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## Dye-Sensitized Solar Cells Based on Nanostructured Semiconductor Oxide Ceramics with Ultra-Thin Barrier Layers

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Nanostructured high band-gap oxide semiconductor ceramics are extensively investigated to understand their unique properties and applications in dye-sensitized solar cells, sensors, supercapacitors and other electronic and electrochemical devices. The unusual properties of these materials originate from large surface-area to bulk-volume ratio, quantum size effects and formation of space charge layers of dimensions comparable to the crystallite size in depletion of carriers. A prototype device demonstrating the unique properties of nanostructured semiconductor ceramics is the dye-sensitized solar cell. The original version of this device is based on TiO<sub>2</sub> and other familiar stable oxides SnO<sub>2</sub> and ZnO yield lower efficiencies owing to faster recombination. SnO<sub>2</sub> admits faster electron transport because of the lower effective electron mass, but the same property enhances recombination. Ultra-thin barrier layers insulating stannates coated over the SnO<sub>2</sub> crystallites by glazing with alkaline earth chlorides increases the efficiency from ~1 to 6.6%.

**Keywords** Nanostructured ceramics; Dye-sensitized solar cells; Tin oxide; Titanium dioxide; Alkaline earth stannates

#### 1. Introduction

Electroceramics constituted of submicron or nano-sized grains and composites incorporating such materials possess unusual electrical, mechanical and chemical properties. They are extensively exploited for applications in diverse variety of areas, notably chemical sensors, catalysts, dye-sensitized solar cells and supercapictors [1–9]. Nanostructured ceramics (NCs) of oxide semiconductors [9, 10] affords ready fabrication into thin films and bulk solids amenable to compositation with inorganic and organic compounds in the solid or liquid form. Their peculiar properties originate from excessively large surface–area to bulk-volume ratio, quantum size effects and the possibility of near complete depletion or accumulation charges, modifying the microenvironment [11–14]. Liquids, polymers and

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nanocrystallites of inorganic substances impregnated into the porous matrix form interpenetrating networks, effectively junctions of area several orders larger than the geometrical cross-section [15–19]. The nature of the surface determines the gross properties of NCs to the same extent as the bulk properties of the constituting chemical material [20]. Trapping and detrapping of carriers greatly influence electrical transport and confinement of charges to the nanocrystalline network [21, 22]. Transport properties can be altered by surface deposition of ultra-thin over layers of inorganic materials, polymers or adsorption of molecular species that bonds to the surface [21, 23]. Again the modulation of the grain interface in NCs is believed to yield systems of giant permittivity [24, 25] for use as a gate dielectric material or in supercapacitors for energy storage.

