

SUPPORTING INFORMATION

Ni(OH)₂ as Hole Mediator for Visible Light-Induced Urea Splitting

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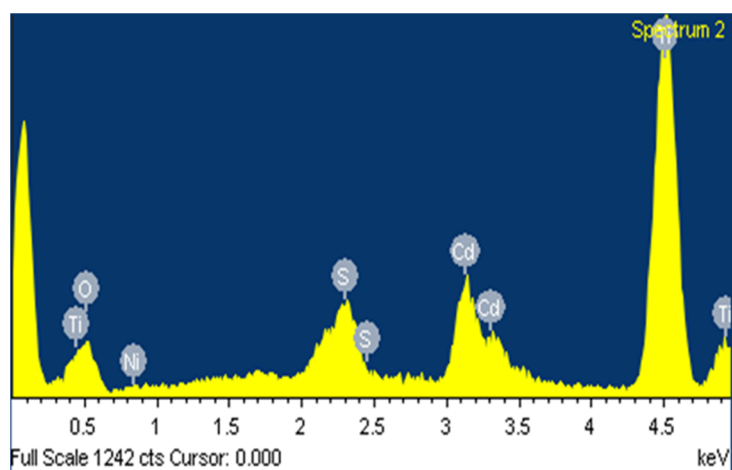


Figure S1. EDS results corresponding to $\text{TiO}_2/\text{CdS}/\text{Ni}(\text{OH})_2$ photoanode. Nickel is detected at very low concentrations as a result of the minimal thickness of the catalyst after only 1 immersion cycle following the SILAR deposition method.

Table S1. Composition of $\text{TiO}_2/\text{CdS}/\text{Ni}(\text{OH})_2$ as calculated by the area under the peaks of the EDS spectra

Element	Weight %	Atomic %
O K	34.20	64.26
S K	3.33	3.12
Ti K	43.78	27.48
Ni K	0.56	0.29
Cd L	18.14	4.85
Totals	100.00	

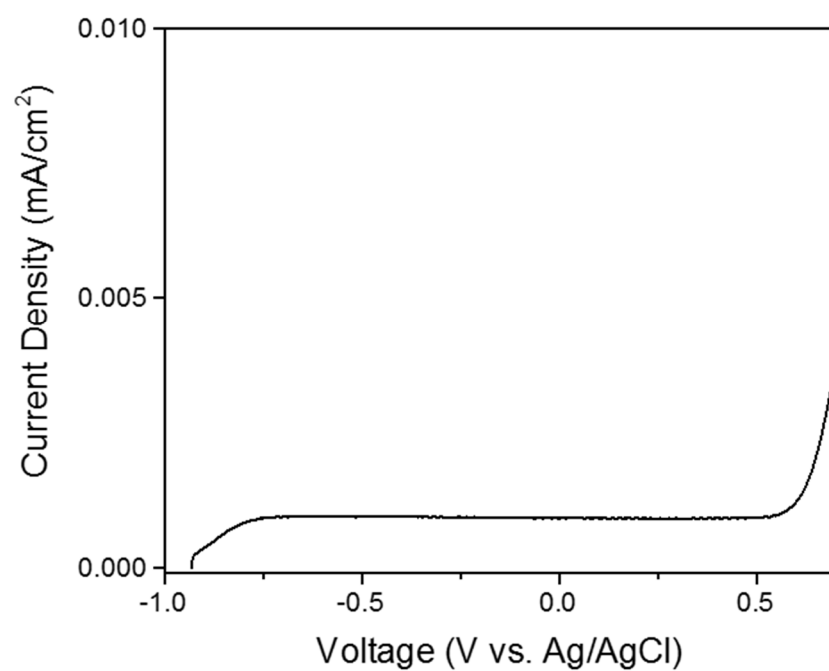


Figure S2. Photoelectrochemical response of a $\text{TiO}_2\text{-CdS-Ni(OH)}_2$ electrode immersed in 1 M NaOH without urea as sacrificial electron donor. The photocurrent is nearly 200 times less than when the electrolyte contains urea.

