

Thiol quenching of CdSe quantum dots in NiO-CdSe-cobaloxime photocathode for H₂ evolution

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Visible-light-driven H₂ evolution has been attracting considerable attention from both environmental and energy points of view and also as a scientific challenge in the artificial photosynthesis community.¹⁻² Many systems have been employed to produce H₂ from sunlight-water splitting in a similar way to the natural photosynthesis systems.³⁻⁵ In general, these systems contain a combination of light harvesting material and an active catalyst that is able to produce H₂ after charge transfer from the light harvester. Therefore, a good understanding of the factors limiting photoinduced charge separation is needed to improve the catalytic activity of these systems.

In this work, we report the photoinduced charge dynamics of both electron and hole in an artificial system for H₂ evolution that consists of CdSe quantum dots (QDs) as light harvester and the well-known molecular CoP catalyst ([CoCl(dmgh)₂(pyridyl-4-hydrophosphonate)]). Both are chemically attached to a mesoporous NiO surface *via* thioglycolic acid and a phosphonate groups, respectively.

QDs have been popular sensitizers for solar cells including solar fuels application due to their high extinction coefficient, broad absorption spectrum, size-dependent tunability of the band gap, and the relatively simple preparation methods. Moreover, the CoP catalyst belongs to the best transition metal complexes known to produce H₂ and is also easy to prepare.

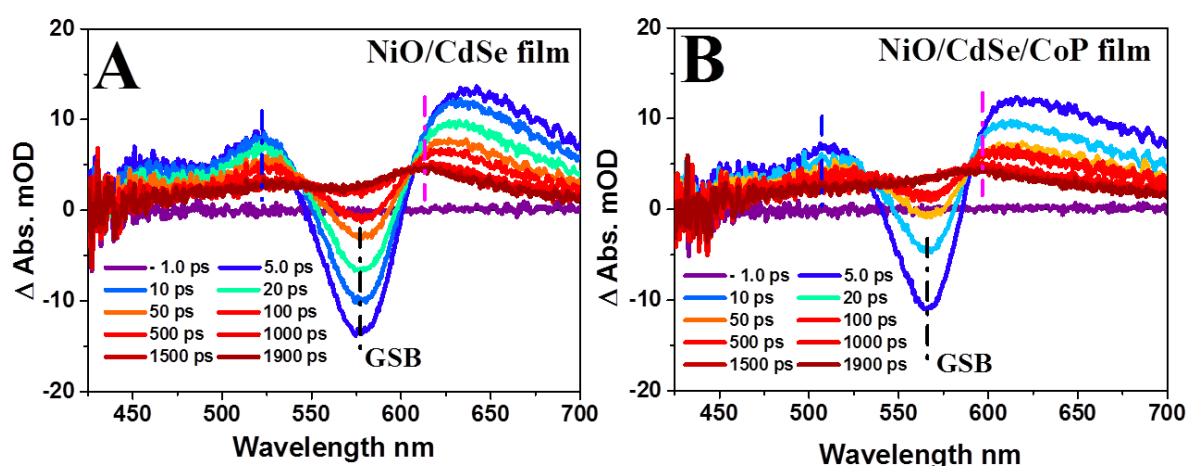


Figure 1. A) Transient absorption spectra for NiO/CdSe film without the catalyst, and B) Transient absorption spectra for NiO/CdSe film with introducing the catalyst.

This system was reported recently as an efficient and stable photocathode for H₂ production. Using time-resolved femtosecond spectroscopy, we managed to investigate that electrons transfer successfully from the excited CdSe QDs to the CoP. On the

other hand, thiol groups from the capping agent, which are used to stabilize the QDs, react with the photo-excited holes. Therefore, most of the photo-excited holes get trapped by the thiol capping agent instead of injected to NiO which will affect the photo-catalytic activity of the system. We believe this behaviour may general for this class of thiol capped QDs and limit their performance.

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