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# Preparation of Nanoporous MgO-Coated TiO<sub>2</sub> Nanoparticles and Their Application to the Electrode of Dye-Sensitized Solar Cells

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Sol–gel-derived Mg(OH)<sub>2</sub> gel was coated onto TiO<sub>2</sub> nanoparticles, and the subsequent thermal topotactic decomposition of the gel formed a highly nanoporous MgO crystalline coating. The specific surface area of the electrode that was prepared from the core–shell-structured TiO<sub>2</sub> nanoparticles significantly increased compared with that of the uncoated TiO<sub>2</sub> electrode. The increase in the specific surface area of the MgO-coated TiO<sub>2</sub> electrode was attributed to the highly nanoporous MgO coating layer that resulted from the topotactic reaction. Dye adsorption behavior and solar cell performance were significantly enhanced by employing the MgO-coated TiO<sub>2</sub> electrode. Optimized coating of a MgO layer on TiO<sub>2</sub> nanoparticles enhanced the energy conversion efficiency as much as 45% compared to that of the uncoated TiO<sub>2</sub> electrode. This indicates that controlling the extrinsic parameters such as the specific surface area is very important to improve the energy conversion efficiency of TiO<sub>2</sub>-based solar cells.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline semiconductors such as TiO<sub>2</sub> are of great interest as an alternative to the conventional solar cells because of their high performance and low-cost production.<sup>1,2</sup> The cell performance is influenced by parameters such as the morphology and optical properties of nanocrystalline oxide films,<sup>3–6</sup> the electrochemical characteristics of redox electrolytes,<sup>7,8</sup> and the photochemical properties of molecular sensitizers.<sup>9–14</sup>

Coating TiO<sub>2</sub> nanoparticles with a different metal oxide has received much attention<sup>15</sup> because the conversion efficiency of the cell is improved by employing a TiO<sub>2</sub> electrode consisting of a core–shell structure. When metal oxides such as ZnO,<sup>16</sup> SrO,<sup>17</sup> Nb<sub>2</sub>O<sub>3</sub>,<sup>18</sup> and SrTiO<sub>3</sub>,<sup>19</sup> were used as the coating layer for TiO<sub>2</sub>, the short circuit current or the open circuit voltage of the solar cell increased, and the overall energy conversion efficiency improved. The improved efficiency of solar cells employing a core–shell-structured TiO<sub>2</sub> electrode has been attributed to the following two factors: First, the wide band gap coating layer retards the back transfer of electrons to the electrolyte solution and minimizes electron–hole recombination.<sup>20</sup> Second, the coating layer enhances the dye adsorption and increases the volume of the optically active component, leading to improved cell performance.<sup>15</sup> If the pH of the coating oxides is more basic than that of TiO<sub>2</sub>, the carboxyl groups in a dye molecule are more easily adsorbed to the surface of the coating layers.

A typical wide band gap oxide, MgO, was employed to improve the energy conversion efficiency of a TiO<sub>2</sub>-based solar cell. Kumara et al.<sup>21</sup> and Taguchi et al.<sup>22</sup> reported that the MgO shell can retard the recombination of holes

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and back-transferred electrons. In addition to the retarded recombination, however, the MgO nanolayer has another potential advantage to improve the conversion efficiency. The specific surface area of the MgO layer can be increased significantly by controlling its preparation route. A topotactic thermal decomposition of hygroscopic  $\text{Mg}(\text{OH})_2$  gel produces a nanoporous MgO layer because of a difference in the density between the  $\text{Mg}(\text{OH})_2$  gel and  $\text{MgO}$ .<sup>23–25</sup> In this study, a nanoporous MgO layer is coated onto  $\text{TiO}_2$  core nanoparticles by using a topotactic reaction for the first time, and the effect of the MgO layer on the solar cell performance is evaluated. The energy conversion efficiency of MgO-coated  $\text{TiO}_2$  increases by 45% compared with that of pure  $\text{TiO}_2$ .

