

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

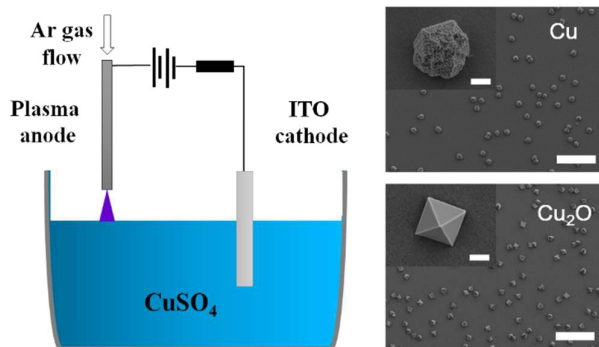
*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## Table of Contents graphic

Atmospheric-pressure microplasma could be applied as gaseous anode for transferring positive charges and controllably electrodepositing of Cu and Cu<sub>2</sub>O nanocrystals.





Journal Name

ARTICLE

## Atmospheric-pressure Microplasma as Anode for Rapid and Simple Electrochemical Deposition of Copper and Cuprous Oxide Nanostructures

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

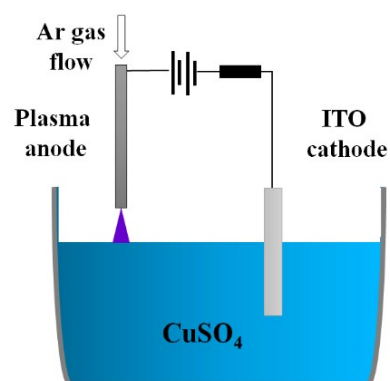
Yuexiang Lu,<sup>\*a,b</sup> Zhonghua Ren,<sup>a,b</sup> Hang Yuan,<sup>a,b</sup> Zhe Wang,<sup>a,b</sup> Bo Yu<sup>\*a,b</sup> and Jing Chen<sup>a,b</sup>

There have been growing attention on plasma electrodes, as they are much cheaper than commonly used metal electrodes such as Pt and have renewable electrodes interface. However, most of researches were mainly focused on plasma cathode, while the research and application of plasma anode have been rarely reported. In this paper, we applied an atmospheric-pressure microplasma as gaseous anode for transferring positive charges and inducing electrochemical reactions in solution. Cu and Cu<sub>2</sub>O nanocrystals have been co-deposited on ITO cathodes in 100 mM CuSO<sub>4</sub> solution at room temperature. By simply changing the precursor concentration and reaction temperatures, pure Cu and Cu<sub>2</sub>O product could be prepared. Our work will expand the application area of plasma electrodes in electrochemistry and nanomaterials synthesis, and it is also a new rapid and simple electrochemical method for preparing copper and cuprous oxide nanostructures.

### Introduction

There have been growing applications of plasma-liquid system in many fields,<sup>1</sup> such as electrochemistry,<sup>2</sup> nanomaterials synthesis,<sup>3-7</sup> spectrochemical analysis<sup>8-10</sup> and wastewater treatment<sup>11,12</sup>. Recently, the research of using microplasma as gaseous electrodes is of great interest for both fundamental studies and technological applications, as they are much cheaper than commonly used metal electrodes such as Pt and have renewable electrodes interface. Although much effort has been done, the charge-transfer reactions at plasma-liquid interface are hardly to be clearly identified because of the complex conditions presented in a plasma. Also, in most of the previous studies, plasmas are usually operated at sub-atmospheric pressure which have limited the further application of gaseous plasma electrodes. Only recently, Sankaran and colleagues provided the evidence of electrolytic synthesis of metal nanoparticles in aqueous solutions by using an Ar microplasma jet as cathode.<sup>13</sup> Subsequently, they reported the evidence of electron-transfer reactions at the plasma-liquid interface by using a nonthermal, atmospheric-pressure microplasma as cathode.<sup>14</sup> Then they found both electron transfer and plasma neutral reactions occurred when

