Supplementary Material (ESI) for *Journal of Materials Chemistry*

Supporting Information

Photocatalytic Activity of Colloidal CdS Nanoparticles with Different Capping Ligands

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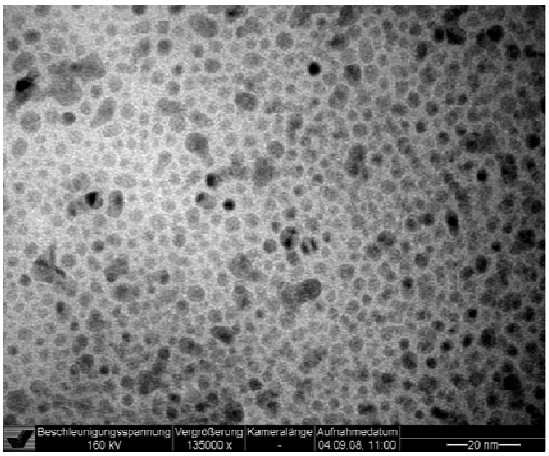
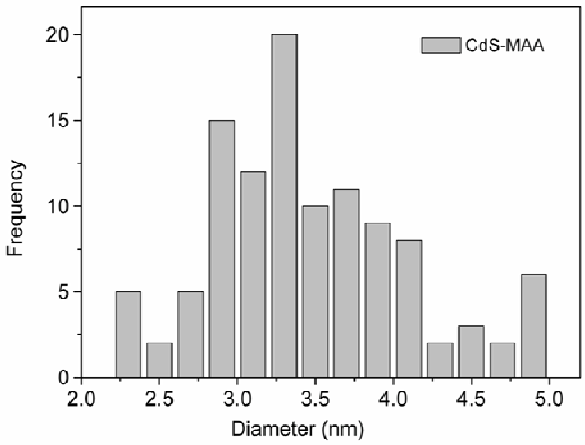
TEM Studies

The size of the QDs was determined using TEM studies. For TEM measurements the dilute solution of QDs (5µM in water) was deposited on the carbon surface of the TEM grid and air dried. The TEM results are shown in Fig S1.

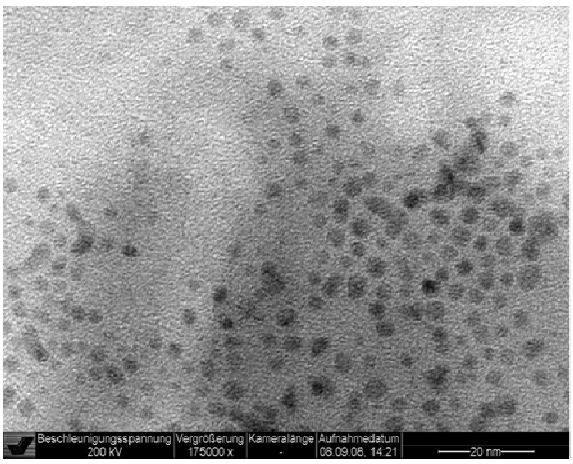
a)

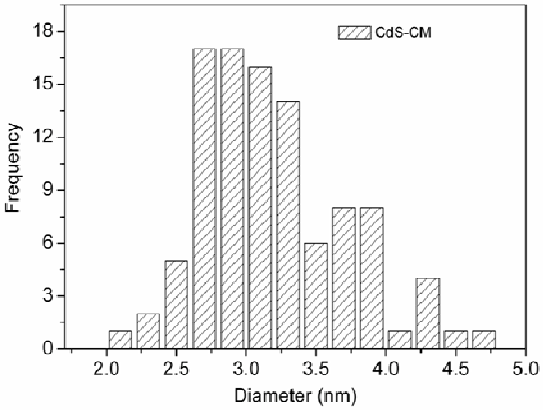




Average diameter of CdS-MAA = 3.4 ± 0.63

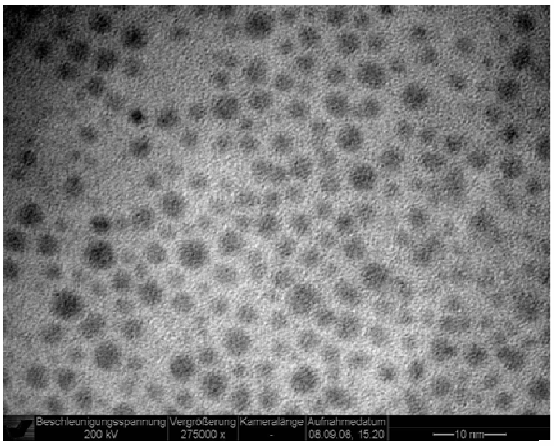
b)

