting carbon is inverse replica of ordered mesoporous silica. Herein, ordered high specific surface area and large porous carbon is synthesized using large porous silica as a template and dye-sensitized solar cells properties of synthesized carbon are investigated as a metal-free counter electrode.

2. Experimental

2.1. Preparation of Large Porous Carbon (LPC) Counter Electrode. Ordered mesoporous carbon material referred to as LPC is synthesized by pyrolysis of sucrose inside the large porous silica (LPS) synthesized at 130°C using P123 surfactant. In a typical synthesis of mesoporous carbon, 1 g of LPS is added to a solution obtained by dissolving 0.75 g of sucrose and 5.0 g of water, and keeping the mixture in an oven for 6 h at 100°C. Subsequently, the oven temperature was raised to 160°C for another 6 h. In order to obtain fully polymerized and carbonized sucrose inside the pores of silica template, 0.5 g of sucrose, 0.06 g of H_2SO_4, and 5.0 g of water are again added to the pretreated sample, and the mixture is again subjected to thermal treatment as described above. Carbonization is performed at 900°C for 5 h under N_2-atmosphere. The resulting carbon/silica composite is treated with HF acid (5 wt%) at room temperature to selective removal of silica. The finally obtained mesoporous carbon paste is coated on FTO glass using doctor blade technique [17, 18].

2.2. Fabrication of Dye-Sensitized Solar Cell. A nanocrystalline TiO_2 photoelectrodes of 20 μm thickness (area: 0.25 cm^2) were prepared by screen printing on conducting glass as previously described [19]. The films were further treated with 0.05 M $TiCl_4$ and 0.1 M HCl aqueous solutions before examination [20]. Coating of the TiO_2 film was carried out by immersing for 45 h in a sensitizer solution (N719) of 3×10^{-4} M acetonitrile/*tert*-butyl alcohol (1/1, v/v) solution. Deoxycholic acid (20 mM) was added to the dye solution as a coadsorbent to prevent aggregation of the dye molecules [21, 22]. Photovoltaic measurements were performed in a two-electrode sandwich cell configuration. The dye-deposited TiO_2 film and a large pore mesoporous carbon on conducting glass were used as the working electrode and the counter electrode, respectively. The two electrodes were separated by a surlyn spacer (40 μm thick) and sealed by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I_2, TBP 0.5 M, and 0.1 M LiI in acetonitrile.

3. Results and Discussion

The unit cell parameters for the LPC and LPS materials are evaluated from the XRD data, which are summarized in Table 1. The hexagonal unit cell a_0 parameter is calculated using the formula $a_0 = 2d_{100}/\sqrt{3}$. It was observed that the

TABLE 1: Textural parameters of large pore silica and carbon materials.

Sample	a_0/nm	A_{BET}/m$^2 \cdot$g^{-1}	V_p (cm^3/g)	dp, BJH (nm) adsorption
LPC	9.02	1317	1.31	4.4
LPS	10.42	530	1.17	10.3

unit cell constant of these LPC material decreases to 9.02 nm compare with unitcell constant of 10.42 for LPS due to structural pore shrinkage after removal of the template. Nitrogen adsorption-desorption isotherms are measured at 77 K on a Quantachrome Autosorb 1 volumetric adsorption analyzer. Before the adsorption measurements, all samples are out gassed at 250°C in the port of the adsorption analyzer. The position of the maximum on pore size distribution is referred to as the pore diameter, which was calculated from adsorption branches by Barrett-Joyner-Halenda (BJH) method. The nitrogen adsorption-desorption isotherm of LPC along with BJH pore size distribution (inset) is shown in Figure 1(a). The isotherm is of type IV and exhibited a H2 type hysteresis loop. As the relative pressure increases ($P/P_0 > 0.4$), the isotherm exhibits a sharp capillary condensation step of nitrogen within uniform mesopores, where the P/P_0 position of the inflection point is correlated to the diameter of the mesopore. The BET specific surface area was obtained from adsorption branches in the relative pressure range of 0.05–0.20. The total pore volume was estimated from the amount of nitrogen gas adsorbed at a relative pressure of 0.98. The position of the maximum on pore size distribution is referred to as the pore diameter, which was calculated from adsorption branch by Barrett-Joyner-Halenda (BJH) method. The specific surface area amounts to 530 m^2/g for LPS and increases to 1317 m^2/g for LPC, while the specific pore diameter decreases from 10.3 nm to 4.4 nm for the same samples. The large pore carbon LPC material possesses pore volume 1.31 cm^3/g, which is higher than large pore silica LPS material. The specific surface area and specific pore volume are higher for LPC than the LPS template, which facilitates for application in dye-sensitized solar cells. It is interesting to note that structural order is retained even after the removal of the template by acid treatment. The HRTEM images are obtained with JEOL JEM-2100F. Hitachi S-4800 HR-FESEM is used to observe the morphology of the material. SEM image in Figure 1(b) reveals that the LPC has hexagonal rod like morphology, which is similar to the morphology of mesoporous silica. Highly ordered linear array of pore channels and pore structure of LPC was confirmed by high resolution transmission electron microscopy (Figures 1(c) and 1(d)).

Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). IPCE at each incident wavelength was calculated from (1), where I_{sc} is the photocurrent density at short circuit in mA cm^{-2} under monochromatic irradiation, q is the elementary charge, λ is the wavelength of

(a)

(b)

(c)

(d)
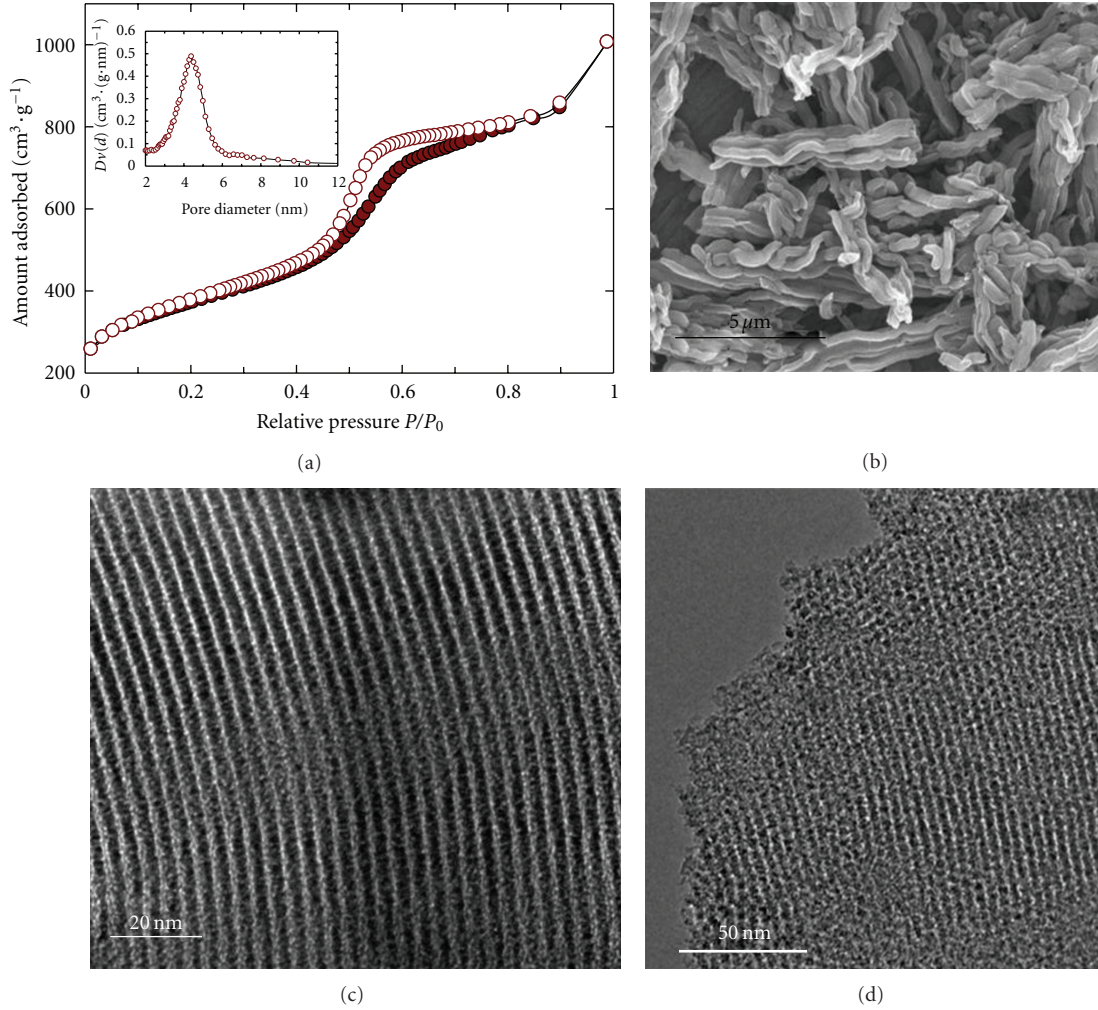
FIGURE 1: (a) Nitrogen adsorption isotherm (• adsorption, ○ desorption) and BJH pore-size distribution (in set) of LPC material. (b) SEM image of LPC material. (c, d) TEM images of LPC.