plasmas interacted with aqueous media and these two kinds of reactions were often in competition with one another but sometime could couple to one other.<sup>15</sup> These researches have opened a new direction for electrochemistry based on reactions between plasma and ionic electrolytes. Their work were mainly focused on plasma cathode, while the research and application of reactions at plasma anode have been rarely reported. The condition at the plasma anode is more complex and the deviation from Faraday's law are commonly observed. In our former work, we have demonstrated that a plasma anode is capable of transferring positive charges and inducing electrochemical reactions in solution.<sup>16</sup> In this paper, for further extending the application area of microplasma electrodes, we have applied an atmospheric-pressure microplasma as anode and used the charge transfer reaction



**Scheme 1.** Schematic of electrochemical cell with an atmospheric-pressure microplasma anode electrode for depositing nanostructures on cathode.

<sup>a</sup> Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China. Email: luyexiang@mail.tsinghua.edu.cn; cassy\_yu@tsinghua.edu.cn. Tel.: +86 10 89796068

<sup>b</sup> Beijing Key Lab of Radioactive Waste Treatment, Tsinghua University, Beijing 100084, China.

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

between plasma electrode and ionic solution for electrodepositing nanostructures on solid cathode.

Cu and Cu<sub>2</sub>O nanoparticles are useful in many fields, such as energy,<sup>17, 18</sup> catalyst<sup>19</sup> and sensors<sup>20</sup>. Among many synthesis methods, electrodeposition is an efficient and inexpensive method for preparing nanostructures.<sup>21-23</sup> In most of the former literatures, potentiostatic method was used to co-deposit Cu and Cu<sub>2</sub>O nanocrystals and obtain pure products. Additives or a high pH value was often needed to obtain Cu<sub>2</sub>O nanoparticles.<sup>24-26</sup> Recently, by controlling the potential Cu<sub>2</sub>O nanocrystals could also be prepared.<sup>27</sup> It is still needed to develop rapid and simple method for depositing Cu and Cu<sub>2</sub>O nanoparticles. In this paper, we have co-deposited Cu and Cu<sub>2</sub>O nanocrystals by using galvanostatic method and pure product could be prepared by simply changing the precursor concentration and reaction temperatures. Also it was the first report on using an atmospheric-pressure microplasma as anode for the electrodeposition of Cu and Cu<sub>2</sub>O nanocrystals in aqueous solution.

## Experimental

### Chemicals and materials

Analytical grade precursor salt, copper (II) sulfate pentahydrate, was used as received without further purification. Stainless steel capillary tube with 180 μm inner diameter was purchased from Dikma Technologies Inc. The metal capillary tube was cleaned by polishing the outside surface with sand paper. Indium Tin Oxide (ITO) glasses (1cm × 4cm, <10 ohm/sq) were washed in turn by methylbenzene, acetone, ethyl alcohol and deionized water for three times and dried by Ar gas blowing.

### Characterization

The scanning electron microscope (SEM) micrographs of the nanoparticles were obtained from a scanning electron microscope (Merlin, Carl Zeiss, Germany). The energy dispersive spectrum (EDS) was obtained from Energy Dispersive X-ray Spectrometer (INCA300, Oxford, USA) equipped on the SEM. The X-ray powder diffraction patterns were obtained on an X-ray diffractometer (Bruker D8 Advance) with Cu Kα radiation (λ=1.54056 Å, operating at 40 kV × 40 mA). X-ray photoelectron spectroscopy (XPS) data were obtained on PHI Quantro SXM (ULVAC-PHI, Japan). Binding energy was calibrated with C1s=284.8eV.

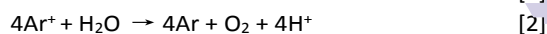
### Electrochemical deposition of nanoparticles

ITO glass was partly immersed in the electrolyte (1cm × 1cm) and served as the cathode. In the anode side, a stainless steel capillary tube was positioned above and normal to the surface of the electrolyte and fed with argon gas flow. The distance between the cathode and anode was set to 2 cm. After a negative high voltage was applied on the cathode by a DC power supply, the anodic capillary tube was moved slowly towards the solution surface using a micrometre-controlled linear stage until a microplasma was ignited and sustained. During experiments, the DC power supply was operated in a current-limiting mode with a constant discharge current.