A prototype device elegantly displaying the virtues of NCs is the dye-sensitized solar cell (DSSC) based on porous films of  $TiO_2$  deposited on conducting tin oxide glass [26]. These films constituted of TiO<sub>2</sub> anatase crystallites of median size  $\sim$ 30 nm, thickness  $\sim 10 \,\mu\text{m}$  have a roughness factor of  $\sim 1000$ . Films are coated with a monolayer of a suitable dye and a lightly platinized conducting tin oxide glass plate pressed onto the dyed surface serves as the counter electrode. The capillary space between the plates is filled with a redox electrolyte. On illumination of the film, excited dye molecules inject electrons to the conduction band of  $TiO_2$  forming immobile dye cations. An electron donor species in the electrolyte quickly scavenge the cation charge and transport it to the counter electrode driving a current through the external circuit. Although the dye lightly covers the  $TiO_2$ crystallites at monolayer level, the large roughness factor of the film ensures almost full absorption of incident photons generating a photocurrent at quantum efficiency very close to unity. The other peculiar property of the system is efficient diffusive transport of injected electrons to the back contact across the interconnected crystallites. Here the depletion of electrons in  $TiO_2$  into the electrolyte and passivation of the  $TiO_2$  surface by the adsorbed dye facilitate electron transport suppressing recombination [23, 27]. The efficiency of the optimized dye-DSSCs based on TiO2 in its present form exceeds 10% [28]. Although oxides of tin and zinc have similar band-gaps and band positions as  $TiO_2$ , cells made from these oxides have efficiencies below 2%, indicating faster recombination. SnO<sub>2</sub> has advantages, because of the lower electron effective mass compared to TiO<sub>2</sub> and therefore faster electron transport. Unfortunately, lower effective electron mass increases the recombination loss (29). Efficiencies comparable to  $TiO_2$  cells have been obtained when small quantities of insulating oxides (MgO, ZnO) are incorporated to the SnO<sub>2</sub> ceramic [29, 30]. Although there is evidence for core/shell structure formation in these systems, thin shell acting as a barrier, the composition and morphology of the ceramic has not been elucidated conclusively. Furthermore the procedure adopted for barrier layer deposition needs to be a relatively low temperature process to prevent the growth of the nano-crystallites and softening glass on which the ceramic is deposited. The parent substance used to produce outer shells of MgO, ZnO are acetates of Mg and Zn respectively [29, 30]. Pyrolysis of acetates during sintering at  $\sim$ 500°C, yields oxides heavily contaminated with carbonaceous material. Alkaline earth oxides interact more strongly with  $SnO_2$  and  $TiO_2$  owing to stronger basicity and expected to create outer shells of  $BaSnO_3$  and  $BaTiO_3$  over the respective grains. Here the acetate route is unsuited because of the thermal resistance of alkaline earth acetates. Low temperature  $(<600^{\circ}C)$  pyrolysis of these acetates, yield carbonates instead of oxides. In this work a procedure for coating outer shells of stannates and titanates of alkaline earths on nanocrystalline films of  $SnO_2$  and  $TiO_2$  is described. Films are characterized and the photovoltaic parameters of the DSSCs fabricated measured. A conspicuous enhancement of the efficiency was observed when the SnO<sub>2</sub> crystallites are covered with shells alkaline earth stannates of appropriate thickness. The dielectric properties of SnO<sub>2</sub> and TiO<sub>2</sub> NCs with core/shell structure are also examined and correlated to DSSC performance.

#### 2. Experimental

Nanocrystalline films of  $SnO_2$  were coated on conducting fluorine doped tin oxide (FTO) glass plates by the following procedure. Colloidal aqueous solution of SnO<sub>2</sub> (Alfa Chemicals) was coagulated by adding HCl and the gel is dispersed in ethanol. Solution was sprayed onto FTO glass plates and sintered in air at 550°C for 30 min. Repetition of spraying enables controlling the film thickness (~10  $\mu$ M). SnO<sub>2</sub> films of core/shell structure with the stannates of alkaline earth elements as the shell were prepared by incorporation of varying amounts of CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub> dissolved in ethanol and following the same procedure as for the preparation of bare SnO<sub>2</sub> films. Films of SnO<sub>2</sub> conformably coated with an over layer of stannates were prepared by soaking the films in  $CaCl_2$ ,  $SrCl_2$  or BaCl<sub>2</sub> solutions and sintering the film in air at  $550^{\circ}$ C for 30 mins. In all experiments the sintered film was rinsed with water to remove any residual chloride and sintered again for few minutes at 400°C. The following procedure was used to prepare TiO<sub>2</sub> films. TiO<sub>2</sub> powder (Degussa P25), propan-2-ol (85%, 5 ml), 0.1 M HCl (0.2 ml) and the non-ionic surfactant Triton X100 are mixed and ground to form a thick paste and a thin film (10- $15 \,\mu$ m) is screen printed on FTO glass. Films are sintered in air  $550^{\circ}$ C for 30 min., allowed cool and coated with the dye Indoline 149 [31] by soaking them in the dye solution for 6 h. DSSCs were constructed with a Pt sputtered counter electrode clamped to the dyed surface and filling the capillary space with the electrolyte containing iodine and iodide. I-V characteristics of the cells were measured using a source meter with a solar simulator lamp (1000 Wm<sup>-2</sup>, 1.5 AM) as the light source and a monochromator was used to record the photocurrent action spectra. The flat-band potentials of NCs deposited on FTO glass were determined by Mott-Schottky measurements. A solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> was used as the supporting electrolyte and potentials were measured with respect to the standard calomel electrode (SCE). Samples for measurement of dielectric properties were prepared as described below. Dry oxide powders are compacted into pellets and sintered in air at 550°C, 750°C and 1000°C for 30 min. Dielectric constant; loss factor and their variation with frequency and temperature are measured using a LCR meter. Film and pellet samples are characterized by ESEM and XRD.