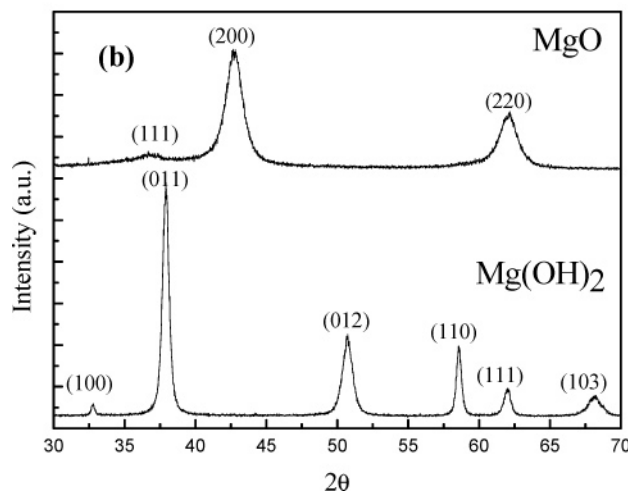
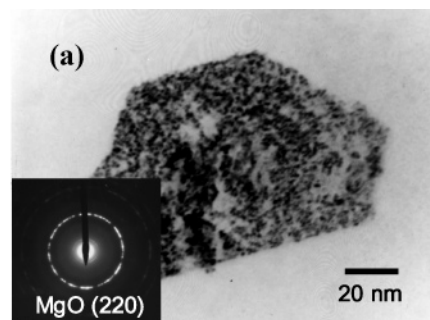
### Experimental Section

For the preparation of MgO-coated  $\text{TiO}_2$  nanoparticles (P25, Degussa), magnesium methoxide (Aldrich; 7.6 wt % in methanol) was used as a coating solution. On the basis of the results of a preliminary experiment, the composition of  $\text{TiO}_2/0.6$  wt % MgO was selected. Mixtures containing 3 g of  $\text{TiO}_2$  powder, 0.62 mL of magnesium methoxide, and 10 mL of methanol were ball-milled. The mixture was then hydrolyzed with 20 mL of deionized water at 80 °C. The hydrolysate was centrifuged and redispersed in a mixture of 10 mL of ethanol, 9.6 mL of deionized water, and 0.4 mL of acetylacetone, resulting in a homogeneous slurry. As a companion set, a batch of pure  $\text{TiO}_2$  without MgO was prepared, and its photovoltaic properties were investigated.

A plate of transparent conducting glass (indium tin oxide, Samsung SDI) was cut into  $2 \times 2$  cm pieces. Strips of Scotch tape (40  $\mu\text{m}$  thick) were used to cover three sides of glass substrate, and approximately 100  $\mu\text{L}$  of the slurry was spread over the surface with a glass rod sliding on the scotch tape spacers. The dimension of the  $\text{TiO}_2$  electrodes was  $0.5 \times 0.5$  cm. After being dried at room temperature, the coated electrodes were heat-treated for 1 h at 400 °C. The thickness of the resultant electrodes was approximately 8  $\mu\text{m}$ .

For the fabrication of the solar cells, the resultant electrodes were immersed overnight in a solution of ruthenium dye [ruthenium (2,2'-bipyridyl-4,4'-dicarboxylate)<sub>2</sub>(NCS)<sub>2</sub> (SOLARONIX)] dissolved in ethanol. Subsequently, the electrode with the dye-adsorbed film was assembled with a Pt-sputtered glass electrode to form a sandwich-type dye cell. A drop of an electrolyte solution (SOLARONIX, Iodolyte TG-50; 90 vol % of tetraethylene glycol dimethyl ether, 2 wt % of iodine) was infiltrated into the cell. The photocurrent–voltage characteristics of each film were measured with a potentiostat (model: CHI 608A, CH Instruments) under the illumination of AM 1.5 (ORIEL 91193 1000 W xenon lamp; intensity = 100  $\text{mW}/\text{cm}^2$ ).

Diffuse reflectance UV–Vis spectra of MgO-coated and uncoated  $\text{TiO}_2$  electrodes were measured using a UV–Vis–NIR spectrophotometer with an integrating sphere accessory. We desorbed the dye molecules from the photoelectrodes by soaking them in alkaline alcoholic solutions. The optical absorption of the dye solutions was also characterized to compare the degree of adsorbed dye molecules. Transmission electron microscopy (TEM; model: JEM 3000F) was used to investigate the uniformity of the MgO layer coated on nanocrystalline  $\text{TiO}_2$ . To prepare the TEM specimens, the hydrolysates, centrifuged and dried at a room temperature, were heat-treated under the same conditions to the photoelectrodes, which yielded powders. The specific surface areas of the MgO-coated and uncoated  $\text{TiO}_2$  nanoparticles



**Figure 1.** (a) TEM micrographs of MgO nanoparticles obtained from the thermal decomposition of  $\text{Mg}(\text{OH})_2$  and (b) XRD powder patterns for  $\text{Mg}(\text{OH})_2$  and MgO obtained by thermal topotactic decomposition.

were measured using Brunauer–Emmett–Teller (BET) analysis (model ASAP 2400, Micrometrics Instrument Group, USA).