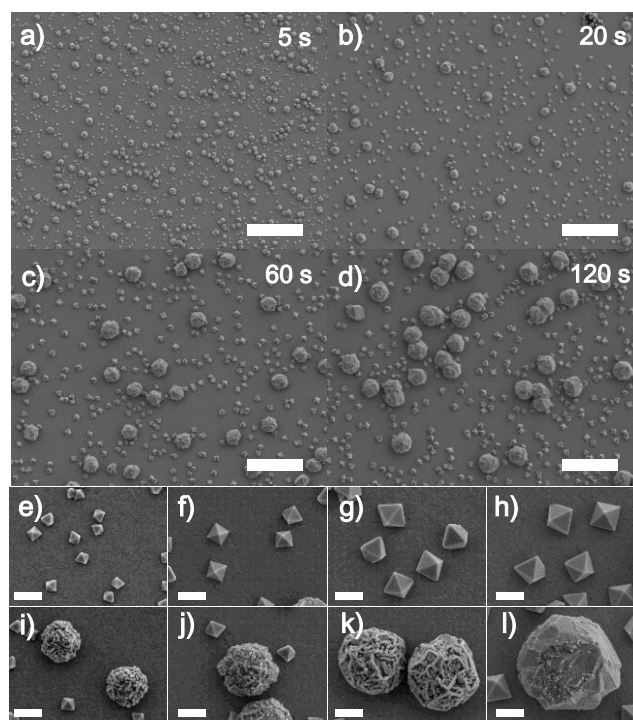
## Results and discussion

The nanostructure deposition was first operated in 0.1 M CuSO<sub>4</sub> electrolyte at room temperature (25°C) with ITO glass as cathode and substrate. Microplasma was ignited and sustained by using a DC power supply and the discharge current was fixed to 6 mA. As shown in Figure 1, two kinds of nanostructures with different morphology and size were obtained on ITO cathodes and the composition of these two nanostructure were identified by EDS. The sphere-like nanoparticles with larger size were mainly composed of Cu, while the composition of the smaller octahedral nanoparticle was Cu<sub>2</sub>O (Figure 2). We found that the size of both nanostructures increased with discharge time. As the reaction time increasing from 5 s to 120 s, the diameter of Cu nanoparticles was increased from 1.37±0.10 μm to 3.52±0.21 μm, while the edge length of Cu<sub>2</sub>O octahedron was increased from 0.39±0.01 μm to 1.00±0.06 μm. We also found that the size of Cu nanoparticles was much larger than Cu<sub>2</sub>O at the same condition.

When the microplasma was ignited, the Ar gas was firstly positively charged in the plasma and then transferred charges to the solution as follows:

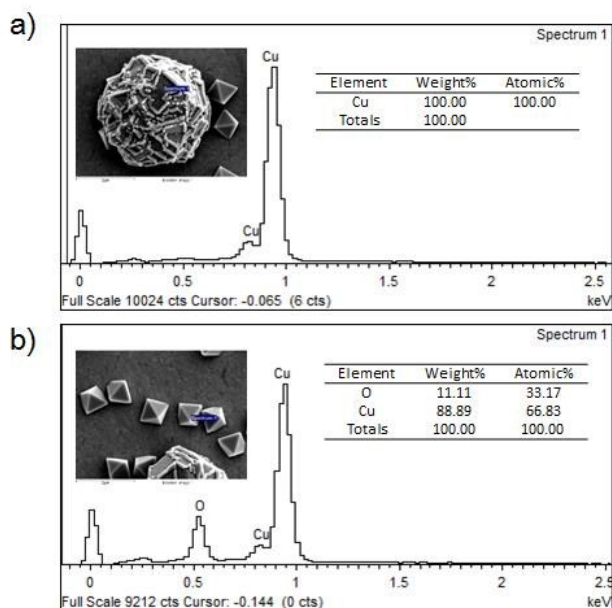


Once the charge transfer happened at the plasma-liquid interface, Cu<sup>2+</sup> ions were driven by the electric field to the