#### 3. Results and Discussion

During sintering alkaline earth chloride  $MCl_2$  (M = Ca, Sr, Ba) reacts with SnO<sub>2</sub> to form a shell of MSnO<sub>3</sub> (SnO<sub>2</sub>/MSnO<sub>3</sub>) over the grains via the reaction,

$$SnO_2 + MCl_2 + 1/2O_2 \rightarrow MSnO_3 + Cl_2$$
(1)

A similar reaction takes at the surface of  $TiO_2$  forming  $BaTiO_3$  (LiCl treatment yield shells of  $Li_2SnO_3$  and  $Li_2TiO_3$ ). The ESEM images of bare  $SnO_2$  and  $BaCl_2$  treated films appear distinctly different, the grain structure is clearer in the latter film (Fig. 1). The dense outer shell on  $SnO_2$  crystallites enhances secondary electron emission improving the image contrast. X-ray diffractogram of a porous  $SnO_2$  ceramic surface sintered after  $CaCl_2$  treatment is shown in Fig. 2. All the prominent peaks are those originating from  $CaSnO_3$  and texturing is evident from the high intensity of (111), (222), (021) peaks. Assuming the grains in ceramic are spheres of mean radius *R*, the shell thickness *T* is estimated from the formula,

$$T = (R/3) \left( W_s / W_c \right) \left( \rho_c / \rho_s \right) \tag{2}$$



Figure 1. ESEM images of ceramic films (a) SnO<sub>2</sub>/BaSnO<sub>2</sub> (b) SnO<sub>2</sub>.

where  $W_c = \text{wt. of the core material}$ ,  $W_s = \text{wt. of the shell material}$ ,  $\rho_c = \text{density of the core material}$ ,  $\rho_s = \text{density of the shell material}$ . In films where the over layer is conformably deposited. The thickness is calculated from the formula,

$$T = (W_s/\rho_s)S^{-1} \tag{3}$$

where *S* is the surface area of the film.

Table 1 gives the optimum efficiencies of DSSCs made from  $SnO_2$  and  $SnO_2/MSnO_3$ and the corresponding open-circuit voltage (Voc), short-circuit photocurrent (Isc), fill factor (FF) and film thickness. I-V plots and photocurrent action spectra are shown in Figs. 3 and 4. The efficiency of cell with the  $SnO_2$  film was 2.2%. In cells with core/shell structured

#### Table 1

Short-circuit photocurrent (Isc/mA cm<sup>-2</sup>), open-circuit voltage (Voc/mV), FF = fill factor (FF/%),  $\eta$  efficiency ( $\eta$ %) and shell thickness (T/nm) of DSSCs made from different films

Film	Т	Isc	Voc	FF	η
SnO <sub>2</sub>	_	9.3	524.4	49.5	2.2
SnO <sub>2</sub> /CaSnO <sub>3</sub>	0.74	15.9	586.6	66.2	6.2
SnO <sub>2</sub> +SrSnO <sub>3</sub>	1.0	14.1	596.3	58.6	4.9
$SnO_2 + BaSnO_3$	1.0	14.4	631.1	61.6	5.6
SnO <sub>2</sub> +CaSnO <sub>3</sub> (Ba doped)	1.0	16.2	628.3	65.1	6.6
SnO <sub>2</sub> /Li <sub>2</sub> SnO <sub>3</sub>	-	11.9	599.4	66.4	4.7



**Figure 2.** X-ray diffractogram of CaSnO<sub>3</sub> glazed SnO<sub>2</sub> ceramic showing peaks originating from textured CaSnO<sub>3</sub> film.



