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A comparative study of Be and Mg ions adsorbed on TiO_2 photoelectrodes on interfacial charge recombination in solar cells

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ABSTRACT

Be^{2+} and Mg^{2+} ions were adsorbed on a TiO_2 surface, and the resulting photoelectrodes were applied in dye-sensitized solar cells. Be^{2+} modification led to an increase in electron collection, electron injection, and dye regeneration efficiency, thereby increasing the short-circuit current. It was also found that the enhancements in both open-circuit voltage and fill factor of the device with Be^{2+}-modified TiO_2 were due to the reduced charge recombination between the photoinjected electrons and I_3^-. Be^{2+} modification resulted in an approximately 14% improvement in power conversion efficiency, whereas charge recombination was barely reduced in the case of Mg^{2+} modification.

Introduction

As a third-generation photovoltaic cell, the dye-sensitized solar cell (DSSC) is a disruptive technology that can be used to produce electricity in a wide range of lighting conditions (indoors and outdoors) enabling the user to convert both artificial and natural light into electrical energy for application in a broad range of electronic devices. Over two decades since the first report on DSSCs [1], a power conversion efficiency (PCE) of 14.3% has been achieved in a co-sensitized solar cell, with a cobalt (II/III) complex redox electrolyte solution and graphene nanoplates as the counter-electrode [2]. However, DSSCs still cannot compete with Si- or inorganic semiconductor-based solar cells in the large-scale energy production market owing to their insufficient PCE and poor reliability. In DSSCs, photon-to-current conversion is achieved through the injection of electrons from the photoexcited dyes into the conduction band of the TiO_2 photoelectrode, the subsequent completion of the dye regeneration, and hole transportation to the counter electrode. The electrons and holes are eventually collected in the front and counter electrodes, respectively. Unlike in other solar cells, in DSSCs, an electron-transporting TiO_2 layer is in direct contact with the hole conductor (electrolyte), inducing interfacial charge recombination between the photoinjected electrons and ions in the electrolyte. This may cause a loss of approximately 300 mV in the open-circuit voltage (V_{oc}) relative to the theoretical value, leading to a rapid decrease in the conversion efficiency [3]. Surface modification of TiO_2 could lead to a reduction in interfacial charge recombination between the TiO_2 electrode and electrolytes by the formation of an energy barrier or surface-state passivation on the TiO_2 surfaces [4]. Thus, to reduce interfacial charge recombination, various surface modifiers have been incorporated on the surface of the TiO_2 photoelectrodes, including metal oxides [5–13], metal carbonates [14,15], organic co-adsorbents [16,17], and others [18,19], and the resulting DSSCs have shown an enhancement in PCE that can be attributed to an improved V_{oc}.

TiO_2 nanoparticles have been widely used for the removal of metal ions from waste water, because they exhibit strong adsorption of metal ions [20–22]. In this study, the metal ion-adsorbing ability of TiO_2 was utilized to control electron transfer in the DSSCs, such as interfacial charge recombination, electron injection, or dye regeneration. We selected Mg^{2+} and Be^{2+} ions as the TiO_2 surface modifiers. The TiO_2 surfaces were directly modified with an aqueous metal sulfate solution via a simple dipping process, and the resulting electrodes were used as the photoelectrodes of the DSSCs. We expected the metal ions adsorbed on TiO_2 surface to reduce the interfacial charge recombination, resulting in an improvement in the performance of the DSSCs. DSSCs with metal ion-modified photoelectrodes were fabricated, and the effects of the surface modification on the photovoltaic performance of the cells were examined.

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Experimental

Materials

Commercial fluorine-doped tin oxide (FTO; sheet resistance ~7 Ω/square) glass (TCO22-7), TiO_2 paste for the photoelectrode (Ti-nanoxide T/SP), TiO_2 paste for the scattering layer (Ti-nanoxide R/SP), N719 dye (Ruthenizer 535-bisTBA), hot-melt adhesive (SX1170-60PF, Surlyn), and iodide-based electrolytes (AN-50) were purchased from Solaronix. Magnesium sulfate ($MgSO_4$, MS), beryllium sulfate ($BeSO_4$, BS), and $TiCl_4$ were purchased from Sigma–Aldrich Co. LLC. Platinum paste (PT-1, Dyesol-Timo) was selected as the source for the Pt counter-electrode. All the chemicals were used without further purification.

Preparation of DSSCs

The FTO glasses were cleaned in a detergent solution using sonication for 20 min and then thoroughly rinsed with deionized water and ethanol. After ultrasonic cleaning, the FTO glasses were immersed in a 40-mM $TiCl_4$ solution at 70 °C for 30 min and then washed with water and ethanol. One active TiO_2 layer, which formed on the FTO glass, was prepared via doctor-blade coating with the TiO_2 paste. Additionally, a TiO_2 layer composed of approximately 400-nm-diameter particles was deposited on the active TiO_2 layer and then calcinated at 500 °C for 60 min. Finally, the TiO_2 films were again treated with a 40-mM $TiCl_4$ solution and annealed at 500 °C for 60 min; thus, TiO_2/FTO electrodes with 10-nm-thick TiO_2 layers were prepared. The electrodes were soaked in an aqueous solution (5×10^{-4} M) of MS or BS for 0–60 min to deposit metal ions onto the TiO_2 layers. Subsequently, the resulting electrodes were rinsed with water and ethanol, and then dried at 65 °C for 10 min to produce the modified photoelectrodes (Mg^{2+}- or Be^{2+}-TiO_2/FTO). The bare TiO_2/FTO and Mg^{2+}- or Be^{2+}-TiO_2/FTO photoelectrodes were separately immersed into 0.5 mM of N719 dye solution (acetonitrile/*tert*-butyl alcohol, v/v = 1) for 24 h to obtain working electrodes.

