Supporting Information

Shape-Controlled Cu_2O Nanospheres as Bifunctional Catalysts Boosting the Oxidations of Glucose and Hydrazine

Li Wang,[a] *Yutai Wu* [b*], *Chaoyang Sun* [b], *Hui Wang* [b], *Jianwei Ren* [c**]

[a] School of Chemistry & Environmental Engineering, Pingdingshan University, Pingdingshan 467000, China

[b] State Key Laboratory Base for Eco-Chemical Engineering, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao, 266042, China

[c] Department of Mechanical Engineering Science, University of Johannesburg, Cnr Kingsway and University Roads, Auckland Park, 2092, Johannesburg, South Africa.

Physical characterizations

The X-ray diffraction (XRD) was done on Shimadzu XD-3A Instrument, which was fitted with filtered Cu-Kα radiation (λ = 0.15418 nm) and operated at 30 mA and 40 kV. The 2θ scan rate for XRD analysis was set at 4 ° min^{-1}. The morphologies of the catalysts were evaluated by a Carl Zeiss Ultra Plus field emission scanning electron microscopy (SEM) measurement using a JEM-2010 Electron Microscope (Japan) with an acceleration voltage of 200 kV.

Electrochemical measurements

An electrochemical work station (CHI 660D) was used to do all electrochemical measurements for this study. A three-electrode electrochemical cell comprises of an

Ag/AgCl as reference electrode (saturated KCl solution), platinum wire as counter electrode, and a working electrode with a thin film catalyst layer coated on a glassy carbon disc (5-mm diameter rotating disc electrode-RDE). The detail procedure of catalyst layer was as follows: 2 mg of as-prepared sample was treated ultrasonically in a 0.4 mL of Nafion® solution (25 wt% Nafion® in ethanol). 8 μL of the ultrasonically treated solution was dropped onto the working electrode and then dried in air. Cyclic voltammetry (CV) measurement was done in the three-electrode system using 0.1 M NaOH solution as electrolyte. The potential scan rate was 50 mV s^{-1} in the potential range 0.20–0.80 V vs. Ag/AgCl. The electrode was firstly scanned in NaOH in the absence of glucose, subsequently scanned in NaOH with 500 μM, 1 mM, 2 mM, 3 mM, 4 mM, 5 mM, 6 mM, 7 mM, 8 mM and 9 mM of glucose, respectively. Responses of the as-prepared electrodes with increasing glucose concentration were carried out in a 0.1 M NaOH solution and the rotation speed of the RDE was set at 1000 rpm. The selectivity of the electrodes was firstly tested in 0.1 M NaOH with 1000 μM of glucose and then 0.1 mM of ascorbic acid (AA), uric acid (UA), NaCl and L-glucose was introduced into the NaOH/glucose solution, respectively.

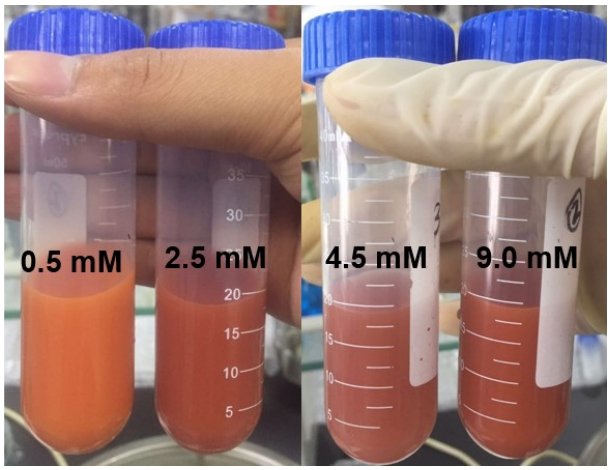

Figure S1. Optical images of Cu_2O solutions prepared with different PVP concentrations.

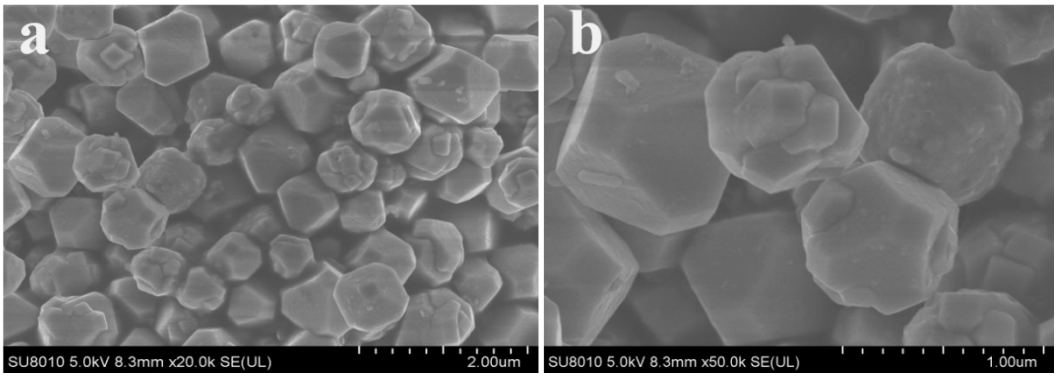

Figure S2. SEM images of Cu_2O nanoparticles synthesized by 4.5 mM PVP.

