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# Glass-Encapsulated Light Harvesters: More Efficient Dye-Sensitized Solar Cells by Deposition of Self-Aligned, Conformal, and Self-Limited Silica Layers

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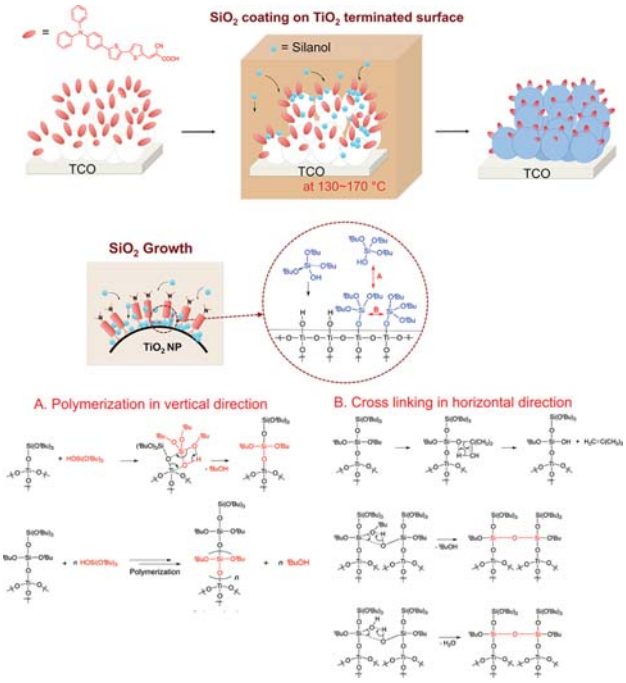
Supporting Information

**ABSTRACT:** A major loss mechanism in dye-sensitized solar cells (DSCs) is recombination at the $TiO_2$/electrolyte interface. Here we report a method to reduce greatly this loss mechanism. We deposit insulating and transparent silica ($SiO_2$) onto the open areas of a nanoparticulate $TiO_2$ surface while avoiding any deposition of $SiO_2$ over or under the organic dye molecules. The $SiO_2$ coating covers the highly convoluted surface of the $TiO_2$ conformally and with a uniform thickness throughout the thousands of layers of nanoparticles. DSCs incorporating these selective and self-aligned $SiO_2$ layers achieved a 36% increase in relative efficiency versus control uncoated cells.

Dye-sensitized solar cells (DSCs) have great potential to compete with conventional p−n junction solar cells due to their relatively low cost.[1] However, their efficiency is limited by the ease with which electrons collected by the nanoparticle (NP) framework can recombine with ions in solution. Therefore, the photovoltaic efficiency of DSCs can be increased by retarding electron recombination at the photoelectrode interfaces. The surfaces of the $TiO_2$ NPs are not fully covered by the dye molecules, as shown schematically in Scheme 1. Thus, an electrical short by direct contact between electrolyte and the areas of $TiO_2$ not covered by dye provides an important loss pathway by which electrons recombine with the electrolyte. This recombination rate could be reduced or eliminated by selectively coating an insulating and transparent layer on these open areas of $TiO_2$. In an effort to minimize such losses, many groups have proposed device architectures that include the coating of inorganic barrier layers,[2] the use of long aliphatic chain on organic framework,[3] saccharides,[4] the introduction of co-adsorbents,[5] encapsulation by cyclodextrins,[6] and post-surface passivation by polymerization.[7] Recently, high band gap metal oxide layers prepared via atomic layer deposition (ALD) have received much attention as efficient interface engineering tools owing to their capability of infiltrating porous structures, thereby ensuring good coverage of the surface of the nanoporous electrode,[8] fine control of thickness,[9] and low-temperature processing.[10] However,

**Scheme 1. Post-dye $SiO_2$ Deposition Process and Plausible Reaction Mechanism on Dye-Coated $TiO_2$ Nanoparticles**




applying ALD layers prior to dye adsorption on $TiO_2$ or related oxides significantly reduces the electron-transfer rate from the dye through the metal oxide overlayers by creating a tunneling barrier.[11] Therefore, a new methodology is needed that does not interfere with electron transfer to or from the dye molecules.

