Tailoring Electron Diffusion in Electrospun Metal Oxide Nanostructures for Dye-sensitized Solar Cells

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ABSTRACT

Metal oxide wide bandgap semiconducting nanostructures lie at the heart of many technologies including dye-sensitized solar cells (DSCs). In DSCs, they act as charge separation and transport medium; and therefore, understanding and controlling charge transport is key to increase the performance level of corresponding devices beyond current thresholds. Unlike bulk semiconductors, in which the electrons diffuse in the conduction band from one transport state to another, electron transport in nanostructured materials occurs through the localized surface energy states that lie within the bandgap. This article focuses on the advances made on controlling the charge transport in electrospun metal oxide nanostructures.

Keywords: Dye-sensitized solar cells, Electron diffusion, Electrospinning, Metal oxide semiconductors

1 INTRODUCTION

Dye-sensitized solar cells (DSCs) have emerged as one of the low-cost photovoltaic device due to less fabrication cost and less-expensive raw materials. The photovoltaic effect in DSCs occurs at the interface between a dye-anchored wide bandgap nanostructured metal oxide semiconductor (n-MOS) and a redox electrolyte [1]. Intensity of solar light is weak at the absorption wavelength window of most MOSs, which is conventionally widened by sensitizing by organic fluorophores (dyes), hence the name dye-sensitized solar cells. On sunlight irradiation, the dye absorbs solar light thereby creates a transiently localized state called exciton. The exciton can be viewed as a quasi particle composing an (e−–h+) pair. If the conduction band energy of the MOS is at lower energies than the lower unoccupied molecular orbital (LUMO) of the dye, then the excited electron decays to the MOS and thereby creating mobile charge carriers [2]. The electrons injected to the conduction band of the oxide material is transported through the mesoporous network to the counter electrode by doing a work equal to the energy difference between the conduction band of the electrode and redox potential of the electrolyte. The oxidized dye is regenerated by a hole-conductor, thereby completing the cycle of operations.

The photoconversion efficiency (η) of DSCs, from a first principle approach, depends on the amount of the dye used in the cell as they are the primary absorbers of solar light. Although the n-MOS absorb solar light, the intensity of the solar spectrum is rather weak at their bandgaps (~3.2 eV). Need for more amounts of dye demands more amounts of active metal oxide surface to bind them, which could be achieved by using mesoporous materials of large specific surface area and/or increasing the thickness of the n-MOS network. However, mesoporous materials are weakly crystalline that are disadvantageous for efficient charge transport. In addition, there are intrinsic limitations to increase the thickness of the electrode film because the photoinjected carriers recombine with the electrolyte if they take longer time to reach the anode than their lifetime. The time required for photoelectrons to reach the anode is known as the electron transit time and is a crucial parameter in DSCs. The electrons travels a distance equals to the electron diffusion length in electron transit time. The diffusion length is given by 

\[ L = (D_e \tau)^{1/2} \]

where \( D_e \) is the electron diffusion coefficient and \( \tau \) is the electron lifetime. The electron lifetime in DSCs is ~10⁻⁶ s, which limits the diffusion length to be several microns assuming the \( D_e \) to be 10⁻⁴ cm²/s [2]. For efficient charge collection in DSCs, the thickness of the mesoporous metal oxide electrode should be one-third of the diffusion length. Therefore, development of materials with high \( D_e \), while maintaining large surface area and high crystallinity are most promising ways to increase the η of DSCs. Research over the past decade brought the η of DSCs to 12% [3]. The state-of-the-art DSC uses a mesoporous TiO₂ particles sensitized by an organic sensitizer organic sensitizer Carbz-PAHTDTT and ferrocene-based electrolyte [3].

This paper describes advanced materials featured by high \( D_e \). The materials were developed by electrospinning a polymeric solution and subsequent controlled annealing [4, 5]. This paper reports four materials characterized by high \( D_e \), viz. one-dimensional (1D) anatase TiO₂, Nb doped TiO₂, Nb₂O₅ and SnO₂.
2 EXPERIMENTAL DETAILS

Samples for analysis were 1D nanostructures developed by electrospinning a polymeric solution and subsequent annealing [4, 5]. Four typical materials are presented here, their respective processing details could be found from the noted references. (1) TiO2 nanofibers, nanowires, and nanorods [6-8]; (2) Nb-doped TiO2 nanofibers [9, 10]; (3) monoclinic Nb2O5 nanonuggets [11, 12]; (4) SnO2 flowers [13].