### Results and Discussion

The physical properties of the MgO particles themselves, which were prepared by using the hydrolysis/condensation and thermal decomposition, were first investigated to demonstrate the production of a highly porous structure with a high specific surface area. Figure 1a shows nanopores (bright spots) in a hexagonal-shaped MgO platelet. This nanoporous feature of the MgO particles (black spots) indicates that the intended topotactic thermal decomposition from  $\text{Mg}(\text{OH})_2$  to MgO was successfully achieved. The X-ray diffraction (XRD) data also supports the phase transformation from  $\text{Mg}(\text{OH})_2$  to MgO, as shown in Figure 1b. The measured specific surface area of the resultant MgO powder was as large as 396  $\text{m}^2/\text{g}$ , which is approximately 8 times larger than the calculated specific surface area of  $\text{Mg}(\text{OH})_2$  with a diameter of 50 nm. This substantial increase in the surface area shows that the topotactic reaction from  $\text{Mg}(\text{OH})_2$  to MgO generates nanopores. The pore size of the MgO powder was in the range of 3–5 nm, which was determined by a TEM micrograph (Figure 1a). This nanopore size is comparable with the reportedly known pore size distribution of MgO obtained via the topotactic thermal decomposition of  $\text{Mg}(\text{OH})_2$ .<sup>23–25</sup> To form highly nanoporous MgO shells on  $\text{TiO}_2$  surfaces, the same hydrolysis/condensation condition used for the fabrication of MgO-only particles was applied to prepare the  $\text{Mg}(\text{OH})_2$  gel-coated  $\text{TiO}_2$  particles, which were then thermally decomposed after being coated onto an ITO glass surface (Supporting Information 1). The particles of the  $\text{TiO}_2$ –MgO core–shell structure exhibited a high surface area, 56.1  $\text{m}^2/\text{g}$ , which was larger than that

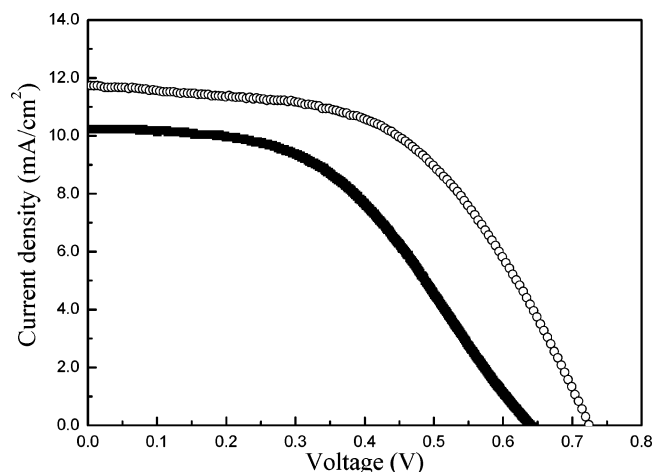
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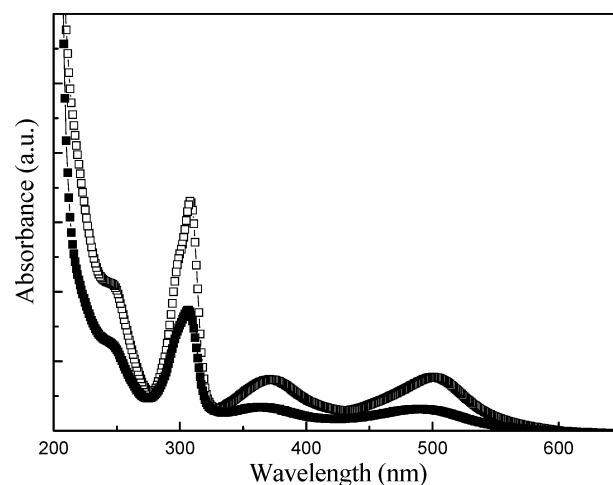
**Figure 2.** Photocurrent–voltage characteristics of dye-sensitized TiO<sub>2</sub> and MgO-coated TiO<sub>2</sub> electrodes (■ = 0 wt %, ○ = 0.6 wt %).