We discovered a method to deposit selectively an insulating and transparent layer of silica ($SiO_2$) only on the open areas of $TiO_2$ surface, but not on the adsorbed dye molecules or between the dye surface-linker and the electrode. Our approach exploits deposition of $SiO_2$ from a precursor that is catalytically

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decomposed by the surface of $TiO_2$. Areas of $TiO_2$ covered by adsorbed dye do not catalyze the deposition of $SiO_2$. Thus the gaps between dye molecules are selectively covered by $SiO_2$. This $SiO_2$ retards the interfacial charge recombination dynamics without hindering electron injection from the dye into the $TiO_2$ or from the solution into the dye. When this $SiO_2$ treatment was applied to a DSC just after coating the $TiO_2$ with an organic dye (**OrgD**, Scheme 1), enhanced performance was obtained, with a higher power conversion efficiency and longer electron lifetime. Another important feature of the $SiO_2$ deposition process is that its thickness is self-limiting, so the same thickness is applied to all levels in the porous multilayer structure of the photoelectrode. In this study, we investigated the conditions needed to make $SiO_2$ deposit selectively on $TiO_2$ between dyes.

We found that $SiO_2$ less than 1 nm thick functions as a barrier to charge recombination and thereby improves the performance of these photovoltaic devices. The $SiO_2$ coating chemistry is related to a process for rapid ALD using alternating exposure of surfaces to vapors of trimethylaluminum (TMA) as a catalyst and tris(*tert*-butoxy)silanol (TBOS) as the $SiO_2$ precursor.[12] In this reaction, aluminum placed on the surface by the TMA plays a crucial role as a Lewis-acidic catalyst for deposition of $SiO_2$ layers up to 15 nm thick on top of the alumina.[13] There have been reports that hafnium and zirconium can also catalyze the growth of $SiO_2$.[14−16] This work suggested to us that titanium might also catalyze the growth of $SiO_2$. Indeed, we have found that anatase titanium dioxide does, in fact, catalyze growth of $SiO_2$ on its surface.

The $SiO_2$ coating process was performed in a home-built hot-wall tubular reactor (Scheme 1). TBOS was used as the precursor for both the silicon and the oxygen. The thickness of $SiO_2$ deposited on planar witness samples of $TiO_2$ is plotted as a function of substrate temperature in Figure 1. The reaction

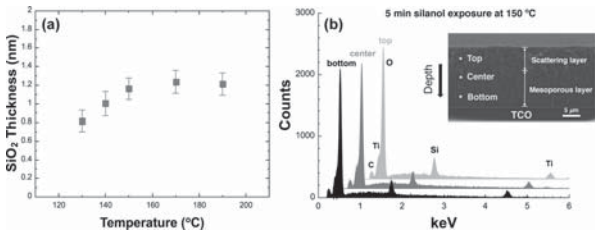


**Figure 1.** (a) RBS data for the thickness of the $SiO_2$ layer as a function of deposition temperature. (b) EDS data showing that the $SiO_2$ is deposited uniformly throughout the porous, nanoparticulate $TiO_2$ electrode.

temperature was varied from 130 to 190 °C, since no $SiO_2$ film was deposited below 130 °C. The amount of $SiO_2$ deposited was measured by the Rutherford backscattering spectroscopy (RBS) technique. The thickness of the $SiO_2$ film was found to increase with temperature from 0.8 nm to about 1.2 nm. These thicknesses represent the self-limited values obtained after initial dosing of about 1 Torr of silanol vapor, which was then allowed to react for 5 min. Other experiments showed that almost all of this deposition occurs within the first 10 s. Energy-dispersive X-ray spectroscopic (EDS) analyses (Figure 1) showed that the $SiO_2$ is evenly distributed throughout the thousands of $TiO_2$ NP layers constituting the photoanode. The coverage and thickness of the $SiO_2$ layer on the $TiO_2$ NPs were further examined with HRTEM (see Figure 2), which also

