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Hollow Cu-TiO₂/C Nanospheres Derived from Encapsulated MOF

coating for Efficient Photocatalytic Hydrogen Evolution

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Figure S1. TEM images of SiO₂@HKUST-1 and TEM element mapping of Si, C, O and Cu in SiO₂@HKUST-1 nanospheres.



Figure S2. TEM EDS of $SiO_2@HKUST-1$ nanospheres (Mo net was used as the support).



Figure S3. The TEM EDS of SiO₂@HKUST-1-Ti nanospheres (Mo net was used as the support).

	Percentage	Percentage	Amount of sample for
	of Ti	of Cu	photocatalysis
SiO ₂ @HKUST-1	0	1.05 %	265 mg
SiO ₂ @HKUST-1-Ti	1.13 %	1.03 %	265 mg
SiO ₂ @ Cu-TiO ₂ /C	1.19%	1.14%	265 mg
Hollow Cu-TiO ₂ /C	30.4 %	27.7 %	5 mg
Cu-TiO ₂ /C	30.4 %	27.7 %	5 mg
P25	60 %	0	5 mg
HKUST-1-800	0	58.5%	5 mg
P25+HKUST-1-800	30.4 %	27.7%	5 mg

Table S1. The ICP result of Ti and Cu percentage in sample of $SiO_2@HKUST-1-Ti$, $SiO_2@Cu-TiO_2/C$ and Hollow Cu-TiO_2/C as well as the amount of the sample for photocatalytic experiments.



Figure S4. The XPS spectra of hollow Cu-TiO₂/C nanospheres.



Figure S5. The XRD of the obtained $SiO_2@Cu-TiO_2/C$.



Figure S6. ESR spectra analyzed in air at room temperature for hollow Cu- TiO_2/C nanospheres.



Figure S7. The UV-vis absorption spectra band gaps of P25, SiO₂@HKUST-1, SiO₂@HKUST-1-Ti, SiO₂@TiO₂-Cu/C and hollow Cu-TiO₂/C nanospheres.



Figure S8. The UV-vis absorption comparison of P25+HKUST-1-800 (mixture of P25 and calcinated HKUST-1) and hollow Cu-TiO₂/C nanospheres.

In order to demonstrate the existence of p-n junction in the catalysis, the UV-vis absorption spectra of two sample with the same Cu/Ti ratio, one was hollow Cu-TiO₂/C nanospheres, another was mixture of P25 and calcinated HKUST-1 (named P25+HKUST-1-800) was studied. The absorption edge of P25+HKUST-1- 800 (mixture of P25 and calcinated HKUST-1) and hollow Cu-TiO₂/C were ~380 and ~430 nm respectively, indicating an obvious shift from UV region to the visible region. Meanwhile, their related band gaps decreased from 3.3 to 2.89 eV. This phenomenon may be attributed to the p-n hetero-junction formation between Cu₂O and TiO₂ in hollow Cu-TiO₂/C after calcination treatment.



Figure S9. The TEM images with element mapping and EDS of hollow $Cu-TiO_2/C$ nanospheres after photocatalytic activity (Mo net was used as the support).



Figure S10. illustration of the band structure and electron transfer process of hollow $Cu-TiO_2/C$ nanospheres during the photocatalytic experiment.