## Novel Au/Cu<sub>2</sub>O Multi-shelled Porous heterostructures for

## enhanced efficiency photoelectrochemical water splitting

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Fig. S1 Powder XRD pattern of the as-prepared Cu<sub>2</sub>O MSP and Au/MSPHs.



Fig. S2 (A) SEM and (B) HRSEM images of the as-prepared Au NPs.

Catalyst	Electrolyte	Light	Bias Potential	Photocurrent Density	References (Year)
Cu <sub>2</sub> O powders	Na <sub>2</sub> SO <sub>4</sub>	> 420 nm	0	~100 uA/cm <sup>2</sup>	[19] (2008)
Cu <sub>2</sub> O nanocubes		AM 1.5G	3 V	8 uA/cm <sup>2</sup>	[20] (2008)
Cu <sub>2</sub> O spheres	Methanol and Na <sub>2</sub> SO <sub>4</sub>	480 nm	-0.1 V vs SCE	25 uA/ cm <sup>2</sup>	[21] (2014)
Cu <sub>2</sub> O cubes	Na <sub>2</sub> SO <sub>4</sub>	> 400 nm	-0.6 V vs Ag/AgCl	$\sim 2 \text{ uA/cm}^2$	[23] (2014)
Cu <sub>2</sub> O octahedrons				$\sim 1.5 \text{ uA/cm}^2$	
Cu <sub>2</sub> O cuboctahedrons				$\sim 6 \text{ uA/cm}^2$	
Cu <sub>2</sub> O nanocubes	$Na_2SO_4$	AM 1.5G	0	10 uA/cm <sup>2</sup>	[10] (2016)
Au/Cu <sub>2</sub> O				30 uA/cm <sup>2</sup>	
Cu <sub>2</sub> O MSP <sup>a</sup>	Na <sub>2</sub> SO <sub>4</sub>	AM 1.5G	-0.45 V vs Ag/AgCl	60 uA/cm <sup>2</sup>	[14] 2016
Cu <sub>2</sub> O MSH <sup>b</sup>				80 uA/cm <sup>2</sup>	
Cu <sub>2</sub> O SSH <sup>c</sup>				70 uA/cm <sup>2</sup>	
Cu <sub>2</sub> O MSP	Na <sub>2</sub> SO <sub>4</sub>	AM 1.5G	0	20 uA/cm <sup>2</sup>	This work (2017)
Au/Cu <sub>2</sub> O				150 uA/cm <sup>2</sup>	

Table S1 Overview of photocurrent density based on Cu\_O and Au@Cu\_O to date.

<sup>a</sup> MSP represents Multi-Shelled Porous (MSP)sub-micron spheres

<sup>b</sup> MSH represents Multi-Shelled Hollow (MSH) submicron spheres

° SSH represents Single-Shelled Hollow (SSH) sub-micron spheres



Fig. S3 (A) and (B) are SEM images of as prepared and after water splitting Au/MSP, respectively.

Fig. S4(A) is the XPS spectrum of the Au/MSP after water splitting. We can see the sample has no obvious change after the photocatalytic reaction. Fig. S4 (B), (C) and (D) are the high-resolution scan XPS spectrum of Cu 2p, Au 4f and O 1s, respectively. The positions and shapes of the peaks of original and after water splitting are almost the same.



Fig. S4 (A), (B), (C), (D) are the XPS spectrum survey, Cu 2p band, Au 4f band and O 1s band of original and after water splitting Au/MSP, respectively.



Fig. S5 Ultraviolet photoelectron spectroscopy (UPS) of Cu<sub>2</sub>O MSP (a) and Au/Cu<sub>2</sub>O MSP (b).



Fig. S6 Photoluminescence (PL) spectra of MSP and Au/MSP.