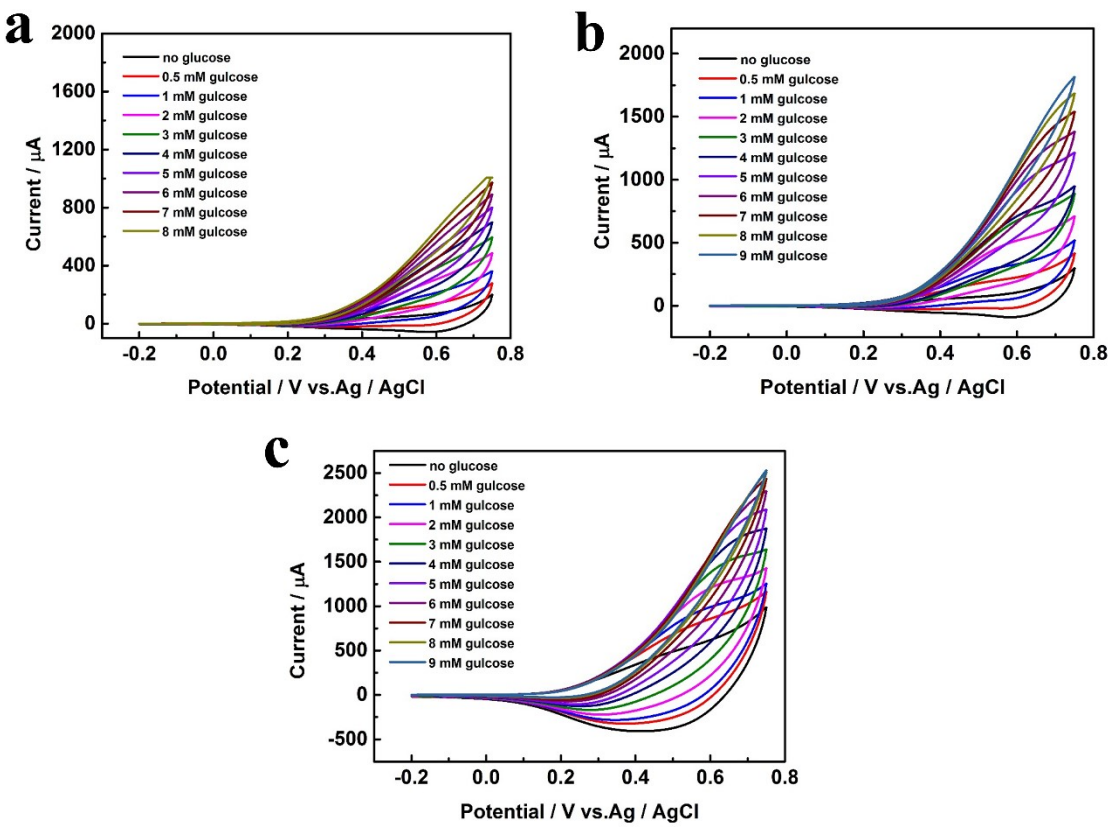

Figure S3. CVs obtained for (a) Cu_2O nanocubes, (b) nanopolyhedron, (c) nanosphere on GCE in 0.1 M NaOH + 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 mM glucose at a scan rate of 50 mV s^{-1}.

