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Bilayer nanoporous electrodes for dye sensitized solar cells

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The fabrication of a new bilayer TiO_2/Nb_2O_5 nanoporous electrode that improves the performance of dye sensitized solar cells by more than 35% is reported.

The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSSCs) may be attributed to the nanoporous TiO_2 electrodes.[1] These electrodes consist of nanosize semiconductor colloids that are sintered on a transparent conducting substrate resulting in a porous geometry and a very large surface area. Both the low absorbance of dye monolayers and the low efficiency of dye multilayers necessitate the large surface area. However, the resulting electrode geometry introduces special characteristics, some of which reduce the performance of the DSSCs.[2–4] One of these characteristics relates to the small size of the individual colloidal particles that cannot support a high space charge.[2,4,5] In other words an energy barrier is not formed at the electrode–electrolyte interface.

Upon illumination of a DSSC, an electron is injected from the dye into the TiO_2 film followed by a hole transfer to the electrolyte[1,6] The injected electrons must cross the TiO_2 film and reach the conducting substrate, while the oxidized ions diffuse towards the back electrode where they are re-reduced.[1,6] The porous geometry that permits the presence of the electrolyte through the entire electrode provides a high surface area for recombination between the injected electrons and the holes in solution[2,7] In the absence of an energy barrier at the electrode–electrolyte interface, the rate of this recombination process may be very high depending on the properties of the hole carrier.[2,5,8,9] For this reason, DSSCs utilizing the I^-/I_3^- redox couple perform better than similar cells consisting of faster couples.[10] Furthermore, part of the low efficiencies observed with solid electrolytes is attributed to this recombination process.[3] The formation of an energy barrier at the surface of the TiO_2 electrode that will enable the use of various mediators has the prospect of improving the performance of DSSCs significantly.

We report here on the fabrication of a nanoporous wide band gap semiconductor electrode that has an inherent energy barrier at its surface. To the best of our knowledge, this is the first time such an electrode has been reported. The new electrode consists of an inner nanoporous TiO_2 matrix covered with a thin layer of Nb_2O_5. The conduction band potential of Nb_2O_5 (0 V *vs.* NHE at pH 0) is *ca.* 100 mV more negative than that of the TiO_2.[11] As illustrated in Fig. 1, this potential difference forms an energy barrier at the electrode–electrolyte interface, which can reduce the rate of recombination processes of the photoinjected electrons. A comparison of two similar DSSCs that differ only in their nanoporous electrodes, shows that the new bilayer electrode is superior to the standard one with respect to all cell parameters. This superiority measured with many cells results in a 35% increase of the overall conversion efficiency.

The TiO_2 nanoporous matrix of 6 μm thickness was prepared from colloids with particles of 23 nm diameter. The colloid and the matrix preparation methods are reported elsewhere.[12] The Nb_2O_5 coating was prepared by dipping the sintered TiO_2 matrix in a dry solution of 0.005 M niobium isopropoxide in isopropyl alcohol for 30 s, followed by washing with dry isopropyl alcohol and sintering at 500 °C in air for 30 min. The dipping was performed under dry nitrogen atmosphere. The thickness of the electrode measured with a Mitutoyo, Surftest SV 500 profilometer did not change upon coating. XPS measurements of the coated electrodes show that the average metal mol fraction of Nb was 36% with the remainder Ti. Given this molar ratio, a 2.7 nm thick Nb_2O_5 layer is calculated when assuming that the TiO_2 colloids are spherical and single sized, and that the Nb_2O_5 coating is uniform.

A sandwich-type configuration was employed to measure the DSSCs. A Pt coated F-doped SnO_2 film was used as a counter electrode, and 0.5 M Li/0.05 M I_2 in 1 : 1 acetonitrile–NMO was used as electrolyte. The dye [*cis*-di(isothiocyanato)-*N*-bis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II), (N3)] was adsorbed by immersing the electrodes overnight in a 0.5 mM ethanol solution of the dye. The oxidation potential of the dye (*ca.* 1.09 V *vs.* NHE in acetonitrile) is sufficient to allow injection into both TiO_2 and Nb_2O_5.[11] The amount of dye adsorbed on the electrode was measured by visible absorption of the electrode using a HP 8453 spectrophotometer. Illumination of the cell was conducted using a calibrated Xe lamp. IPCE measurements were performed using a ScinceTech 9010 monochromator scaled to 6 nm bandwidth.

