

**Dye-sensitized Photoelectrochemical Cells
Based on Nanocrystalline SnO₂ Films:
Implications on Nature of Charge
Recombinations and Transport in
Dye-sensitized Semiconductor Nanostructures**

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Dye-sensitized (DS) photoelectrochemical cells (PECs) made from nanocrystalline films of TiO₂ have efficiencies (η) 10 short-circuit photocurrents I_{sc} 18 mA cm⁻², open circuit voltages V_{oc} 800 mV. When the Ru-N3 dye is used as the sensitizer. Attempts to construct cells of comparable performance with other familiar high band gap semiconducting oxides ZnO and SnO₂ has not been successful. However, the DS composite oxide system SnO₂/ZnO yields photovoltaic out-put similar to that of TiO₂ based cells. There are also other reports, which suggest that composite films improve the incident photon to photocurrent and energy conversion efficiencies of the DS PECs 3-5.

We have found that although nanocrystalline SnO₂ (crystalline dimension 5- 10 nm) based DS PECs have very low V_{oc} (325-375 mV) and η (< 1). However, on coating an ultra-thin film of MgO (1 nm), V_{oc} and η are increased to 650-700 mV and 6.5% enhancement of I_{sc} as well. Even more remarkable is our observation on dye-sensitization of Sb-doped nanocrystalline SnO₂ films. DS PECs made from Sb-doped SnO₂ films have barely detectable photovoltaic response (I_{sc} < 0.1 mA, V_{oc} < 0.1 mV at 1000 W m⁻² 1.5 AM illumination). However when a thin MgO shell is deposited on Sb-doped SnO₂ crystallites, the cell was found to generate I_{sc} 6.0 mA cm⁻², V_{oc} 550 mV under same conditions.

Simple experiments proved that dye is coated on the outer MgO shell. Therefore we conclude that the excited dye molecules on the thin insulating MgO shell injects electrons to the conduction band (CB) of SnO₂ via tunneling. When the electron relaxes to the bottom of the CB of SnO₂, the MgO barrier prevents recombination (e⁻ with D⁺ or an acceptor in the electrolyte). Important questions, we could answer on basis of above findings are: (1) Why does DS PECs made from nanocrystalline films of TiO₂ show excellent photovoltaic response in contrast to cells made from SnO₂ or ZnO only. (2) Why is insulating or semiconducting shells on DS TiO₂ based cells do not show significant photovoltaic enhancement. Our explanation is that a crucial parameter determining the extent of recombinations in DS semiconductor nanocrystalline cells is the effective mass of the electron. Electrons injected in to the CB falls into shallow thermally extractable traps located DE ($\sim kT$, T- room temper-

ature) below the bottom of the CB. Such electrons are described by the wave function $Y(r) = \text{Exp}(-r/a)$, where r = distance measured from the trapping site and $a = (\hbar/2m^*DE)^{1/2}$. For SnO₂ ($m^* = 0.1 m_e$) the parameter a (~ 4 nm) becomes same order of magnitude as the crystallite dimension. In this situation, the trapped electron would readily leak to the out-side instead of getting thermally excited back to the CB. Recombinations reduce I_{sc} and also V_{oc} is decreased as the build up of the quasi-fermi level is prevented. The effect is more pronounced in Sb doped SnO₂, because the ionized donor acts as a trapping site and in the absence of a MgO shell, recombinations occur very rapidly. The general belief is that the charge transport in DS nanocrystalline semiconductor films depends on traps. Two possibilities are trap to trap hopping or transport via CB as a result of trapping and detrapping. Thus when the effective mass is small, trap mediated transport leads to recombinations. In the case of TiO₂, the large electron effective mass ($\sim 10 m_e$) confines the trapped electron to the crystallite. The low m^* is advantageous in other aspects. When the m^* is small, distinct minibands could be formed permitting dissipationless transport. We believe that DS composite nanocrystalline systems could lead to more efficient solar cells and find other device applications.

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