Title:	Confinement Matters: Stabilization of CdS Nanoparticles inside a Postmodified MOF toward Photocatalytic Hydrogen Evolution
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Abstract:	Insights into developing innovative routes for the stabilization of photogenerated charge-separated states by suppressing charge recombination in photocatalysts is a topic of immense importance. Herein, we report the synthesis of a metal–organic framework (MOF)-based composite where CdS nanoparticles (NPs) are confined inside the nanosized pores of Zr4+-based MOF-808, namely, CdS@MOF-808. Anchoring l-cysteine into the nanospace of MOF-808 via postsynthetic ligand exchange allows the capture of Cd2+ ions from their aqueous solution, which are further utilized for in situ growth of CdS NPs inside the nanosized MOF pores. The formation of CdS@MOF-808 opens up a possibility for visible-light photocatalysis as CdS NPs (1–2 nm) are a well-studied semiconductor system with a band gap of ~2.6 eV. The confinement of the CdS NPs inside the MOF pores, close to the Zr4+ cluster, opens up a shorter electron transfer route from CdS to the catalytic Zr4+ cluster and shows a high rate of H2 evolution (10.41 mmol g–1 h–1) from water with a loading of 3.56 wt % CdS. In contrast, a similar composite in which CdS NPs are stabilized on the external surface of MOF-808 reveals poor activity (0.15 mmol g–1 h–1). CdS NPs stabilized on the MOF-808 surface show slower and inefficient electron transfer kinetics compared to CdS stabilized inside the nanospace of the MOF, as realized by the transient absorption measurements. Therefore, this work unveils the critical role of stabilizing the photosensitizer NPs in close proximity of the catalytic sites in MOF systems towards developing highly efficient H2 evolution photocatalysts.
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