We describe here a comparison of two typical DSSCs that differ in their type of electrode. One cell contained the new bilayer electrode and the other served as a reference, consisting of a standard nanoporous TiO_2 electrode. Both cells were studied under similar conditions. The reference electrode and the TiO_2 matrix were made from the same batch and separated only after the first sintering process. After the Nb_2O_5 coating of the TiO_2 matrix was performed, both electrodes were sintered again to ensure similarity. The thickness of both electrodes was 6 μm, and the same amount of dye was adsorbed on both films as confirmed by absorption spectra. Finally, the undyed electrodes had the same transparent appearance showing transmission spectra that differed slightly only in the band gap region. Under illumination equivalent to sunlight, Nb_2O_5 coating of the TiO_2 resulted in an increase of all cell parameters. The photocurrent increased from 10.2 to 11.4 mA cm^{-2}, the photovoltage from 659 to 732 mV, and the fill factor from 51.1 to 56.4%. As a result, the maximum power of the cell was increased from 3.45 to 4.70 mW cm^{-2}.

The improved cell performance achieved by the new bilayer electrode may be attributed to the energy barrier formed by the

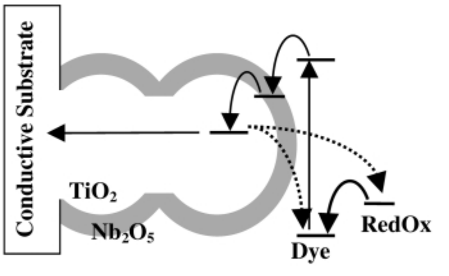

Fig. 1 A schematic view of the new bilayer nanoporous electrode which consists of a nanoporous TiO_2 matrix covered with a thin layer of Nb_2O_5. The Nb_2O_5 coating forms an inherent energy barrier at the electrode–electrolyte interface, which reduces the recombination rate of the photoinjected electrons.

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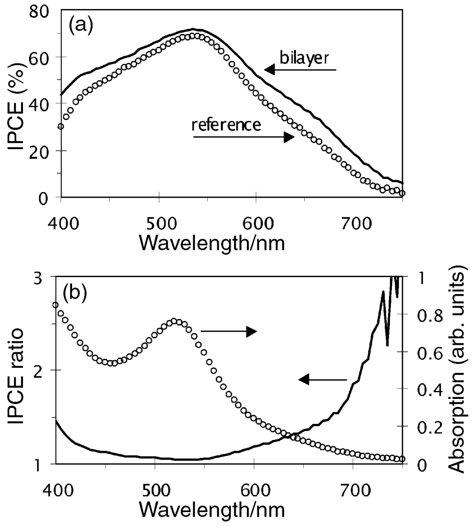

Fig. 2 (a) IPCE curves of the reference dye sensitized solar cell and the cell containing the bilayer electrode. The IPCE curves resemble the absorption spectrum of the electrodes shown in (b) which shows the ratio between the IPCE values of the two solar cells as a function of the illumination wavelength revealing its wavelength dependence.

deposition of the thin Nb_2O_5 layer. The Nb_2O_5 layer apparently decreases the rate of recombination of the photoinjected electrons with the dye and the electrolyte. This phenomenon is revealed best from incident photon to current efficiency (IPCE) measurements for the two cells. As shown in Fig. 2(a) the curves of both cells resemble the absorption spectrum of the N3 dye. The measured IPCE values of the cell containing the bilayer electrode are higher than those of the reference cell throughout the visible spectrum. However, the improvement in the conversion efficiency is wavelength dependent as indicated by the ratio between the IPCE values of the two cells (the improvement factor). Fig. 2(b) shows that this factor increases at illumination wavelengths in which the absorption coefficient of the dye becomes low.

The improved performance evident from Fig. 2(a) is not necessarily the result of a change in the collection efficiency. This improvement can be related to other factors, such as the injection yield.[1] However, the wavelength dependence of the improvement factor can be directly related to the electron collection.[13] The mean distance a photoinjected electron must diffuse in order to reach the current collector increases as the absorption coefficient of the dye decreases thus changing the light absorption profile. This phenomenon means that recombination events are expected to increase as the absorption coefficient of the dye decreases.[13] In other words, a change in the rate of recombination is expected to have a more significant effect at the low dye absorption coefficient regions. Fig. 2(b) indicates that this is the case of the new bilayer electrode.

The results presented above clearly demonstrate that the bilayer electrodes are superior to the standard single material nanoporous electrodes in terms of the performance of DSSCs. These results suggest that the improvement is achieved by the formation of an energy barrier at the electrode–electrolyte interface, which slows the recombination process. However at this stage of research we lack information on the quality of the coating with respect to its homogeneity throughout the film which affects the ability to determine the exact thickness of the coating. In addition, it is still unclear to what extent the new electrode can improve the performance of DSSCs in which mediators other than the I^-/I_3^--based electrolyte are used. Research towards better understanding of this system and further performance improvement are currently being undertaken.

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