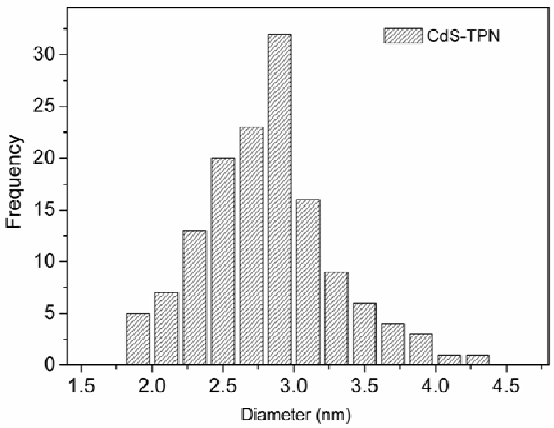




Average diameter of CdS-CM= 3.2 ± 0.52

c)





Average diameter of CdS-TPN = 2.8 ± 0.46

Fig. S1 TEM images and corresponding size distribution histograms of a) CdS-MAA, b) CdS-CM , c) CdS-TPN.

Electrostatic adsorption of HRP to different types of CdS quantum dots

To investigate whether HRP electrostatically adsorbs to the three different CdS QDs, we used fluorescence titration method, in which the fluorescence of the respective CdS QDs is quenched by continuous addition of the enzyme HRP. In a typical experiment, defined volumes of HRP were added to a stock solution of CdS QDs and the change in the fluorescence intensity was monitored.

From the results shown in Fig. S2, it is evident that the QD's fluorescence decreased gradually upon addition of HRP. In the case of CdS-MAA and CdS-TPN QDs the fluorescence intensity continuously decreased until about four molar equivalents of HRP were added. At higher ratios, no significant change in the fluorescence intensity was observed, thus suggesting that each QD is covered with 3-4 HRP molecules. The CdS-CM QDs revealed the similar descrease in fluorescence emission until about three molar equivalents of HRP were added, thereby also confirming the physical adsorption of approximately three HRP molecules per QD.