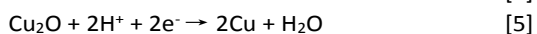
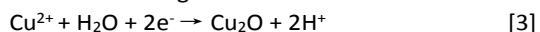
**Fig. 1** The SEM image of nanostructures deposited on ITO cathodes with discharge time of a) 5s, b) 20s, c) 60s and d) 120s. The scale bar is 10 μm. Magnified SEM image of nanostructures with discharge time of e, i) 5s, f, j) 20s, g, k) 60s and h, l) 120s. The scale bar is 1 μm. The electrolyte is 100 mM CuSO<sub>4</sub> solution. The discharge current is 6 mA.





**Fig. 2** The EDS patterns of nanostructures deposited on ITO cathodes with discharge time of 120s. The electrolyte is 100 mM CuSO<sub>4</sub> solution. The discharge current is 6 mA.

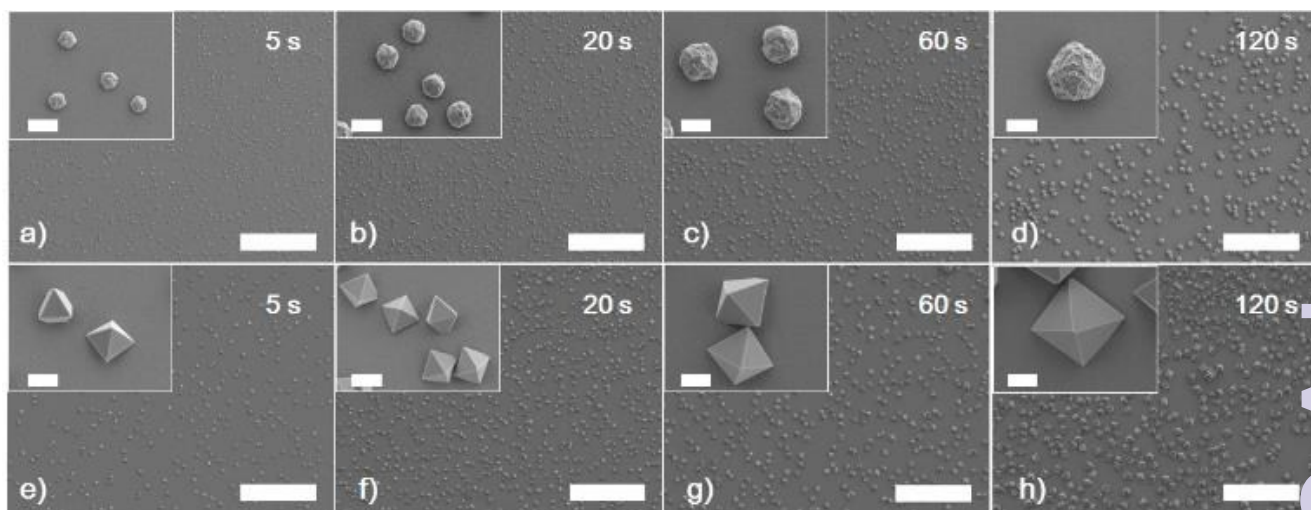
cathode and reduced there. It is known that there are two reductive peaks on the cyclic voltammogram of copper sulfate, which correspond to two electrochemical reduction steps of Cu (II), the reduction of Cu (II) to Cu (I) and the reduction of Cu (I) to Cu metal. So the possible electrochemical reactions on the cathode were as following:



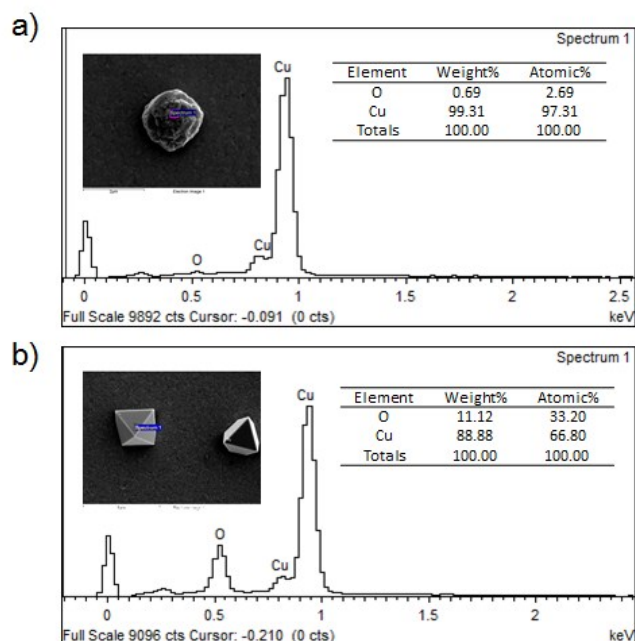
In our experiments, as the Cu and Cu<sub>2</sub>O were co-deposited in 100 mM CuSO<sub>4</sub> at 25 °C, it meant that under this condition

the over-potential at the cathode was large enough to allow both reduction step to occur. The nucleation of Cu<sub>2</sub>O might occur first on ITO glass according to Eq. 3, and then some of them might be further reduced to Cu nanocrystals according to Eq. 5. It was also possible for the Cu<sup>2+</sup> to be reduced to Cu directly on the substrate according to Eq. 4 and Eq. 6. Once Cu nanocrystals were formed in either way, as they had much higher electrical conductivity than Cu<sub>2</sub>O, Cu (II) were preferentially attracted to the surface of Cu nanocrystals and got reduced. That was why the size of Cu nanostructures was much larger than that of Cu<sub>2</sub>O under the same condition. It was found that on some of the Cu nanospheres surface, the elements composition was not 100% copper but with small amount of oxygen, which indicated that Cu<sub>2</sub>O could be formed on the surface of Cu nanoparticles and then be reduced to Cu according Eq. 5. On the other hand, as the size of Cu<sub>2</sub>O nanostructures also grew larger with reaction time, the reduction of Cu<sub>2</sub>O to Cu might be very rare or even did not occur on Cu<sub>2</sub>O octahedron once the Cu<sub>2</sub>O nanocrystals were grown to a certain size.

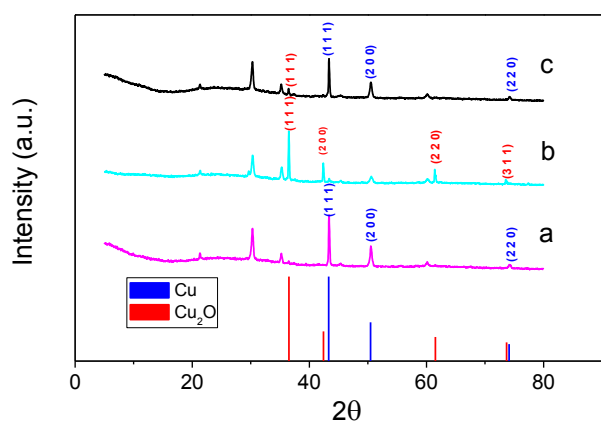
More interestingly, by simply modifying the electrodeposition condition, uniform nanoparticles with different morphology were obtained (Figure 3). When raising the concentration of CuSO<sub>4</sub> to 1 M, the products were mainly sphere-like copper nanoparticles. When keeping the concentration of CuSO<sub>4</sub> as 0.1 M but raising the deposition temperature to 70 °C, the products were nearly all octahedral Cu<sub>2</sub>O nanoparticles. The composition of these nanostructures were confirmed by both EDS and XRD (Figure 4, 5). XPS was also used to determinate the chemical state of Cu in both nanostructures (Figure S1). Both samples showed two bands of the binding energies at 932.2 eV and 952.1 eV, which attributed to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> respectively. As it was hard to distinguish the oxidation states between Cu<sup>+</sup> and Cu<sup>0</sup> only by 2p XPS signals, the Cu LMM Auger spectra were also collected. According to previous reports, the main LMM peaks