To fabricate the counter electrode, two holes were formed in the FTO glass with a drill, and then cleaned using the method described above. A Pt layer was formed on the FTO glass via the doctor-blade method using Pt paste, followed by a calcination process at 400 °C for 30 min. The thermally treated platinum counter-electrodes were placed on the photoelectrodes and sealed with a 60-μm-thick sealing material. The electrolyte was introduced into the cells through one of the two small holes drilled on the counter-electrodes to produce DSSCs with a 25 mm^2 active area.

Measurements

X-ray photoelectron spectroscopy (XPS) was performed using a VG Multilab ESCA 2000 (ThermoVG Scientific) instrument with Mg Kα radiation. The C 1s photoelectron peak (binding energy of 284.6 eV) was used as an energy reference. The photocurrent–voltage measurement was performed using a CompactStat (Ivium Technologies B.V.) potentiostat and a PEC-L01 solar simulator system equipped with a 150 W xenon arc lamp (Peccell Technologies, Inc.). The light intensity was adjusted to 1 sun (100 mW/cm^2) with a silicon photodiode (model PEC-SI01, Peccell Technologies, Inc.). The ultraviolet-visible light (UV–vis) absorption spectra were obtained using a SINCO NEOSYS-2000 spectrophotometer. Both the electrochemical impedance spectroscopic (EIS) analysis and the open-circuit voltage decay (OCVD) measurements were performed using an electrochemical analyzer (CompactStat, Ivium Technologies B.V.). The active areas of the dye-adsorbed TiO_2 films were estimated using a digital microscope camera (OLYMPUS SZ61) with an image analysis software.

Results and discussion

Adsorption of metal ions on TiO_2 surface

It is well known that TiO_2 nanoparticles have strong adsorption capacities for metal ions such as Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} [20–22]. To incorporate the metal ions on the TiO_2 surface, the bare TiO_2/FTO was soaked in an aqueous MS or BS solution, then rinsed with water and dried. The soaking time was varied from 15 to 60 min to produce Mg^{2+}(15, 30, 45, and 60)-TiO_2/FTO or Be^{2+}(15, 30, 45, and 60)-TiO_2/FTO, where "(15)" indicates that the dipping time was 15 min, and so on. The incorporation of Mg^{2+} and Be^{2+} on the TiO_2 surface was verified by XPS measurements. Fig. 1 shows XPS spectra for Mg^{2+}(15)-TiO_2/FTO and Be^{2+}(15)-TiO_2/FTO. The peaks detected at 1305.26 and 50.80 eV correspond to the binding energy of Mg 1 s and Mg 2p, respectively. For Be^{2+}(15)-TiO_2/FTO, a peak was observed at 113.88 eV, which corresponds to the binding energy of Be 1s. Thus, it was confirmed that by simple dipping in each solution, metal ions were adsorbed on the TiO_2 surface. In addition, S $2p_{3/2}$ peaks originating from sulfate ions were also detected at approximately 169 eV in both electrodes (not shown).

Performance variations of DSSCs with bare and metal ion-modified TiO_2 photoelectrodes

The DSSCs with the metal ion-modified photoelectrodes were fabricated, and their photovoltaic properties were compared with

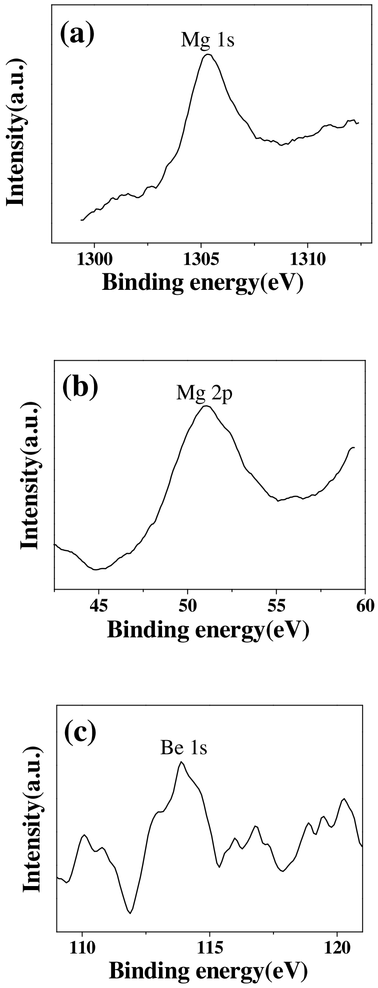

Fig. 1. XPS spectra for (a) Mg 1s, (b) Mg 2p from Mg^{2+}(15)-TiO_2/FTO, and (c) Be 1s from Be^{2+}(15)-TiO_2/FTO.

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