**Table 1. Photoelectric Conversion Efficiency ( $\eta$ ) of DSSCs Based on TiO<sub>2</sub> and MgO-Coated TiO<sub>2</sub> Electrodes**

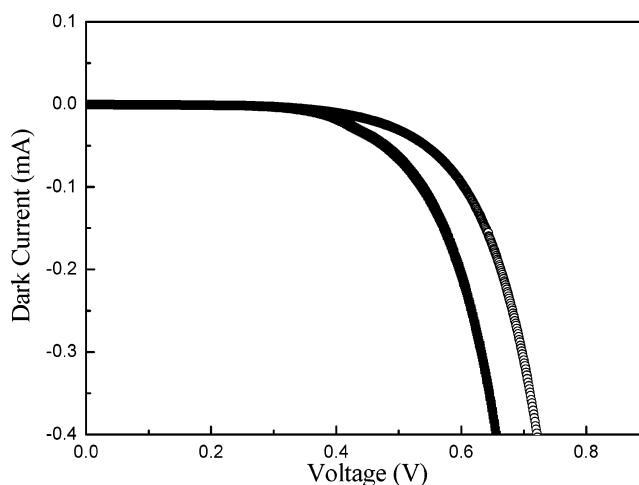
sample	$V_{oc}$ (V)	$I_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
bare TiO <sub>2</sub>	0.64	10.2	47.3	3.1
MgO-coated TiO <sub>2</sub>	0.72	11.7	53.5	4.5

of the uncoated TiO<sub>2</sub> particles, 47.5 m<sup>2</sup>/g. Because only 0.6 wt % of the MgO coated the TiO<sub>2</sub> particles, the increase in the specific surface area indicates that the coated MgO layer itself, obtained by the topotactic reaction, has a very high nanoporous structure.

Figure 2 shows the photocurrent–voltage curves of the DSSCs having the bare TiO<sub>2</sub> and the nanoporous MgO-coated TiO<sub>2</sub> electrodes. As summarized in Table 1, the short circuit current,  $I_{sc}$ , increases to 11.7 mA/cm<sup>2</sup> from the 10.2 mA/cm<sup>2</sup> of the bare TiO<sub>2</sub>. The open circuit voltage,  $V_{oc}$ , and the fill factor (FF) also increase by using the MgO nanolayer. Thus, the cell efficiency is significantly improved from 3.1 to 4.5% (Supporting Information 2). In previous works on MgO-coated TiO<sub>2</sub>,<sup>21,22</sup> the MgO was prepared from a non- or slightly hydrolyzed solution, and a significant increase in the short circuit currents was not observed. This indicates that the enhanced cell performance of previous works on nonporous MgO was obtained mainly by retarding the charge recombination at interfaces; that is, the back electron transfer from TiO<sub>2</sub> to electrolyte, though the basicity of nonporous MgO slightly increases the dye adsorption.<sup>20</sup> In this report, however, the improvement in cell efficiency is attributed to the enhanced dye adsorption as well as retardation of the back electron transfer. The increase in the surface area of MgO-coated TiO<sub>2</sub>, as shown in the BET analysis, demonstrates that the MgO layer from topotactic reaction favors the dye adsorption because of the nanoporous structure in the MgO layer. A change in the relative amount of adsorbed dye molecules demonstrates the merit of our approach to utilize the nanoporous MgO layer in fostering the dye adsorption. Figure 3 shows the optical absorbance spectra of solutions in which the dye molecules on the surface of the electrode were dissolved. The degree of dye adsorption on the electrode is proportional to the intensity of the optical absorption of dye. The coating of the MgO nanolayer apparently increases the amount of adsorbed dye molecules (approximately 2 times). The difference between the 20% increase in surface area and the 100% increase in dye adsorption may be attributed to dyes that fill the nanopores in the MgO layer. The dye penetrating the nanopores in the MgO layer is expected



**Figure 3.** UV-visible absorption spectra of the desorbed dye solution from each TiO<sub>2</sub> photoelectrode (■ = 0 wt %, □ = 0.6 wt %).



