

Significantly Enhanced Open Circuit Voltage and Fill Factor of Quantum Dot Sensitized Solar Cells by Linker Seeding Chemical Bath Deposition

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Detailed description of the LS-CBD experiment: As shown in Scheme S1, LS-CBD can be divided into three basic steps. Step 1 presented linker anchoring process. We found that a higher temperature could accelerate the anchoring after several series of experiments. Considering MPA linkers weren't stable in high temperature, we finally fixed the temperature at 40°C. Step 2 represented the $-S-(Cd^{2+})_x$ seeds formation. In this step, we also found that mixture solvent of ethanol and water for Cd^{2+} was a great benefit for seeds formation compared to pure water from our experience of experiment, which was attribute to the poorer solubility of MPA in H_2O after $-COOH$ tethering on TiO_2 . We also fixed the temperature at 40°C for fast seeds formation. Step 3 presented the CBD process. The effectiveness of the CdSe deposition process by subsequent CBD at a given deposition temperature and time was judged by comparing the color changes when viewed from the top and from the bottom of the photoanode film. After the cool precursor reagents Na_2SeSO_3 and $CdCl_2$ were successively injected into the vessel containing the $Cd_x-S-(CH_2)_2-COO-TiO_2$ film, the film turned yellow in a minute and then to red as time went by and the precursor solution also turned from yellow to red subsequently. The temperature was controlled in such a way that the reaction on the surface of TiO_2 was preferred to that in solution so as to supply sufficient CdSe source to sustain the QD film growth. Besides, we swayed the vessel from time to time for facilitating precursor permeation into the film and observe the color change to decide on the necessary reaction time. It was quickly concluded that a moderate temperature ($\sim 30^\circ C$) and accordingly a long deposition time (1 h) could achieve a full and even coverage of CdSe on TiO_2 . Shown in Figure S2a are photographs of the as deposited CdSe on the agglutinate microsphere film at $30^\circ C$. From the front view and back view of the film, a very even QD coverage is evident in such a large area and more important, such even coverage of CdSe is nearly the same on both sides, much like even color printed on the TiO_2 surface. In contrast, higher temperature ($\sim 45^\circ C$) induced

fast growth of CdSe in solution and thus undermined the QD film growth, which ended up with a higher coverage of CdSe at the top but a lower coverage at the bottom of the film (Figure S2b). Therefore, the appropriate deposition time and temperature in essence reflect the balance between the needed pervasion of the precursor reagent Na_2SeSO_3 and CdCl_2 into the TiO_2 film and the undesirable accretion CdSe in solution, which would fatefully determine the quality of the resulting QD film.