incident radiation in nm, and P_0 is the incident radiative flux in Wm^{-2}

$$\text{IPCE}(\lambda) = 1240 \left(\frac{I_{SC}}{q\lambda P_0} \right). \tag{1}$$

The photocurrent density-voltage curves and incident photon-to-current efficiency (IPCE) spectra of the cells are based on N719 dye under the illumination of air mass (AM) 1.5 sunlight (100 mW/cm^2, WXS-155S-10: Wacom Denso Co. Japan).

Photovoltaic performances of DSCs based on the mesoporous carbon and activated charcoal are shown in Figure 2. The short circuit current (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), and the overall conversion efficiency (η) are summarized in Table 2. The results indicate that the activated charcoal shows poor performance compare with mesoporous carbon. The LPC counter electrode shows J_{sc} of 12.07 mA/cm^2, V_{oc} of 0.80 V and FF of 0.66% superior over J_{sc} of 12.07 mA/cm^2, and V_{oc} of 0.76 V and FF of 0.15% of activated charcoal material. The overall conversion efficiency

TABLE 2: Photovoltaic parameters of DSCs based on mesoporous carbon and activated carbon electrodes.

Sample	J_{sc}/mA cm^{-2}	V_{oc}/V	FF%	η/%
LPC	13.41	0.80	0.66	7.1
AC	12.07	0.76	0.15	1.4

achieved is 7.1% and 1.44% for LPC and AC, respectively. The higher FF and η indicate that LPC is more efficient than AC material.

4. Conclusions

High surface area and large mesoporous carbon LPC with ordered pore structure has been explored as the metal-free counter electrode for DSCs. Nitrogen adsorption isotherm measurement indicates that LPC material shows very high surface area and large pore volume than mesoporous silica LPS material. SEM and TEM analyses confirm that LPC material retain morphology and order pore structure of
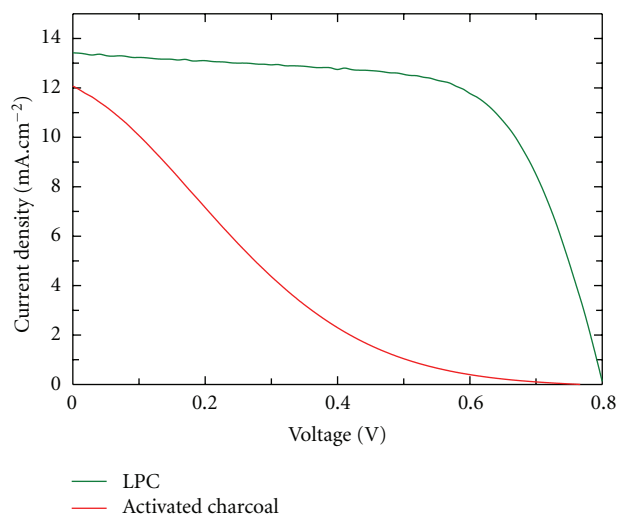
Figure 2: Photocurrent-voltage characteristics of dye-sensitized solar cells of LPC and activated charcoal materials.

the template LPS even after acid treatment. Large porous structure of LPC helps for the penetration of electrolyte and high-specific surface area of ca. $1300 \, m^2/g$, interconnected pore structure facilitate for high energy conversion efficiency than activated charcoal.

Acknowledgments

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