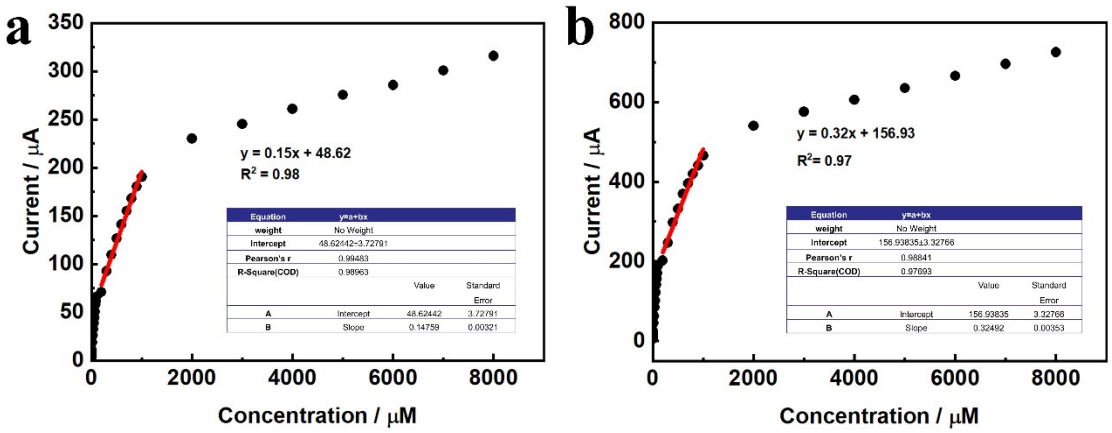

Figure S4. The corresponding calibration curves of (a) Cu_2O nanocubes and (b) Cu_2O nanopolyhedron.

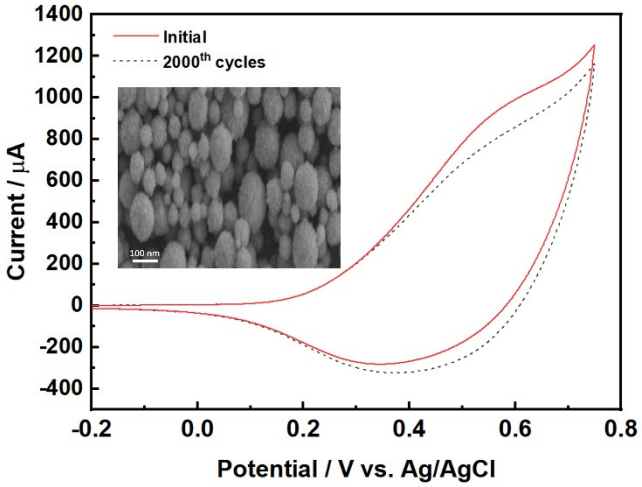

Figure S5. CVs obtained for initial Cu_2O nanosphere sample and after 2000th cycles Cu_2O nanosphere sample in 0.1 M NaOH + 1 mM glucose at scan rate of 50 mV s^{-1}. (Inset: the SEM image of Cu_2O sphere after electrochemical degradation tests)

Table S1. An indicator of HOR activity (re. HOR onset potential) of Cu_2O nanosphere catalyst compared with previously Cu-based HOR catalysts.

Catalyst	The oneset potential of hydrazine oxidation	The electrolyte	Scan rate /mV s^{-1}	Reference
Cu_2O nanosphere	-0.107V vs. Ag/AgCl(0.857V vs.RHE)	0.1 M KOH + 0.1 M N_2H_4	50	This work
Cu metal electrode	-0.193V vs. RHE	1.0 M KOH + 5 wt% N_2H_4	20	1
Cu-GP	-0.10V vs SCE (0.91V vs. RHE)	0.1 M KOH + 10 mM N_2H_4	100	2
NPCF	-0.87V vs. SCE (0.23V vs. RHE)	3 M NaOH + 1 M N_2H_4	50	3
Nanotextured Cu foam	-0.70V vs. Ag/AgCl (0.37 vs. RHE)	6 M KOH+1 M N_2H_4	50	4
S-RGO	-0.21V vs. SCE(0.23V vs. RHE)	0.1 M KOH + 10 mM N_2H_4	100	5
Cu (hydr)oxide	-0.10V vs. Ag/AgCl (0.87V	0.1 M NaOH+10 mM N_2H_4	50	6

	vs. RHE)			
Flower-CuO	-0.104V vs. Ag/AgCl (0.789V vs. RHE)	0.1 M KOH + 0.1 M N_2H_4	50	7

1. K. Asazawa, K. Yamada, H. Tanaka, M. Taniguchi and K. Oguro, *J. Power Sources*, 2009, **191**, 362-365.
2. H. C. Gao, Y. X. Wang, F. Xiao, C. B. Ching and H. W. Duan, *J. Physical Chem. C*, 2012, **116**, 7719-7725.
3. F. L. Jia, J. H. Zhao and X. X. Yu, *J. Power Sources*, 2013, **222**, 135-139.
4. B. Filanovsky, E. Granot, I. Presman, I. Kuras and F. Patolsky, *J. Power Sources*, 2014, **246**, 423-429.
5. C. Liu, H. Zhang, Y. Tang and S. Luo, *J. Mater. Chem. A*, 2014, **2**, 4580-4587.
6. G. Karim-Nezhad, R. Jafarloo and P. S. Dorraji, *Electrochim. Acta*, 2009, **54**, 5721-5726.
7. Y. Ma, H. Wang, J. Key, S. Ji, W. Lv and R. Wang, *J. Power Sources*, 2015, **300**, 344-350.