2.1 Fabrication and Characterization of DSCs

The TiO2 electrodes were prepared as described before [6-15]. The TiO2 nanorod electrodes (area ~1 cm²) were soaked in a 1:1 vol. mixture of acetonitrile and tert-butanol with ruthenium dye (RuL2(NCS))2-2H2O; L=2,2′-bipyridyl-4,4′-dicarboxylic acid (0.5 mM, N3 Solaronix) for 12 h at room temperature. The soaked electrodes were washed with ethanol to remove non-anchored dye molecules and then dried in the air. Pt sputtered FTO glasses were used as counter electrode. The Pt counter electrode and the dye anchored TiO2 electrode were assembled into a sealed sandwich type cell using a sealing material (SX1170-25, 4-methoxystyrene). Acetonitrile containing 0.1M lithium iodide, 0.03M iodine, 0.5M 4-tert-butylpyridine, and 0.6M 1-propyl-2,3-dimethyl imidazolium iodide was used as redox electrolyte solution. The electrolyte solution was injected into the cell through a small opening drilled on the counter electrode. Finally the opening was sealed by a piece of glass.

Current-voltage characteristics and electrochemical impedance spectroscopy (EIS) data were obtained using a potentiostat (Autolab PGSTAT30, Eco Chemie B.V., The Netherlands). The EIS measurements were carried out in the dark using 10 mV ac voltage superimposed on a forward-biased DSC (0.4–0.7 V) with frequency ranging from 30 kHz to 0.05 Hz. The electron transport were also studied using transient photocurrent technique, the details of which are available in our earlier publications [8, 9].

3 RESULTS AND DISCUSSION

3.1 Charge transport Mechanism in n-MOS

Electron transport through metal oxide nanostructures has been fairly well understood. In bulk single crystalline n-MOS, electrons in the conduction band move from one transport state to another with a free electron diffusion coefficient (Dn) of ~10⁻⁷ cm²/s. The extended periodicity in the bulk crystal is altered in amorphous and nanocrystalline semiconductors, and thereby, alter their electronic band structure and eventually the free electron diffusion mechanism become less dominant. In n-MOS, electrons move via extended band-tail states at the bottom of the conduction band as well as broad distribution of localized energy states lie within the bandgap [16]. Density of those localized states is higher at the bottom of the conduction band and exponentially decreases in the energy scale towards the top of the valence band (Fig.1). The carriers injected to the n-MOS are trapped by the band-tail states and subsequent thermal activation leads the electrons to deeper energy levels and retrap again (Fig. 1). The injected carriers thus move via a trap-detrap, otherwise called multiple trapping (MT), mechanism through the transport level (ETR); the ETR is a function of Fermi level [17]. In the case of DSCs, the photoinjected electrons increase the chemical capacitance (Cp) of n-MOS [18] and the consequent Dn through ETR typically is ~10⁻⁷–10⁻⁵ cm²/s for lower photoexcitation density (Φ ≤ 10¹⁶ cm⁻³) [19], typically for n-TiO2, i.e., the Dn in n-TiO2 is several orders of magnitude lower than Do due to the above described trap-limited diffusion process. Kopidakis et al showed that higher Φ (≥10¹⁷ cm⁻³) uplift the Fermi level of n-TiO2 close to its extended band-tail states and result in a diffusion mechanism similar but lower in magnitude (Dn ~10⁻⁴ cm²/s) to that of the bulk TiO2[19].

![Figure 1: Cartoon depicting the charge transport process in nanostructured metal oxide semiconductors. The E_F and E_F0 are the Fermi and pseudo-Fermi energies, E_TR is the electron transport energy, and E_C is the conduction band energy.](image)

### Table 1: Photovoltaic properties of the devices used for the current study.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>JSC (mA/cm²)</th>
<th>VOC (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2 Fibers [6]</td>
<td>9.45</td>
<td>0.78</td>
<td>57</td>
<td>4.2</td>
</tr>
<tr>
<td>TiO2 rods [7]</td>
<td>13</td>
<td>0.83</td>
<td>49</td>
<td>5.2</td>
</tr>
<tr>
<td>TiO2 wires [8]</td>
<td>8.46</td>
<td>0.82</td>
<td>60</td>
<td>4.3</td>
</tr>
<tr>
<td>Nb:TiO2 [10]</td>
<td>14.79</td>
<td>0.72</td>
<td>57</td>
<td>6</td>
</tr>
<tr>
<td>TiO2 NPs [21]</td>
<td>17.05</td>
<td>0.86</td>
<td>76</td>
<td>11</td>
</tr>
</tbody>
</table>
Figure 2 show s the Nyquist plots of a representative nanofiber device recorded at under different bias in the dark. The high frequency offset is the series resistance $R_s$ of the cell, primarily due to the FTO resistance. The platinum/electrolyte interface can be seen as the small arc at high frequencies. The transport and charge transfer processes in the Nb:TiO₂ nanofibers, prominent at low bias, show up as a straight line followed by the larger arc at intermediate frequencies, respectively. Diffusion in the electrolyte can be detected as a small arc at low frequencies.