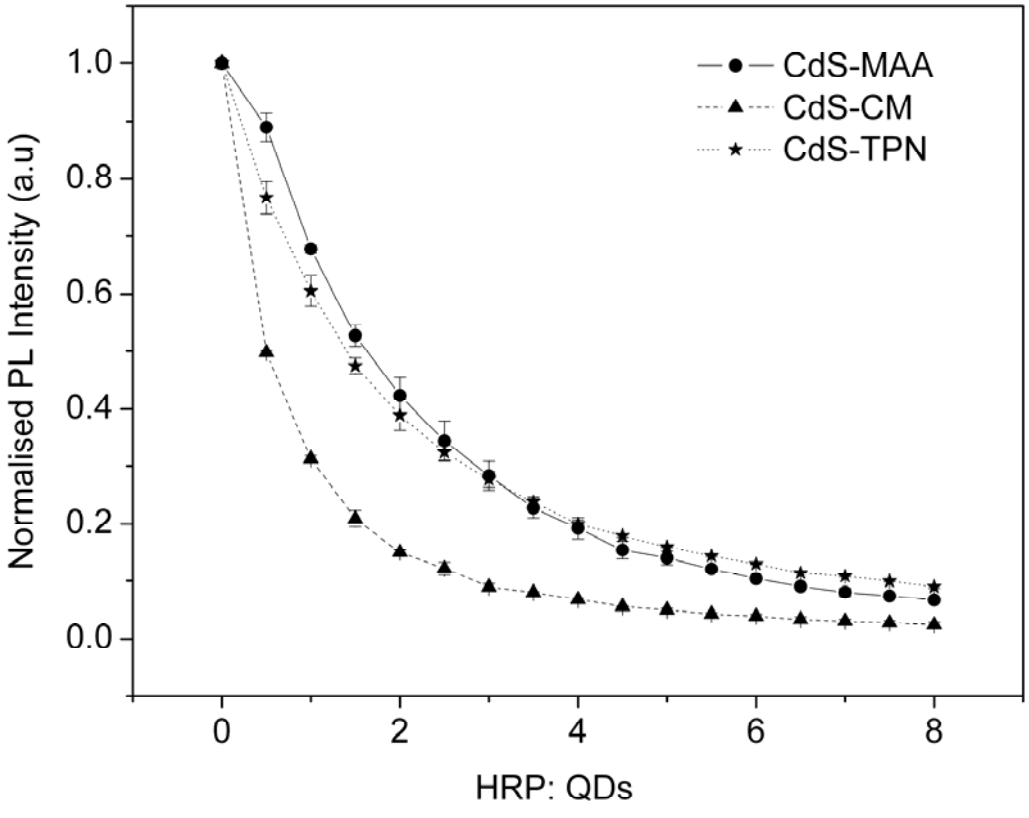


Fig. S2 Fluorescence quenching of QDs upon addition of various molar equivalents of HRP.

We also tried to verify physical attachment of HRP to QDs by electrophoretic shift assays, using 0.4 – 1% agarose gels. This method has been frequently used for analysis of QD-protein interactions, for instance, to study binding of hexahistidine-tagged proteins to CdSe/ZnS QDs (see e.g., H. Lu, O. Schoeps, U. Woggon, C. M. Niemeyer, *J. Am. Chem. Soc.* 2008, **130**, 4815.). In the case of the CdS QDs investigated here, however, the results were less clear, since no typical shift of the QD-protein band in dependence of protein concentration could be observed (Fig. S3). Nonetheless, bands of CdS-HRP conjugates were visible only, when both components were present in the samples (lanes 2, 3, 5, 6, 8, 9). In contrast, HRP only produce only one band (lane 10) and samples lacking HRP revealed no bands (lanes 1, 4, 7). Comparison of these results with those obtained from hexahistidine-tagged protein binding to CdSe/ZnS QDs (Lu, et al., J. Am. Chem. Soc. 130, 4815) indicates that the purely electrostatic interaction between HRP and the CdS QDs is less stable than that occurring between his-tagged proteins and CdSe/ZnS QDs, which also involves additional stabilization by Zn-histidine coordination (I. L. Medintz, A. R. Clapp, H. Mattoussi, E. R. Goldman, B. Fisher, J. M. Mauro, *Nat. Mater.* 2003, **2**, 630).

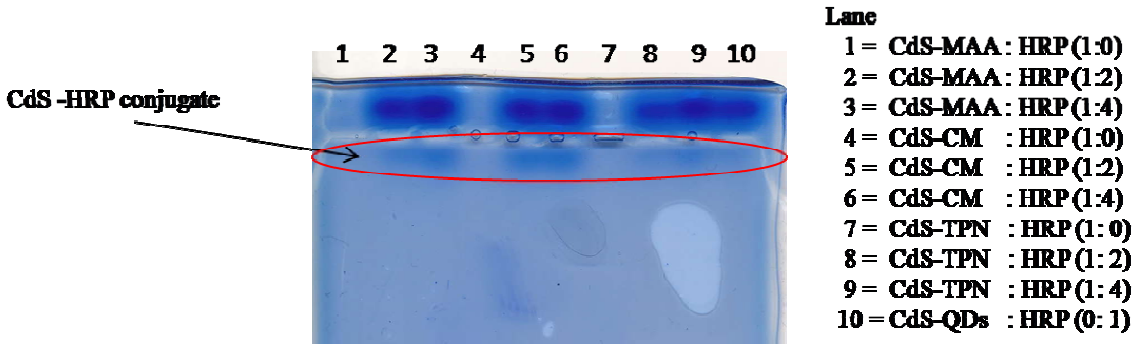


Fig. S3 Mobility shift assay using a 0.4% agarose gel, 50 V at 4 °C. Gels were stained with coomassie brilliant blue (CBB) for 20 min and destained in deionized water over night. Note that CBB staining was necessary since the QD's fluorescence could not be observed directly, likely due to quenching by the agarose gel matrix.