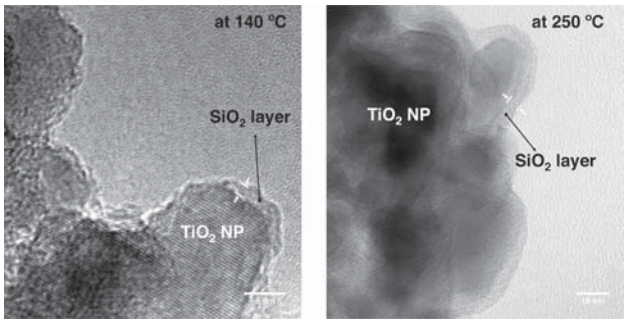


**Figure 2.** TEM images of $TiO_2$ NPs coated with $SiO_2$ at substrate temperatures of 140 and 250 °C.

shows a uniform and conformal $SiO_2$ layer. The thickness of the $SiO_2$ layer was ∼1 and ∼3 nm at 140 and 250 °C, respectively, showing the temperature dependence of the thickness, consistent with thicknesses determined by RBS.

Although it is not ideal to compare the thickness of $SiO_2$ on the dye-loaded $TiO_2$ surface with that on a flat surface, it should be noted that the real thickness of $SiO_2$ deposited is similar to the vertical dimension of dye molecules as evidenced by the stable oxidation of dyes within $TiO_2/SiO_2$ films (Figure S1) and the corresponding $I-V$ performance studied below (see Table 1). (Thicker layers might shut-off dye electrochemistry.)

**Table 1. Photovoltaic Performance of DSCs**

| sample | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [V] | ff | $\eta$ [%] |
|---|---|---|---|---|
| **OrgD** | 9.95 | 0.62 | 0.71 | 4.36 |
| **OrgD**/$(SiO_2)_{130}$ | 11.03 | 0.66 | 0.69 | 5.02 |
| **OrgD**/$(SiO_2)_{140}$ | 12.63 | 0.69 | 0.68 | 5.94 |
| **OrgD**/$(SiO_2)_{150}$ | 12.17 | 0.68 | 0.69 | 5.70 |
| **OrgD**/$(SiO_2)_{170}$ | 12.07 | 0.67 | 0.65 | 5.29 |
| **N719** | 13.58 | 0.77 | 0.71 | 7.39 |

In UV/vis spectra of $TiO_2$/**OrgD**/$SiO_2$ films, no significant decrease in absorbance is observed after $SiO_2$ deposition, indicating the sensitizing dye molecules are not affected by the $SiO_2$ precursor or the thermal stress during $SiO_2$ deposition (Figures S2 and S3). Given the fact that the sensitized dye molecules are partly surrounded by the $SiO_2$ layer, resulting in a change of the external dielectric field, the unchanged $\lambda_{max}$ in the films arises from the low dielectric constant of $SiO_2$ ($\varepsilon \approx 4$), which acts as a nonpolar medium.

Enshrouding dyes with a glass ($SiO_2$) coating of precise and uniform thickness substantially improves the photovoltaic performance of the DSC devices. Figure 3 shows action spectra in the form of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSCs based on **OrgD** (electrolyte: 0.6 M DMPImI, 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile). The post-dye-treated **OrgD**/$(SiO_2)_x$ ($x$ = $SiO_2$ deposition temperature ranging from 130 to 170 °C) cells clearly exhibited an increased response over the entire spectral region, but especially the red region, relative to the nontreated **OrgD** cell. The IPCE of **OrgD**/$(SiO_2)_{130-170}$ showed plateaus of over 75% from 400 to 590 nm. Significantly higher responses were observed over the wavelength range of 500−700 nm for **OrgD**/$(SiO_2)_{130-170}$ cells compared to **OrgD** cell. The broadened IPCEs of these coated cells suggest superior electron collection capability (greater collection length) versus untreated cells. If we examine IPCE as