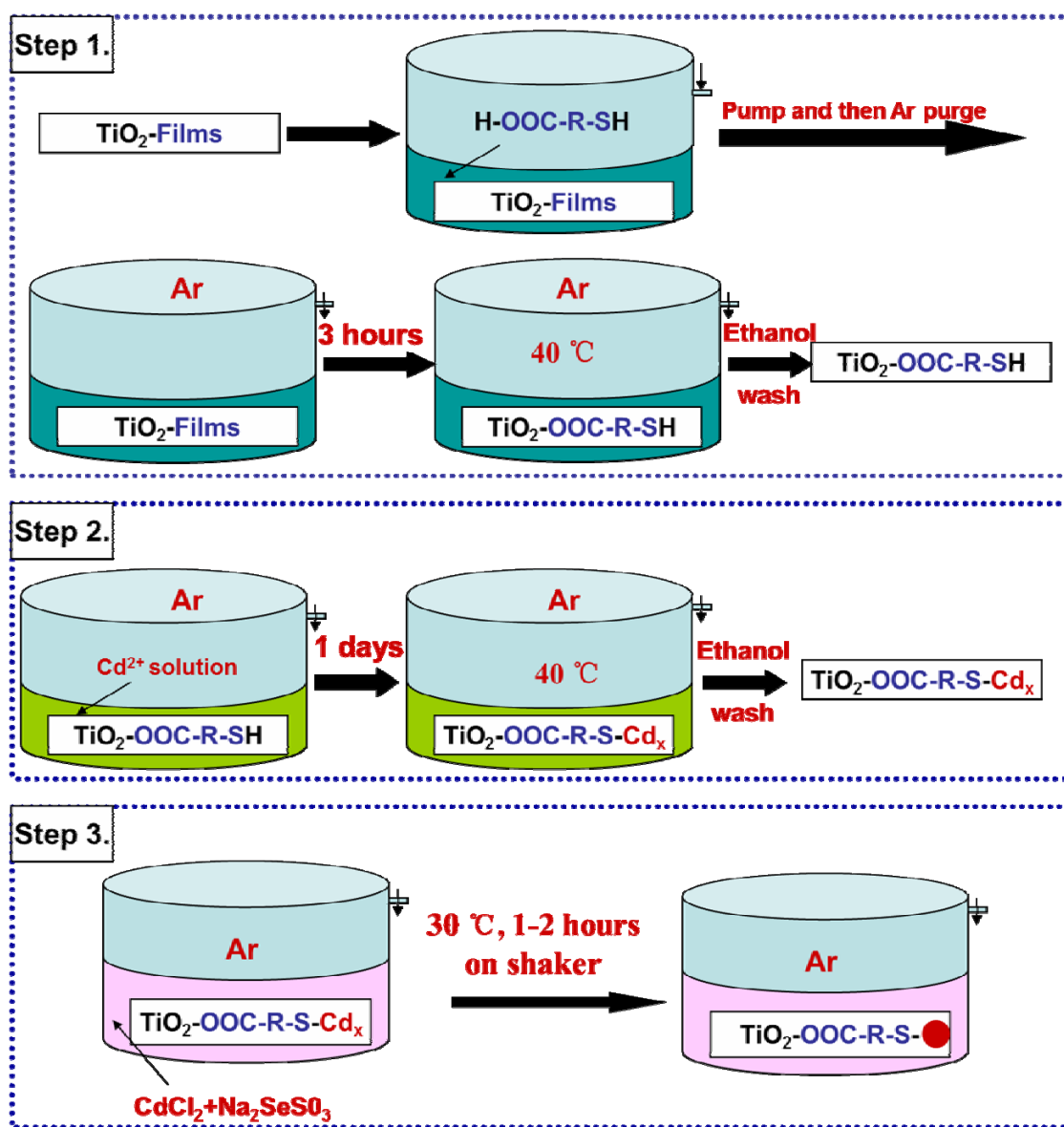
Discussion of other methods: Deficiently, however, the QD layer on the same TiO_2 mesoporous microspheres film deposited by the direct-CBD method appears unsightly, with lighter and uneven color intensity on both sides of the photoanode, and even obviously exposed white TiO_2 uncoated by QDs, as can be seen in the photograph in Figure S2c. We performed CBD processes for several times and could gain the red dark color photoanodes finally. However, the V_{oc} (around 0.5 V) and FF (below 40% with Pt) were still inferior to LS-CBD deposited photoanodes. The CdS-CBD deposited photoanodes are shown in Figure S2d. Despite the coverage of QDs seems better than direct-CBD, the anchorage can't stand comparison with those by LS-CBD from the appearance (Figure S2d), resulting in lower photovoltage (around 0.46-0.55 V).

We used the mixture of Cd^{2+} , S^{2-} and MPA solutions to assist anchoring but found that it didn't work as well as expected. Yellow floccules precipitated in solution immediately during mixing. The addition with some sodium hydroxide to adjust PH around 10 could disperse them but it broke the anchorage of COOH onto TiO_2 .

We also tried to use linkers in SILAR. At first, for Cd^{2+} anchoring to form $\text{TiO}_2\text{-COO-CH}_2\text{-S-Cd}$, there is no problem. But second step, we dipped Cd^{2+} anchored film into S^{2-} or Se^{2+} solution and observed some yellow precipitate in the solution, which can be explained that some tethered Cd^{2+}

disconnected from linkers because of excess of S^{2-} . (The much stronger binding of CdS compared to $TiO_2-COO-CH_2-S-Cd$).