**Figure 3.** I-V characteristics of DSSCs made from the films (a) SnO<sub>2</sub> (b) SnO<sub>2</sub>/CaSnO<sub>3</sub> (c) SnO<sub>2</sub>/BaSnO<sub>3</sub> (d) SnO<sub>2</sub>/SrSnO<sub>3</sub> (e) SnO<sub>2</sub>/Li<sub>2</sub>SnO<sub>3</sub> (f) SnO<sub>2</sub>/CaSnO<sub>3</sub> (Ba doped). (See Color Plate XVII)



**Figure 4.** Photocurrent action spectra of DSSCs made from the (a)  $\text{SnO}_2$  (b)  $\text{SnO}_2/\text{CaSnO}_3$  (c)  $\text{SnO}_2/\text{BaSnO}_3$  (d)  $\text{SnO}_2/\text{SrSnO}_3$  (e)  $\text{SnO}_2/\text{Li}_2\text{SnO}_3$  (f)  $\text{SnO}_2/\text{CaSnO}_3$  (Ba doped). (See Color Plate XVIII)

films, a dramatic increase in the efficiency is observed. Efficiency reached the highest value  $\sim 6.6\%$  when the grains are covered with a shell of CaSnO<sub>3</sub> doped with barium (Ba:Ca = 1:32). The shells on SnO<sub>2</sub> crystallites also increased Isc, Voc and FF. It is interesting to note that in all cases, the efficiency reaches the optimum value when the thickness of shells (CaSnO<sub>2</sub>, SrSnO<sub>3</sub> and BaSnO<sub>3</sub>) is  $\sim 1$  nm. These stannates have lattice constants (*a*) around 0.4–06 nm, therefore the optimum shell thickness is of the order of 1–2 lattice constants. Mott-Schottky (MS) plots (plot of  $1/C^2$  vs applied potential, C = capacitance) for SnO<sub>2</sub> and SnO<sub>2</sub>/CaSnO<sub>3</sub> films are shown in Fig. 5. The flat band potential (FBP) of the latter film is shifted in the negative direction by  $\sim 0.8$  V. Table 2 summarizes the FBPs of different films, the apparent shift in the FBP originates from the capacitance and resistance of the barrier



**Figure 5.** Mott-Schottky plots (i—kHz, ii —1.5 kHz) of (a) SnO<sub>2</sub>/CaSnO<sub>3</sub> (b) SnO<sub>2</sub> films. (See Color Plate XIX)

Film	Flat-band position V vs SCE
SnO <sub>2</sub>	0.10
SnO <sub>2</sub> /CaSnO <sub>3</sub>	-0.73
SnO <sub>2</sub> /BaSnO <sub>2</sub>	-0.61
SnO <sub>2</sub> /CaSnO <sub>2</sub> (Ba doped)	-0.67

 Table 2

 The flat-band positions (V vs SCE) of different ceramic films as determined from Mott-Schottky plots

layer. MS plots are frequency dependent, but the plots at 1 kHz and 1.5 kHz converges to a point and gives a donor density in  $SnO_2 \sim 10^{21} \text{ m}^{-3}$ .

