Electronic Supplementary Information

Controllable synthesis of Cu₂O Hierarchical Nanoclusters with High Photocatalytic Activity

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Fig. S1 (a and b) Typical TEM images of Cu_2O nanocrystals (S1) under high magnification Note: It can be seen clearly that there are many "aggregation units" marked with white circles shown in Fig.S1. And sizes of the "units" are different ranging from 40 to 65 nm.



Fig. S2 Typical SEM images of the Cu₂O NCs (S2) under low magnification

Note: It can be seen obviously that S2 has uniform size distribution even under the large scanning scale.



Fig. S3 XRD patterns of different shaped Cu_2O nanocrystals. "cps" is the abbreviation of the phrase of "counts per second".



Fig. S4 FT-IR spectra of various shaped Cu₂O nanocrystals

(a)				8	(b)				-
Dark	Dark	Light	Light	Light	Dark	Dark	Light	Light	Light
0 min	30min	3 min	6min	12min	0 min	30min	20min	40min	65min

Fig. S5 Digital pictures of the color changes with the irradiation time of Cu₂O NCs (S2) by using different initial concentrations of MO solution: (a) 10 mg/L (b) 40 mg/L

Further work has been done to prove that the effect observed is indeed photocatalysis, and not just continued adsorption. The experimental results are listed in Tab. S1 as following. For convenient discussion, the decoloration rate of MO is determined by the formula $\eta \% = (C_0 - C_t)/C_0 \times 100 \%$. Where, C_0 and C_t represent the initial absorbance and the real time absorbance of MO solution in dark or under irradiation, respectively.

Initial concentration of	Experimental presedure	Decoloration rate	
MO aqueous solution	Experimental procedure	of MO	
40 mg/I	30 mins (dark) plus 65 mins (dark)	51 %	
40 mg/L	30 mins (dark) plus 65 mins (irradiation)	100 %	
10 mg/I	30 mins (dark) plus 12 mins (dark)	55 %	
10 mg/L	30 mins (dark) plus 12 mins (irradiation)	100 %	
40 mg/L	16 hours in the dark	100 %	
10 mg/L	15 hours in the dark	100 %	

Tab. S1 Adsorption property and photocatalytic activity of S2

Note: The amount of S2 keeps the same (0.01g) in all the experiments with MO aqueous solution of 100 ml.

According to Tab.S1, it is obviously that photocatalysis really exists by using the most active Cu_2O sample (S2). Moreover, the adsorption rate of S2 becomes very very slow after 30 mins in the dark. Further experimental results indicate that MO can be completely adsorbed after 16 hours (40 mg/L) and 15 hours (10 mg/L) in the dark, respectively. Therefore, the effect observed is indeed photocatalysis.

Initial concentration of MO aqueous solution	S 1	S2	S3	S4	S5
40 mg/L	0.0404	0.0533	0.0362	0.0293	0.0017
10 mg/L	0.0859	0.2033	0.0829	0.0818	0.0053

Tab. S2 Constants (k) of each sample under different conditions

Morphologies of Cu ₂ O	Average particle size of Cu ₂ O	Composites	The quality ratio between Cu ₂ O and MO	Irradiation time	Degradation ratio of MO	Ref.
Porous sphere	~300 nm	Pure Cu ₂ O	10 mg:1.5 mg=20:3	3 h	~3%	1
26(18)-facet Polyhedral	2 µm	Pure Cu ₂ O	50 mg:1.5 mg=100:3	3 h	73%	2
Sphere	200 nm	rGO-Cu ₂ O	20 mg:1 mg=20:1	60 mins	96.6%	3
Sphere	1-2 μm	Cu-Cu ₂ O	50 mg:2.5 mg=20:1	20 mins	99.77%	4
Hollow sphere	200 nm	Au-Cu ₂ O	20 mg:16 mg=5:4	4 h	~70%	5
Irregular sphere	20-40 nm	TiO ₂ -Cu ₂ O	25 mg:1.5 mg=50:3	60 mins	90%	6
Quasi- sphere	100-300 nm	Fe ₃ O ₄ -Cu ₂ O	100 mg:3 mg=100:3	60 mins	90%	7
Octahedral	60 nm	Ag-Cu ₂ O	25 mg:2.5 mg=10:1	60 mins	~98%	8
NCs	25nm	Pure Cu ₂ O	10 mg:1 mg=10:1	12 mins	100%	This work
NCs	25 nm	Pure Cu ₂ O	10 mg:4 mg=5:2	65 mins	100%	This work

Tab. S3 Photocatalytic activities of Cu₂O with different morphologies and composites

Notes: (1) The definition of the degradation ratio is the same with the decoloration rate discussed before. (2) Porous sphere Cu₂O. The degradation ratio of MO was not provided with accurate value but with curve at different time.¹ (3) rGO-Cu₂O composites with weight ratio 2:5.³ (4) Cu-Cu₂O composites with weight ratio 6:125.⁴ (5) Au-Cu₂O composites with molar ratio 1:20. The degradation ratio of MO was not provided with accurate value but with curve at different time.⁵ (6) TiO₂-Cu₂O composites with molar ratio 1:9.⁶ (7) Fe₃O₄-Cu₂O composites with weight ratio 4:6.⁷ The degradation ratio of MO was not provided with accurate value but with curve at different time. (8) Ag-Cu₂O composites with molar ratio 3:10.⁸

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