IMPS/IMVS discussion: Interestingly, we observed two IMPS response features for the QDSSCs under weak light irradiation as shown in Figure S5c (below 50 W m^{-2}). However, the DSSC with the same photoanode architecture as QDSSCs exhibits only one IMPS response feature, as shown in Figure S5a. Then we sprayed 1-2 micrometer QD films on FTO ($CdSe_{FTO}$) and we found that the QD_{FTO} solar cells also showed only one IMPS response feature, as shown in Figure S5b. This difference may be caused by the fact that both QDs and TiO_2 had contribution on electron transport. Turning to the IMVS measurement, we observe only one response feature for all of three basic types of solar cells we tested. This is understandable because it is only the interface with the electrolyte which suffers the most significant charge recombination.



Scheme S1. Schematic illustration of the basic procedure for the linker seeding chemical bath deposition (LS-CBD) method.

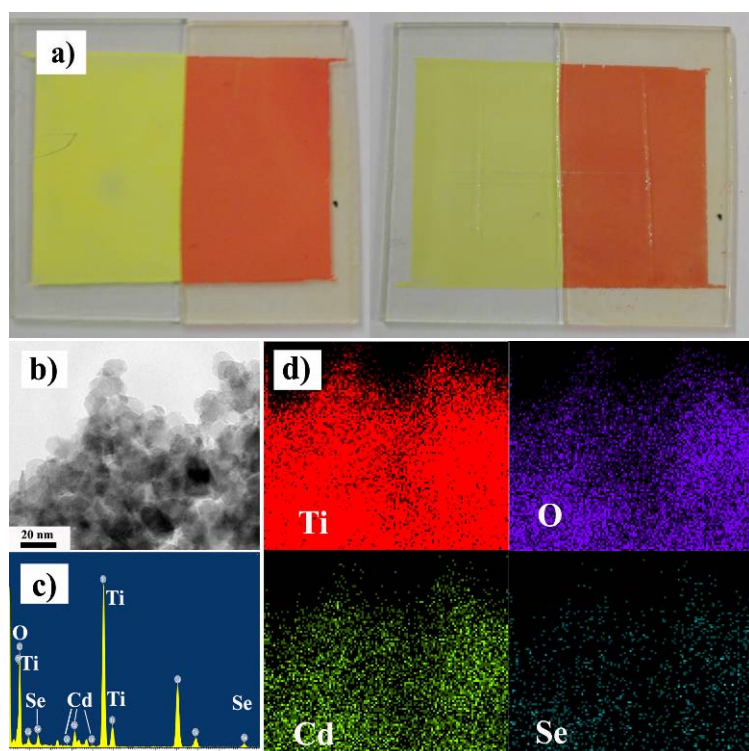


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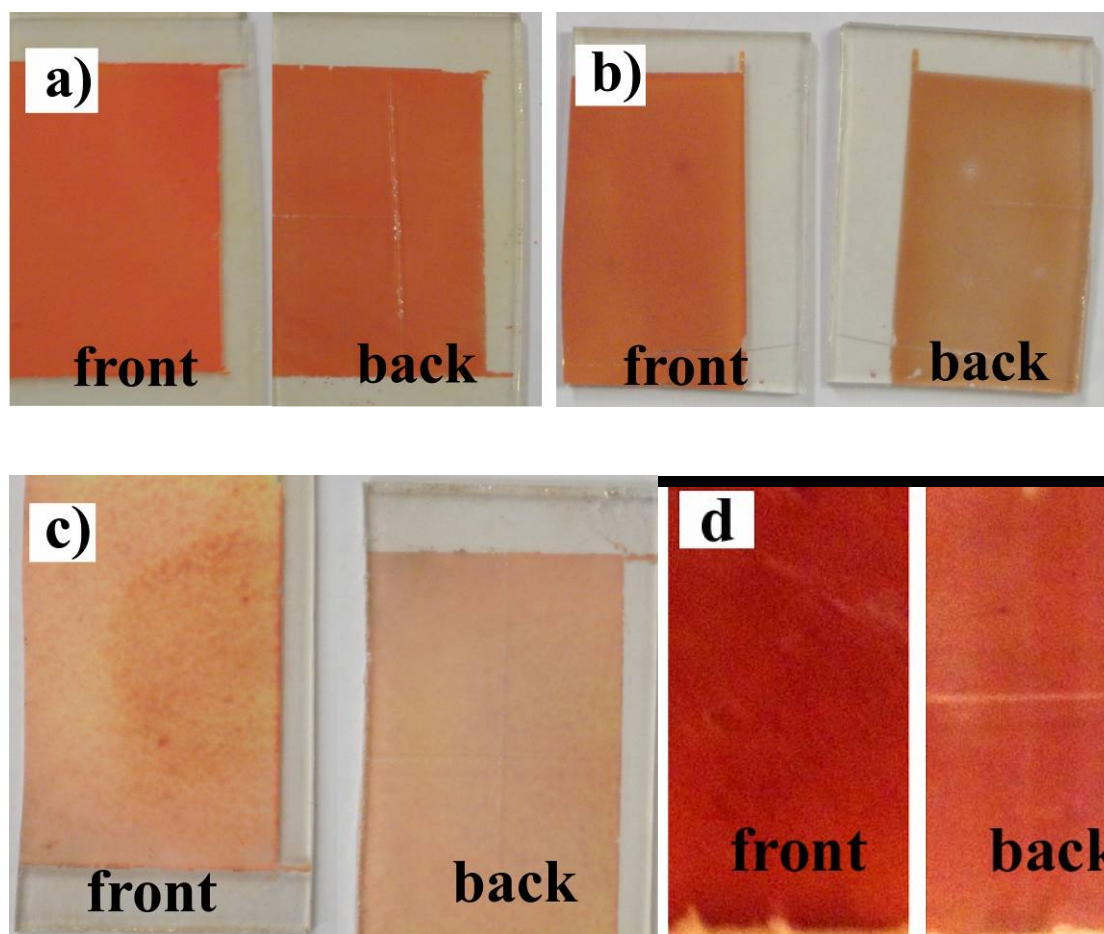


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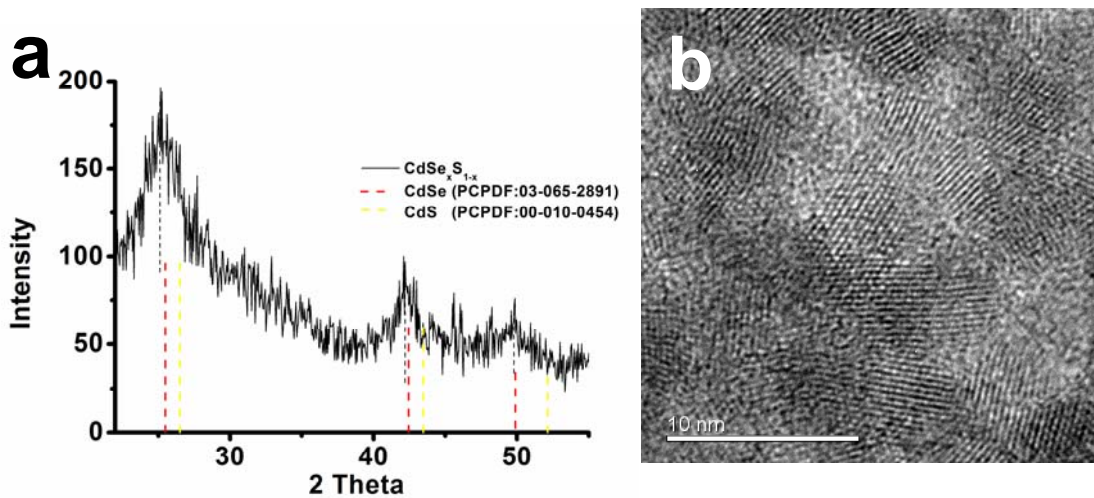


Figure S3. XRD (a) and TEM (b) of S doped CdSe (CdSeS)



Figure S4. The photographs of gel polysulfide electrolyte placed upright (Left) and upside down (Right), which was used for quasi-solid state QDSSCs.

