## **Supporting Information**

## Role of surface states in photocatalysis: study of chlorine-passivated CdSe nanocrystals for photocatalytic hydrogen generation

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**Figure S1.** X-ray photoelectron spectra of CdSe NCs after Cl treatment with (a) in-situ, (b) exsitu and (c) modified process, and (d) without Cl treatment. (e) Normalized Cl 2p spectra by area of Cd 3d signal. Intensity reveal relative fraction of Cl in nanocrystal depending on Cl treatment method.



**Figure S2.** UV-vis spectra of CdSe NCs after (a) *in-situ* and (b) *ex-situ* treatment processes at various Cl concentrations.



Figure S 3. Photograph of ex-situ Cl:CdSe NCs disperse in hexane (right) and N-methylformamide (left).



**Figure S4.** X-ray photoelectron spectra of OA and MUA capped CdSe NCs with and without Cl treatment after light irradiation. The binding energy of SeO<sub>2</sub> is 58.8 eV..



**Figure S5.** (a) Time-resolved photoluminescence (TRPL) decay of MUA-capped CdSe (black) and Cl:CdSe (red) NCs and OA-capped CdSe NCs (blue). (b) TRPL (straight line) and transient absorption (TA) (dotted line) kinetics of Cl-treated (red) and untreated CdSe NCs (black) showing the different decay traces up to 1 ns.



**Figure S6.** Cyclic voltammogram of CdSe NCs before and after Cl treatment. (Inset) cyclic voltammogram magnified in the range of 0 to -2.0 V vs. Ag/AgCl. The shift of reduction potential after Cl treatment is distinct from the plots.



**Figure S7.** <sup>1</sup>H NMR spectra of (a) OA- and (b) MUA- capped CdSe NCs dispersed in 0.1M of ferrocene and ethanol as reference solution, respectively. Insets of (a) and (b) show peaks of the resonances from vinyl in OA and methylene proton in MUA, respectively.

## Ligand quantification.

OA- and MUA- capped CdSe NCs are dispersed in 0.1 M of ferrocene d-benzene and 0.1 M of ethanol water solution, respectively, for <sup>1</sup>H-NMR analysis. In order to estimate ligand density of NCs, NC concentration of prepared solution is calculated using UV-vis spectrum based on Beer-Lambert law, and number of ligand is quantified by comparing the integrated areas of resonance peak from ligand and reference (*i.e.*, ferrocene and ethanol) as shown in Figure S7.