![Figure 2: EIS spectra of nanofiber based devices](image)

The EIS data was fitted to the well-accepted diffusion-recombination model, the resistors and capacitors in which represents various interfacial and transport processes in DSCs, to extract the effective electron diffusion coefficient in TiO₂, electron transit time, and lifetime [20, 21] Details of the transmission line model are as described elsewhere [21]. For a device of electrode thickness $L$, the electron transport resistance in the TiO₂ nanofiber is $R_T=r_L$. The strong dependence arise from the trap-detrap diffusion as explained before. Two regions were observed in the $D_n$ vs. applied voltage graph of Nb:TiO₂ (i) $0.4 – 0.6$ V region a region with two orders of magnitude higher photovoltaic performances [2] and (ii) >0.6 V region, where $D_n \sim 10^{-3} \text{ cm}^2/\text{s}$ is independent of the applied voltage indicating the diffusion through the extended states. Enhanced $D_n$ and weak dependence on applied voltage should arise from the larger $C_p$ of the Nb:TiO₂ achieved through doping. In contrast, for the $n$-TiO₂ based devices, the $D_n$ depended strongly on the applied voltage, which was explained on the basis of trapping-detrapping model. The Fermi level increases with the applied voltage and removes some of the deep traps, and therefore, $E_{TR}$ level shifts near to the extended band tail states and result in $D_n \sim 10^{-4} \text{ cm}^2/\text{s}$, typically in $n$-TiO₂. The Nb:TiO₂ showed similar diffusion behavior even at lower bias voltages, which indicate that doping shifted the $E_{TR}$ to the extended states. Further enhancement of the applied voltage above 0.6 V did not change the $D_n$ and this quantity was two orders of magnitude lower than $D_o$. This difference would probably arise from the inferior crystallinity of Nb:TiO₂ nanofibers compared to the bulk crystals.

![Figure 3: Electron diffusion coefficients of TiO₂ morphologies considered in this work](image)

### 3.3 Charge transport through Nb₂O₅ and SnO₂ nanostructures

In addition to TiO₂, which have the advantages of getting mesoporous materials relatively easy, there are other wide bandgap metal oxides such as Nb₂O₅ and SnO₂. Both SnO₂ and Nb₂O₅ has definite advantages over TiO₂: Nb₂O₅ has a higher conduction band edge compared to TiO₂ hence offer possibilities for higher $V_{OC}$ and SnO₂ has higher electron mobility compared to TiO₂ hence possible to attain higher photovoltaic performances [2].

The Nb₂O₅ has several polymorphs: choice of proper polymorph has been recently addressed by us and identified that monoclinic Nb₂O₅ has desirable charge transport properties [11]. Samples for the present study were nano-nuggets. Due to high processing temperature involved, specific surface area of the of the materials used for device fabrication was rather poor and the efficiency of the corresponing device was ~2%. Figure 4 shows the electron lifetime and $D_n$ of the DSCs fabricated using monoclinic Nb₂O₅. Both lifetime and $D_n$ depend strongly on the applied...
voltage thereby indicating trap limited diffusion behavior. The $D_n$ of Nb$_2$O$_5$ based devices were comparable with that of Nb doped TiO$_2$.

The SnO$_2$ nanostructures with different morphologies such as fibers and flowers were synthesized, their details will be published elsewhere [13]. The differences in electrical properties of these two morphologies were determined EIS measurements of the DSCs in the dark under forward bias. The Nyquist plots (Data not shown) showed that radius of the right semicircle of the flower based device is larger compared to that made using the fibers. The apparently larger semicircle indicates increase in the charge transfer resistance; and therefore, an increased electron lifetime. The $D_n$ determined from the EIS spectra were $\sim 10^{-3}$ cm$^2$/s at 0.7 V, which is comparable to that of the Nb doped TiO$_2$ and Nb$_2$O$_5$ nanonuggets.

Finally, the charge mobility through the above nanostructures were studied by transient photocurrent measurements. The $D_n$ derived from the EIS plots were in good agreement the transient photocurrent measurements. Table 2 summarizes the electron mobility values of the various nanostructures considered under present study. Among them Nb doped TiO$_2$ showed the highest electron mobility among them followed by SnO$_2$ flowers. The Nb doped TiO$_2$ could, therefore, soon find electronic applications requiring high electron mobility and optical transparency.

### Table 2: Electron Mobilities of the samples used in this study

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Normalized Transit time [ms]</th>
<th>Normalized Electron Mobility $[\text{cm}^2 \text{V}^{-1} \text{s}^{-1}] \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$ Fibers</td>
<td>10</td>
<td>3.75</td>
</tr>
<tr>
<td>SnO$_2$ Flowers</td>
<td>2</td>
<td>18.5</td>
</tr>
<tr>
<td>Nb: TiO$_2$</td>
<td>0.2</td>
<td>185</td>
</tr>
<tr>
<td>TiO$_2$ Nanowires</td>
<td>5.5</td>
<td>6.74</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>15</td>
<td>2.47</td>
</tr>
</tbody>
</table>

### ACKNOWLEDGEMENTS

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### REFERENCES