Dielectric measurements with pellets also shows clear distinction between  $SnO_2$  and  $SnO_2$  with barrier layers over the crystallites. Figure 6 compares the frequency variation of the dielectric constant and loss of a  $SnO_2$  pellet and a  $SnO_2$  pellet treated with  $CaCl_2$  to cover



Figure 6. Dielectric loss (a) SnO<sub>2</sub> (b) SnO<sub>2</sub>-crystallites coated with a shell of CaSnO<sub>2</sub>.

the crystallite conformably with CaSnO<sub>3</sub>. In the latter sample, loss in the frequency range 100–2000 Hz is nearly an order of magnitude smaller and flat after a peak structure around 500 Hz. Similar features are seen in BaSnO<sub>3</sub> coated films. Trapping and detrapping of carriers at the surface, causes dielectric loss—an effect more significant in nanocrystalline materials because of the large bulk to volume ratio. Ultrathin barrier layers passivate surface trapping sites and/or make electrons inaccessible to traps, decreasing the loss. The loss peak seems to originate from the Maxwell-Wagner effect in the composite system. In contrast to SnO<sub>2</sub>, TiO<sub>2</sub> did not show a significant decrease in loss when the crystallites were coated with CaTiO<sub>3</sub> or BaTiO<sub>3</sub> indicating that the carrier trapping-detrapping contribution to dielectric loss is less in the case of TiO<sub>2</sub>. Thermally excitable carriers undergo trapping-detrapping encounters in a distribution of frequencies  $\omega_j$ . If a damped simple harmonic oscillator model is assumed, the dielectric dispersion takes the form,

$$\varepsilon(\omega) = \varepsilon_{\infty} + (4\pi e^2/\mathrm{m}^*) \sum \mathrm{N}_{j} \left(\omega_{j}^2 - \omega^2 - \mathrm{i}\Gamma_{j\omega}\right) \tag{4}$$

where  $N_j$  = number of carriers undergoing trapping-detrapping at frequency  $\omega$  and  $\Gamma_j$  = width of resonance,  $m^*$  = effective electron mass. The effective mass of electrons in TiO<sub>2</sub> exceed that in SnO<sub>2</sub> by factor ~100, thus term in front of the summation sign in (4) is larger for SnO<sub>2</sub>. Furthermore, trapped electrons have hydrogenic wave functions [21] and ionization energy increase with the decrease of  $m^*$  and  $N_j$  in SnO<sub>2</sub> greatly exceed that in TiO<sub>2</sub> based DSSCs, faster trapping greatly enhances recombination.

The dark I-V characteristics of DSSCs made from  $SnO_2$  and core-shell structured  $SnO_2$  films ( $SnO_2/MSnO_3$ ) are presented in Fig. 7. Clearly, cells with core-shell structured films show better rectification and the onset of the current occurs at more negative potentials, suggesting that these films resists recombination by electrons leaking to the electrolyte.

The indoline 149 dye (structural formula shown in Fig. 8) anchors to oxide surfaces via the carboxylate ligand and establishes electronic coupling with the conduction band of the semiconductor. On photo-excitation of the chromopore, an electron injects to the



**Figure 7.** Dark I-V characteristics of DSSCs made from the films (a) SnO<sub>2</sub> (b) SnO<sub>2</sub>/CaSnO<sub>3</sub> (c) SnO<sub>2</sub>/BaSnO<sub>3</sub> (d) SnO<sub>2</sub>/SrSnO<sub>3</sub> (e) SnO<sub>2</sub>/Li<sub>2</sub>SnO<sub>3</sub> (f) SnO<sub>2</sub>/CaSnO<sub>3</sub> (Ba doped). (See Color Plate XX)

![](_page_10_Figure_2.jpeg)

Figure 8. Structural formula of Indoline 149.

conduction band forming the dye cation. The injected election could recombine geminately with the dye cation or with an acceptor in the electrolyte on its way to back contact of the cell. Geminate recombination being generally very slow, the dominant loss mechanism in a DSSC happens to be the latter process (i.e., combination electrons with  $I_3^-$  ion in the electrolyte). SnO<sub>2</sub> seems to be more susceptible electron leakage compared to TiO<sub>2</sub> and the outer shell acts as barrier [29, 30]. Electron injected in photo-excitation of the dye molecule, attached to the surface of the shell, tunnels across the barrier. Although thicker barriers, more effectively screen electron leakage, the tunneling probability falls exponentially with the barrier width. The compromise of the two opposing effects occurs at a barrier thickness of ~1 nm. Suppression of recombination and favorable shift of the flat-band potential increases the efficiency of the cell.