Influence of QDs concentration on the photocatalytic generation of hydroxyl radicals

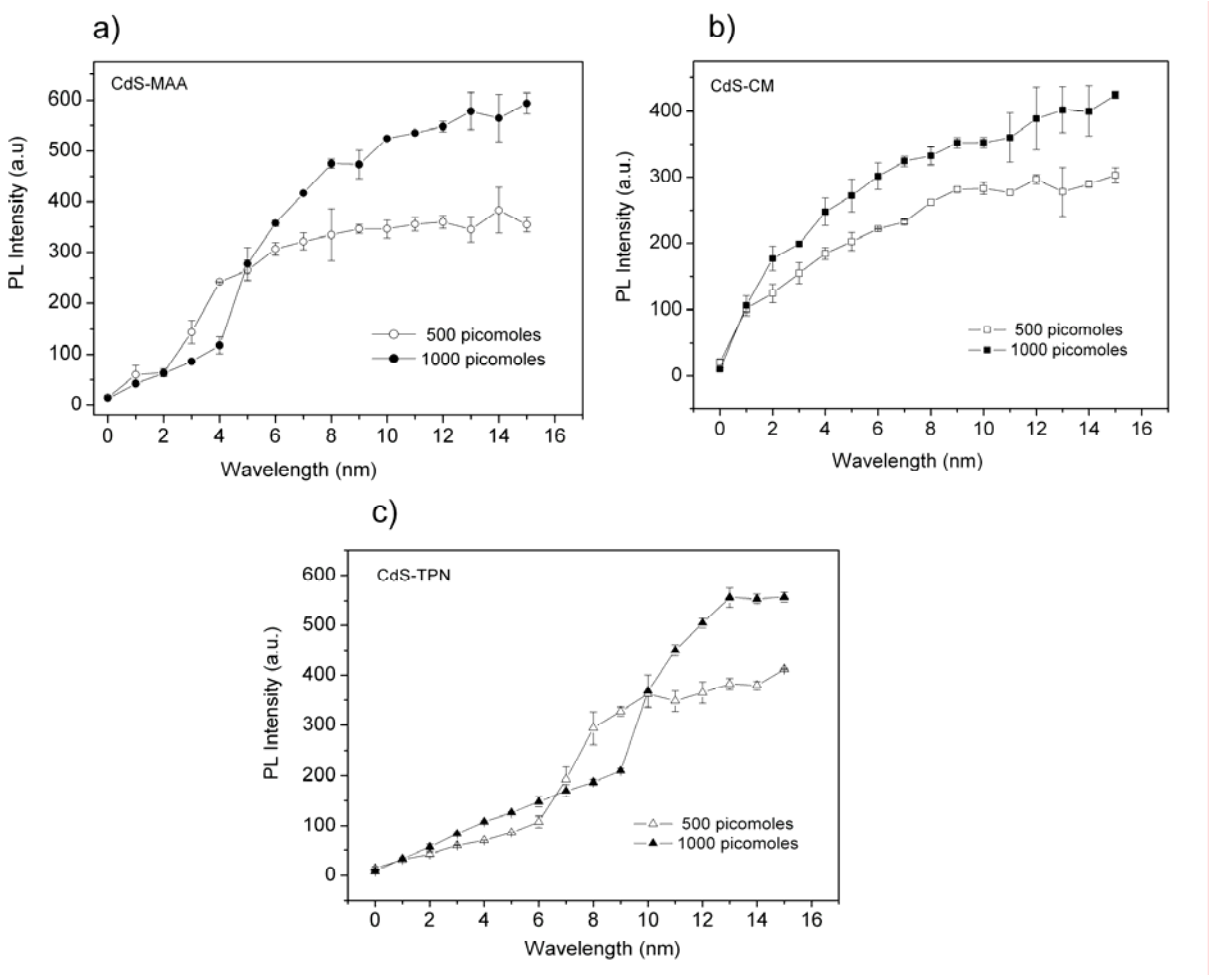


Fig. S4 Fluorescence intensity of 2-hydroxyterephthalate anion, generated by irradiation of different concentration of a) CdS-MAA, b) CdS-CM, and c) CdS-TPN as a function of irradiation time.