Reviewer(s)' Comments to Author:

Referee: 1

Comments to the Author

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Summary:

In this work “CdSe on a mesoporous transparents Conducting Oxide Scaffold as a Photocathode,” Norris and Cossairt describe efforts to prepare a high surface area photocathode based on CdSe quantum dot sensitized nanoITO electrodes. They demonstrate the use of a mesoporous ITO (nanoITO) substrate leads to an increase in surface area of the electrode in comparison to a planar substrate, sensitize these nanoITO electrodes with CdSe QDs, and observe an increase in activity for the photochemical reduction of MV2+ with MPA as a sacrificial donor as compared to a solution of suspended CdSe QDs. They fall short at what appears to be their ultimate goal—replacement of the sacrificial with an applied electrochemical potential—but offer insight into the challenges associated with this endeavor.

Significance:

It has previously been shown that photoexcited CdSe QDs are able to reduce both MV2+ as well as some H2 evolution catalysts. Sensitization of ITO has also been shown via spin casting and other depositing techniques. The novelty of this work lies in the construction of a photocathode material with high surface area that can effectively drive the reduction of MV2+ upon irradiation. In comparison to photoanode materials, comparatively few photocathode materials are known. This work represents a first step towards a new paradigm of p-type semiconductor materials which will find extensive applications in the field of solar fuels. While ultimately replacing the sacrificial donor with an applied bias would be an impactful contribution, this work is meritorious. In general, the experiments carried out are of the highest quality. For instance, I note that the experiments employed to determine the active surface area of the modified nanoITO electrodes are a very nice example of electrochemical quantification

Recommendation:

I would recommend that this article be published with major revisions. Additional control experiments need to be done to address the concerns detailed below and help further support the authors’ claims. These additional experiments will provide more concrete evidence for the claims made in this work.

Changes (Major):

1. Per the experimental procedure in the SI, it appears that the CdSe QDs with native (oleic acid) ligands are added to an aqueous solution with MPA, followed by sonication. Presumably ligand exchange from OA to MPA occurred during this process to yield water soluble QDs. This should be noted. These experiments should be repeated with isolated MPA-capped QDs (carry out a complete ligand exchange to MPA and isolate the MPA-capped dots, as opposed to doing the exchange in situ). Along these lines the following concerns should be addressed:

a. Do the authors think the sacrificial donor is the surface bound MPA or the free MPA in the solution? Is the sacrificial donor the same in both the solution and surface anchored system?

b. If surface bound MPA is the donor, it is important that the same amount of MPA is bound in both the slides and solution. An incomplete ligand exchange could account for the lower yield of reduced MV observed for the solution sample.

c. If surface bound MPA is the donor, how will this affect the integrity of the films? Assuming the oxidized MPA dimerizes to the dithiol, the films may lose QD sensitizer during the course of multiple photochemical reduction cycles.

d. Could the order of the photochemical reaction differ? Photoexcitation followed by hole trapping via MPA THEN electron transfer from the conduction band the methyl viologen? If bound MPA is the sacrificial donor this pathway seems more likely as trapping by bound MPA will likely be much faster than the bi-’molecular’ electron transfer to MV2+. Figure 4 should be changed to account for this possible pathway if the authors agree it is viable.

e. I think if would be helpful of the authors to better hypothesize why the films perform significantly better than solutions. As written, this is the main basis of the manuscript.

2. I think that being able to apply a bias to drive this photochemical reduction is the main goal the authors are striving for and they should make a few more efforts to push this part of the manuscript. I think this could really increase the significance. Below are some possibly experiments and considerations for these experiments:

a. By applying a -0.30 V potential, any MV2+ reduced by the QDs (MV•+) can be directly reoxidized to MV2+ if the small molecule has direct communication with the electrode. This seems to be an equally or more viable option to that proposed—that back electron transfer between MV•+ and the CdSe valence band hole occurs rapidly before the hole transfer to nanoITO can occur via tunneling through the organic linker ligand (as an aside, the authors may want to cite tunneling literature here).