**Figure 4.** Dark current characteristics of dye-sensitized TiO<sub>2</sub> and MgO-coated TiO<sub>2</sub> electrodes (■ = 0 wt %, ○ = 0.6 wt %).

to fill the pores as well as form a monolayer coating on the surface of the MgO layer. Similar increases in the photocurrent (15%) and the BET specific surface area (18%) in MgO-coated TiO<sub>2</sub> confirm this suggestion that a part of adsorbed dye fills the nanopores, because the photocurrent of DSSC mainly results from the dye directly contacting the TiO<sub>2</sub> electrode.

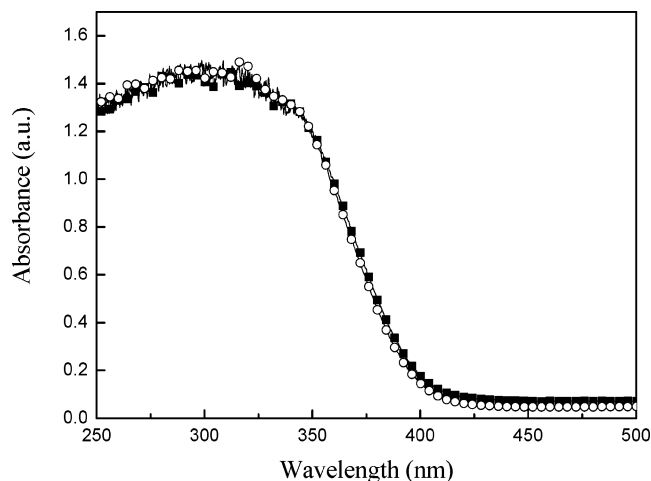
In addition to the enhanced dye adsorption, the retarded charge recombination behavior can contribute to the increase in the solar cell performance of our study. The dark current characteristics in Figure 4 show that the nanoporous MgO shell in this study reduces the charge recombination. The observation of retarded charge recombination is consistent with previous reports on various thin insulating layers.<sup>15,20</sup>

To clarify the origin of the enhanced solar cell performance, the effects of other possible parameters on the cell surface, such as light scattering and light absorption, should be examined. Light scattering, which can increase the energy conversion efficiency, becomes significant in the regime of red light (over 700 nm) when the effective scattering diameter of the particles is over hundreds of nanometers.<sup>4,26–28</sup> However, the particle size in this study is in the range of 20–30 nm in diameter. Thus, the change

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**Figure 5.** UV-visible absorption spectra of  $\text{TiO}_2$  and MgO-coated  $\text{TiO}_2$  electrodes (■ = 0 wt %, ○ = 0.6 wt %).

in light scattering caused by the MgO overlayers is negligible. Another possible factor to change the energy conversion efficiency is the change in the light absorption. The UV–Vis spectra in Figure 5 show that the light absorption of MgO-coated  $\text{TiO}_2$  is similar to that of bare  $\text{TiO}_2$ , indicating that an MgO layer does not influence the overall light absorption. The negligible change in the light absorption by MgO coating can be explained by the difference in the band gap. Because the band gap of MgO

(6–7.8 eV) is much wider than that of  $\text{TiO}_2$  (3.0–3.2 eV), MgO coating does not change the light absorption of the  $\text{TiO}_2$  core in UV–Vis range. These results confirm that the enhanced dye adsorption and the retardation of the interfacial recombination are responsible for the enhanced solar cell performance.

In summary, the coating of a MgO layer onto  $\text{TiO}_2$  nanoparticles by the topotactic reaction improves the performance of the  $\text{TiO}_2$  electrode-based solar cell. The increase in the short circuit current for nanoporous MgO-coated  $\text{TiO}_2$  indicates that the high specific surface area of the nanoporous MgO layer promotes the adsorption of dye molecules and enhances the cell performance. In addition to improved dye adsorption, the MgO coating layer increased the energy conversion efficiency by retarding the electron–hole recombination, as shown in the increased open circuit voltage. These results demonstrate that the extrinsic factors, such as specific surface area, are very important to improving the performance of  $\text{TiO}_2$ -based solar cells.

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**Supporting Information Available:** TEM image of a MgO-coated  $\text{TiO}_2$  surface (Supporting Information 1) and the photocurrent–voltage characteristics and photoelectric conversion efficiency of various weight percents (wt %) of MgO coating (Supporting Information 2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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