Splitting growth of novel CuO straw sheaves and the improved photocatalytic activity by active {110} facets exposed

Yunxuan Zhao, Huaxia Shi, Mingdong Chen and Fei Teng*

Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Innovative Research Laboratory of Environment and Energy, School of Environmental Sciences and Engineering, Nanjing University of Information Sciences and Engineering, Nanjing 210044, China. Corresponding author. Email: tfwd@163.com (F. Teng); Phone: 86-25-58731090



Fig. S1 Intensity ratios of {002}/{110} peaks



Fig. S2 SEM images of the samples prepared at different reaction temperatures: (a) $80 \ ^{\circ}C$; (b) $100 \ ^{\circ}C$; (c) $120 \ ^{\circ}C$; (d) $140 \ ^{\circ}C$



Fig. S3 XRD patterns of the samples at different reaction temperatures corresponding to Fig. S2



Fig. S4 SEM images (a-c) and XRD patterns (d) of the samples prepared at different molar ratios of HMT/Cu(II): (a) 5; (b) 10; (c) 15; HMT, hexamethylenetetramine



Fig. S5 SEM images of the sample prepared without adding HMT



Fig. S6 Total organic carbon (TOC) variation (a), Degradation curves of RhB (b) and phenol (c) over CuO straw sheaves

The variation of total organic carbon (TOC) represents the mineralization extent of organic chemical. The TOC values during the degradation process are determined on Apollo 9000 analysis instrument (Tekmar Dohrmann). It is clear that the TOC values decrease gradually with the proceeding of reaction. In the initials stage, the TOC values decrease fast; the TOC value varies slowly with the decrease of RhB

concentration. After 140min, about 24.5% of RhB are mineralized (Fig. S10a,b). Generally, de-ethylation can only result in slightly variation of the TOC value [1-3]. Some researchers have reported that the RhB photodegradation usually occurs through two competitive processes: de-ethylation and the destruction of the conjugated structure. De-ethylation and breakage of cabonyl first occurs to form colorless inner ester-like isomers; and then latters are completely mineralized. The destruction of the conjugated structure occurred in this case [4-7]. Also, we have measured the degradation of colorless phenol at 270 nm (Fig. S10c).

Ref.s:

- [1] P. Wilhelm, D. Stephan, Photochem. Photobio. A-Chem., 185(1) (2007) 19.
- [2] C.-C. Chen, W. Zhao, P.-X. Lei, J.-C. Zhao, N. Serpone, Chem. Eur. J., 10 (2004) 1956.
- [3] P.-X. Lei, C.-C. Chen, W.-H. Ma, J.-C. Zhao, Acta Chim. Sin., 63(17)(2005)1551.
- [4] C. Chen, X. Li, W. Ma, J. Zhao, J. Phys. Chem. B, 106 (2002) 318.
- [5] G.A. Somorjai, Chem. Rev., 96 (1996) 1223.
- [6] M. Kiskinova, Chem. Rev., 96 (1996) 1431.
- [7] F. Seker, K. Meeker, T.F. Kuech, A.B. Ellis, Chem. Rev., 100 (2000)2505.



Fig. S7 XRD patterns of the CuO samples

Samples	^[a] Surface area (m^2/g)	^[b] Crystallinity (%)
Irregular CuO	27.0	41.7
CuO flowers	28.5	57.7
CuO straw sheaves	21.8	75.9
^[a] Surface area,	calculated by the	Brunauer-Emmett-Teller (BET

Table S1 The BET areas and crystallinity of the CuO samples

^[a] Surface area, calculated by the Brunauer-Emmett-Teller (BET) method; ^[b] Crystallinity, calculated using JADE5 software on base of XRD patterns, compared with bulk CuO



Fig. S8 SEM micrographs and lattice fringe image of CuO flowers

The lattice fringe spacing is determined to be 0.23 nm, which can be indexed to the (111) facet of monoclinic CuO, suggesting that the CuO crystals grow preferentially along the [111] direction. However it is difficult to determine the facets exposed due to the compact microstructures.



Fig. S9 Atom distribution of different facets

Facets	Copper number /unit Å ²	Oxygen number /unit Å ²
(110)	0.1255	0.1339
(200)	0.1054	0.1264
(002)	0.1229	0.1153
(111) or (-111)	0.1108	0.1108

Table S2 Atom numbers per area over different facets

It is clear that atom density on (110) facet is higher than those of (200), (002) and (111) or (-111) facets.



Fig. S10 Photocurrent responses of CuO straw sheaves, irregular CuO and CuO flowers electrodes

Fabrication of electrode: 50 mg of powders are dispersed into 5 mL of distilled water under ultrasonic stirring. After 60 min, the powders were coating onto $10\text{mm}\times10\text{mm}\times2\text{mm}$ ITO glass (Indium tin oxide, 50Ω) and then dried at 120 °C for 3h. The photocurrent of the as-prepared electrode was measured under visible light irradiation (\geq 420nm) at electrochemistry working station.

The photoresponses of CuO straw sheaves, irregular CuO and flower-like CuO electrodes have been measured and the results are shown in Fig. S10. The photocurrent of CuO straw sheaves electrode is the highest than those of irregular and flower-like ones under visible light irradiation. The improved photocurrent of CuO straw sheaves electrode may originate from an enhanced photoinduced charge separation, which benefits to the improved photocatalytic properties.