It is important to understand why the incorporation of a small quantity of Ba into the CaSnO<sub>3</sub> shell on SnO<sub>2</sub> grains enhances the Isc and the efficiency significantly above the undoped system (i.e., the cell where the shell material is CaSnO<sub>3</sub>). A clue is evident in the photocurrent action spectra of different cells (Fig. 3). Alcoholic solutions of indoline 149 absorb light most strongly at ~530 nm. Photocurrent action spectra of DSSCs generally have peaks red-shifted with respect to the absorption spectra in dilute solution. The red-shift indicates the bonding of the dye to the solid surface, stronger the binding greater is the red-shift. The peak positions of the action spectra  $\lambda_{max}$  of different cells are depicted in Table 3. The  $\lambda_{max}$  of the action spectra of cells with films SnO<sub>2</sub>/BaSnO<sub>3</sub> or SnO<sub>2</sub>/SrSnO<sub>3</sub> are red shifted with respect to the SnO<sub>2</sub>/CaSnO<sub>3</sub> system. However, the  $\lambda_{max}$  of the cell with Ba doped CaSnO<sub>3</sub> is same as the cell with BaSnO<sub>3</sub> (Figure 3 and Table 2). This observation suggests that in the system with a Ba doped shell of CaSnO<sub>3</sub> the dye molecules anchor to the Ba sites on the surface of CaSnO<sub>3</sub>. Further evidence supports the above suggestion, the Ba doped BaSnO<sub>3</sub> surface contains approximately (N)<sup>2/3</sup> Ba sites ~10<sup>12</sup> cm<sup>-2</sup>, where

Table	3
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Positions $(\lambda_{max})$	of the absorption	spectrum of indoline	e 149 solution and
action spec	ctra of different sys	stems sensitized with t	the same dye

System	$\lambda_{max}/nm$
Indoline 149 solution	530
SnO <sub>2</sub> /Dye	600
SnO <sub>2</sub> /CaSnO <sub>3</sub> /Dye	614
SnO <sub>2</sub> /SrSnO <sub>3</sub> /Dye	625
SnO <sub>2</sub> /BaSnO <sub>3</sub> /Dye	540
SnO <sub>2</sub> /CaSnO <sub>3</sub> -Ba (shell)/Dye	540

N = volume concentration of Ba atoms in the CaSnO<sub>3</sub> (calculated from shell thickness,core radius and the level of Ba doping). The surface concentration of dye molecules is also of the same order of magnitude as (N)<sup>2/3</sup> indicating that each dye molecule anchors to a Ba site on the surface. Presumably, as dye bonds more strongly to Ba than to Ca, the above mode of dye attachment to the surface prevents aggregation of dye molecules. Prevention of dye aggregation increases efficiency avoiding quenching of excited dye molecules due to their mutual interaction [31].

#### 4. Conclusion

Treatment with alkaline earth chlorides and sintering at relatively low temperature effectively covers crystallite surface of  $SnO_2$  ceramics with corresponding alkaline earth stannates. The efficiencies of DSSCs increase dramatically on covering the crystallite surface with ultra-thin barrier layers of alkaline earth stannates. Barriers effectively suppress recombination while permitting dye-sensitized injection via tunneling of electrons across the barrier. Capacitance measurements indicate that the barrier raises the flat-band potential of  $SnO_2$  and reduce the rate of trapping-detrapping of electrons. Co-doping of the CaSnO<sub>3</sub> barrier layer with Ba enhanced the efficiency further, i.e., from 6.6 to 6.6%. It is suggested that in the co-doped film, dye molecules binds preferentially to the Ba sites preventing dye aggregation. Efficiency varies sensitively with the barrier thickness and further increase of the efficiency may be possible when the system is fine tuned choosing other sensitizers.

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