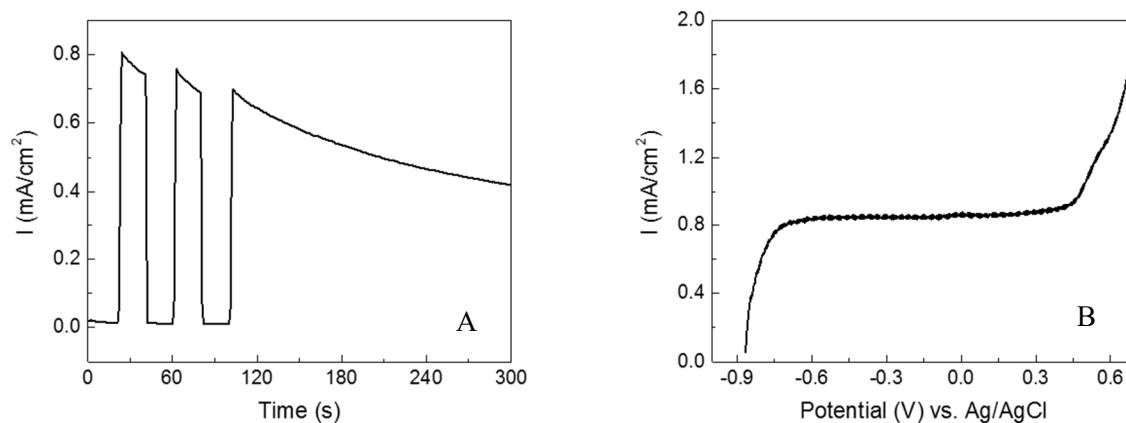


Figure S3. $\text{TiO}_2\text{-CdS}$ electrode response in 1 M NaOH - 0.33 M urea solutions. Photostability (A) and photocurrent density are both poor relative to the CdS-Ni semiconductor-catalyst assembly response in the urea photooxidation.

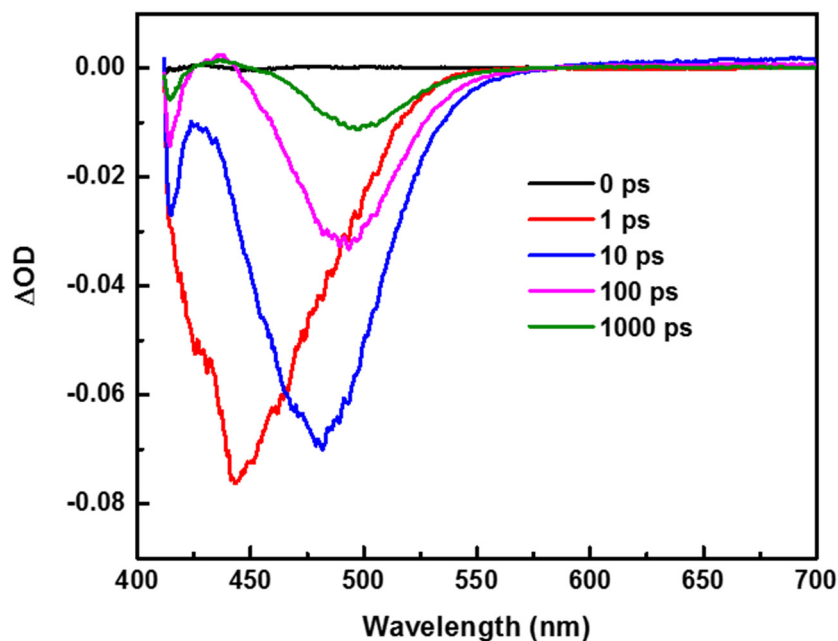


Figure S4. Transient absorption spectra of TiO_2/CdS in 1 M NaOH. The transient absorption observed when urea is in the electrolyte solution is absent when only NaOH is present. This implies the transient absorption peak (720 nm) that evolves when urea is present in the electrolyte solution is related to a still unveiled mechanism that is speculated to involve urea cation radical species. One can also observe the noise in the band edge bleach and the slow red-shifting of the bleach until >100 ps, which is likely a result of the instability of CdS in pure NaOH.

Table S2. Bleach recover fitting parameters and values

A ₁	tau1 (ps)	A ₂	tau2 (ps)	A ₃	tau3 (ps)	Tau (ave) (ps) 95% confidence interval	System
0.33	1.9	0.3	17.4	0.34	141.4	126.6 ± 8.3	TiO ₂ -CdS-Ni(OH) ₂ in urea/NaOH
0.49	1.9	0.3	23.7	0.21	188.6	160.7 ± 6.4	SiO ₂ -CdS-Ni(OH) ₂ in urea/NaOH
0.34	2.1	0.7	38.2	0.44	263	214.4 ± 8.2	SiO ₂ -CdS in vacuum
0.12	290.1	0.5	2.1	0.34	32.5	222.9 ± 11	TiO ₂ -CdS-ZnS-Ni(OH) ₂ in urea/NaOH

Table S3 Absorption decay fitting parameters and values

A ₁	tau1 (ps)	A ₂	tau2 (ps)	A ₃	tau3 (ps)	Tau (ave) (ps) 95% confidence interval	System
0.74	1.5	0.17	14.5	0.08	126.3	97.1 ± 2.3	TiO ₂ -CdS-Ni(OH) ₂ in urea/NaOH
0.78	1.4	0.18	19.3	0.05	167.6	113.2 ± 1.9	SiO ₂ -CdS-Ni(OH) ₂ in urea/NaOH
0.81	1.5	0.12	21.4	0.07	266.9	221 ± 3.9	TiO ₂ -CdS-ZnS-Ni(OH) ₂ in urea/NaOH
0.7	1.5	0.23	17.3	0.07	210.6	162.8 ± 3.3	TiO ₂ -CdS-Ni(OH) ₂ in NaOH