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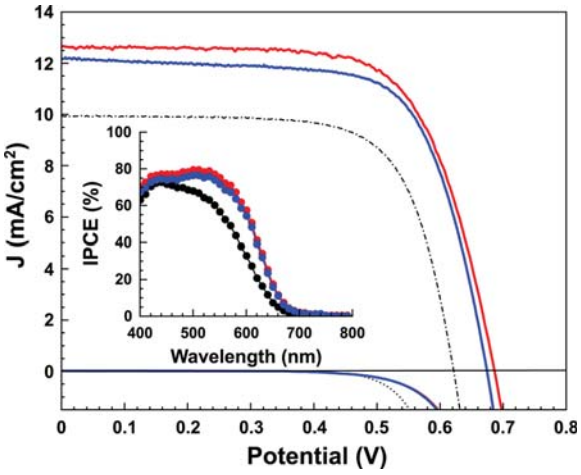


**Figure 3.** *J*–*V* curves, dark currents, and IPCE plots (inset) of **OrgD** (black dashed line), **OrgD**/$(SiO_2)_{140}$ (red line), and **OrgD**/$(SiO_2)_{150}$ (blue line).

a function of light harvesting efficiency over the wavelength (Figure S4), the results suggest that the coated films have much longer *effective* light infiltration compared to uncoated ones ("effective" means ability to inject electrons that are subsequently collected as a photocurrent rather than lost to interception by $I_3^-$ or recombination with oxidized dye). An additional minor contributor to the IPCE broadening could be a red shift in dye absorption following encapsulation. Extinction measurements suggest that, depending on the wavelength, the shift could be as large as 15 nm. The measurements were complicated, however, by baseline shifts presumably due to light scattering.

The photovoltaic performances of the **OrgD** sensitized cells are listed in Table 1.[17] The optimal condition for the $SiO_2$ barrier was that produced at 140 °C (~1.0 nm by RBS), which resulted in 36% increase in efficiency ($\eta$) compared to the reference cell, with the highest $\eta$ achieved being 5.94%; both the open-circuit photovoltage ($V_{oc}$) value of 0.69 V and the short-circuit photocurrent ($J_{sc}$) value of 12.63 mA/cm$^2$ are larger than for the uncoated control.[18] This value agrees well with that obtained by integrating solar-spectrum-weighted IPCE. Under the same conditions, the **OrgD** cell gave $J_{sc}$ = 9.95 mA/cm$^2$, $V_{oc}$ = 0.62 V, and fill-factor (ff) = 0.71, which correspond to $\eta$ = 4.36%. When the deposition temperature was increased to 150 °C, the resulting device showed slightly poorer characteristics than the **OrgD**/$(SiO_2)_{140}$ cell. Of particular importance is the 60–70 mV increase in the $V_{oc}$ value of the **OrgD**/$(SiO_2)_{130-170}$ cell relative to the **OrgD** cell. This result implies that the $SiO_2$ surrounding the dye results in retardation of interfacial charge recombination losses in the device, as confirmed by the dark current data (Figure 3). Charge lifetimes ($\tau_e$) determined from $V_{oc}$ decay measurements are shown in Figure 4a. The $\tau_e$ values are successively shifted to larger values with increase of reaction temperature from 130 to 170 °C, demonstrating that the electron-recombination process was effectively retarded by the $SiO_2$ deposition. Specifically, the increase of $\tau_e$ by the post-dye $SiO_2$ layer is saturated with the amount produced at 140 °C, showing that as little as 1.0 nm of $SiO_2$ (about 4 monolayers) is sufficient to insulate the $TiO_2$ surfaces very efficiently. These results are also in good agreement with the $V_{oc}$ results shown in Table 1.

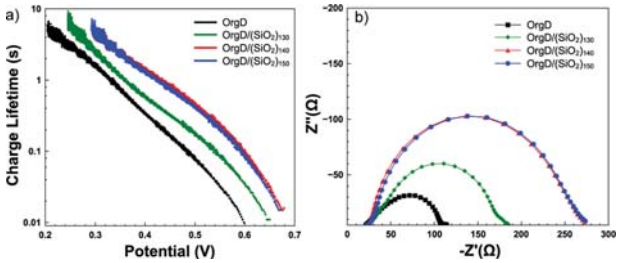


**Figure 4.** (a) Charge lifetimes from open-circuit photovoltage decays. (b) Dark electrochemical impedance spectra at 575 mV of **OrgD**, **OrgD**/$(SiO_2)_{130}$, **OrgD**/$(SiO_2)_{140}$, and **OrgD**/$(SiO_2)_{150}$ cells.