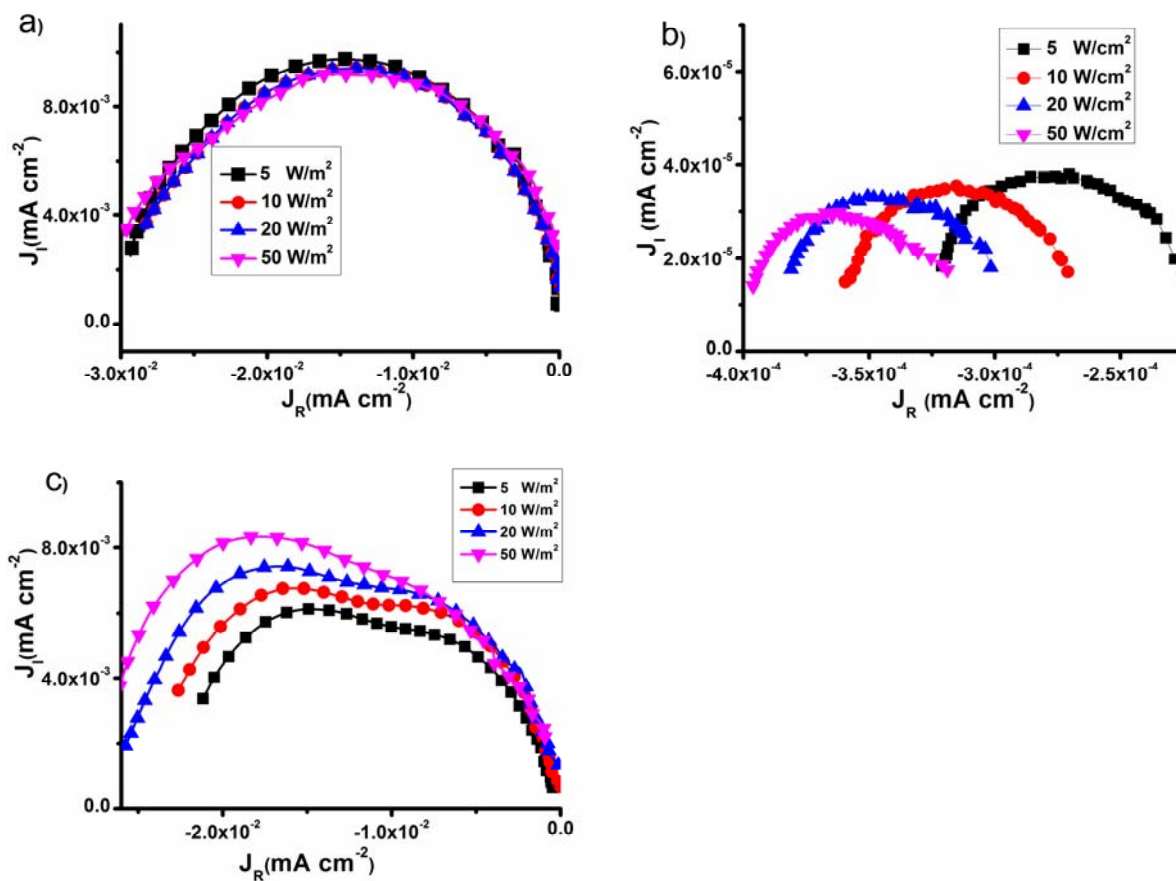


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