b. If the above case is true, the proposed experiment to add a p-type tunneling barrier to the surface via electrodeposition or ALD would help significantly as if would block MV•+ from being directly reduced at the electrode surface. This proposed experiment suggests that the authors do believe that oxidation of the MV•+ by the applied bias may be possible.

c. One experiment to test the mechanism suggested in 2a is to apply a negative applied bias, one insufficient to reduce the CB of CdSe, but sufficient to reduce MV2+. If the signature blue color of the viologen radical appears, the violgen can readily be oxidized/reduced at the sensitized nanoITO surface.

d. Linking the MV2+ to the quantum dot surface via a carboxylate linker, as opposed to free in solution would also help eliminate MV•+ from being directly reduced at the electrode surface.

e. Doing a post ligand exchange with a short chain or ionic ligand may help communication between the quantum dot and electrode surface. This is done often in DSSC applications. You may also try using a conjugated linker ligand.

Changes (Minor):

1. The crystal structure of CdSe produced by the ‘heat-up method’ should be noted (zinc blende, not the wurtzite produced from hot injection synthesis)

2. A reference noting the size estimation from the LEET should be provided (Page 2, paragraph 3)

3. Can the authors provide a short explanation of the broadening observed on the slide-loaded CdSe?

4. In Figure 4, the D/D+ label in the figure should be defined as MPA.

5. The line “in order to compare the rate of MV2+ reduction by the slide…divided by the number of moles of CdSe in the reaction” seems a little out of place. Perhaps a “see below” should be added, since the slide chemistry had not yet been introduced.

Other Notes:

The manuscript is clearly written, and an appropriate length.

Referee: 2

Comments to the Author

The manuscript “CdSe on a Mesoporous Transparent Conducting Oxide Scaffold as a Photocathode,” by Norris et al. presents the use of an of a mesoporous nanoITO framework as a platform to attach CdSe quantum dots. In this communication, the authors briefly characterize their electrodes and evaluate their ability to function as a photocathode. The title of this manuscript is potentially misleading since MV2+ is not reduced photoelectrochemically. Rather the reaction occurs only photochemically with a sacrificial donor. Accordingly, the impact of the stated claims in the manuscript are better suited for the Journal of Materials Chemistry. A revised manuscript requires a responise to several critical issues to bolster the conclusions, as outlined below.

1. The authors should use a better light source for the photoelectrochemical experiments. In this work, the authors resort to using white LEDs as their light source. They do not mention the lamp power nor do they present the spectrum of their light source. This is problematic for two reasons: 1) they may simply not be providing enough photons to their photocathode, which could be why they see no photoresponse, and 2) without a spectrum of their light source, they do not know what fraction of the light they are using is actually capable of exciting an electron from the VB to the CB in the quantum dots. This reviewer notes that it is possible that the light source choice is not the cause for the photocathode’s poor performance since the QDs are independently capable of turning over MV2+/+• using the same light source.

2. The authors should try different linkers to attach the CdSe quantum dots to the nanoITO surface. If back electron transer is truly the issue at hand, then the authors should probe how different anchoring groups may mitigate this phenomenon. Performing a systematic set of experiments using these materials could be beneficial to the field. It may perhaps be worthwhile to begin studying the use of phosphonates or hydroxamic acid anchors (known to be more hydrolytically stable for aqueous solution work) if the authors wish to engage in this endeavor.

3. The authors should provide experimental evidence (often carried out by Raman spectroscopy) that the CdSe QDs are chemically bound to the surface of the nanoITO. It is not clear if the QDs are physisorbed or covalently bound to their nanoITO surface. If the goal is to present basic reactivity, this questions is not of major significance. However, in order to glean mechanistic insight, answering this question is crucial. If a majority of their QDs are simply adsorbed to the surface, then the QD/nanoITO interface could behave as a recombination center, which would prevent charge transfer from the QD to the ITO.

4. The authors should provide more photoelectrochemical characterization. The authors perform a single bulk electrolysis experiment at –0.3 V vs. Ag/AgCl, but they should also include linear sweep voltammetry performed in the light and in the dark to determine the photocurrent onset potential. It is possible that the authors may simply have not applied a suitably negative bias to drive the photoelectrochemical reduction. However, without a chopped light LSV there is no way of knowing if this is the case.