Electrochemical impedance spectroscopy (EIS) was performed under dark conditions (Figure 4b) with the forward bias ranging from −0.5 to −0.7 V. The semicircular curve obtained in the intermediate-frequency regime shows the dark reaction impedance caused by electron transport from the $TiO_2$ conduction band to the $I_3^-$ ions in the electrolyte.[19] The radius of the intermediate frequency semicircle showed the increasing order of **OrgD** (72 Ω) < **OrgD**/$(SiO_2)_{130}$ (133 Ω) < **OrgD**/$(SiO_2)_{140}$ (239 Ω) ≤ **OrgD**/$(SiO_2)_{150}$ (241 Ω), which is in agreement with the trends of the $V_{oc}$ and $\tau_e$ values. EIS also revealed that the effective length of **OrgD**/$(SiO_2)_{140}$ is roughly 2.5 times greater than that of **OrgD**, confirming that $SiO_2$ inhibits the interception of injected electrons by the $I_3^-$ ions in the electrolyte (Figure 5).[20] Figure S5 shows that the untreated

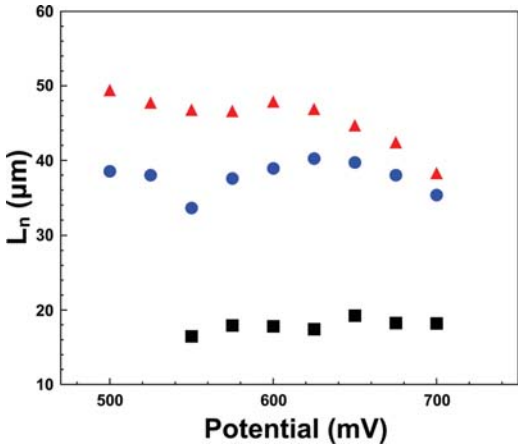


**Figure 5.** Effective electron diffusion lengths (from dark EIS) for the electrodes coated with **OrgD** (black squares), **OrgD**/$(SiO_2)_{140}$ (red triangles), and **OrgD**/$(SiO_2)_{150}$ (blue circles).

and treated cells have a similar capacitance, indicating that the band-edge of the nanoporous $TiO_2$ network is not affected by the $SiO_2$ deposition (Figure S5). We envision that this strategy could be even more useful for the bulky outer-sphere redox shuttles. Such studies are currently in progress and will be presented elsewhere.

In summary, we have demonstrated that self-aligned, conformal, and self-limiting deposition of $SiO_2$ on $TiO_2$ in DSCs is an effective tool for retarding charge recombination, leading to enhanced charge collection and substantially increased overall conversion efficiency. The $SiO_2$ layer forms only on the $TiO_2$ and does not cover the dye molecules. Moreover, this new architecture provides an insulating layer that retards interfacial charge recombination without reducing


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electron transfer from the dye into the $TiO_2$ NPs or from the solution to the dye. Optimization of DSCs using this $SiO_2$ post-dye treatment as well as application to other, more strongly absorbing dyes is currently being investigated. We believe that the development of highly efficient DSC devices with excellent stabilities is possible through this interfacial engineering.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental conditions and results of cyclic voltammetry, UV/vis spectra, $J-V$ curves, chemical capacitance experiments, and TEM image. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Author Contributions

[‖]H.-J.S. and X.W. contributed equally.


### Notes

The authors declare no competing financial interest.

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(18) In contrast, the commonly utilized co-adsorbent, chenodeoxycholic acid (see ref S1 in SI), yielded no improvement in efficiency, indicating that here it is ineffective in preventing electrolyte interception of injected electrons.

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