**Fig. 3** The SEM image of nanostructures deposited on ITO cathodes with discharge time of a) 5 s, b) 20 s, c) 60 s and d) 120 s in 1 M CuSO<sub>4</sub> solution at 25 °C and e) 5 s, f) 20 s, g) 60 s and h) 120 s in 100 mM CuSO<sub>4</sub> solution at 70 °C. The scale bar is 50 μm. The insert figures are magnified SEM image of nanostructures and the scale bar is 2 μm. The discharge current is 6 mA.



**Fig. 4** The EDS patterns of nanostructures deposited on ITO cathodes (6 mA, 120 s) at a) 25°C, 1 M CuSO<sub>4</sub> and b) 70°C, 100 mM CuSO<sub>4</sub>.



**Fig. 5** The XRD patterns of nanostructures deposited on ITO cathodes with discharge time of 120 s at a) 25°C, 1 M CuSO<sub>4</sub>, b) 70°C, 100 mM CuSO<sub>4</sub> and c) 25°C, 100 mM CuSO<sub>4</sub>. The discharge current is 6 mA.

for Cu<sup>0</sup> and Cu<sub>2</sub>O are located at 568 eV and 570 eV, respectively.<sup>28,29</sup> The octahedral nanoparticles only showed the peak at 570 eV, confirming that they were Cu<sub>2</sub>O. The sphere nanostructures showed both peaks at 568 eV and 570 eV. It indicated that at the surface of the nanosphere there were small amount of Cu<sub>2</sub>O and the results was in agreement with the EDS analysis. These results further confirmed that Cu<sub>2</sub>O could be formed on the surface of Cu nanoparticles and then be reduced to Cu according Eq. 5. The size of both nanostructures also increased with discharge time. As the reaction time increasing from 5 s to 120 s, the diameter of Cu nanoparticles was increased from 1.39±0.09 μm to 3.92±0.18

μm, while the edge length of Cu<sub>2</sub>O octahedron was increased from 1.97±0.10 μm to 5.13±0.28 μm (Figure S2).

At a high CuSO<sub>4</sub> concentration (1 M), even with a very short reaction time (5 s), nearly no Cu<sub>2</sub>O octahedron was observed (Figure 3a). As the reaction time increasing from 5 s to 120 s, the diameter of Cu nanoparticles was increased from 1.39±0.09 μm to 3.92±0.18 μm, which were nearly the same with that at a lower CuSO<sub>4</sub> concentration (0.1 M). It meant that the nucleation and growth speed of the Cu nanoparticles were not changed much. While the distribution density of these Cu spheres were obviously increased. These results suggested that under a high Cu<sup>2+</sup> concentration, abundant Cu metal seeds were formed in a short time and occupied most of the active sites. As Cu (II) were preferentially attracted to the surface of Cu nanocrystals and there had been plenty of Cu metal seeds, nearly all Cu<sup>2+</sup> were attracted to these seeds and grew to larger particles. As a result, Cu<sub>2</sub>O nanocrystals had little chance to take up active site and grow larger under this condition.

When operated at a high temperature (70 °C), only octahedral Cu<sub>2</sub>O nanoparticles were observed on the SEM images (Figure 3e-f). As the reaction time increasing from 5 s to 120 s, the edge length of Cu<sub>2</sub>O octahedron was increased from 1.97±0.10 μm to 5.13±0.28 μm, which was about 5 times larger than those obtained at room temperature. According to the Arrhenius formula, higher reaction temperature led to higher rate constants and increased the diffusion rate, nucleation and growth rates. Under this condition, the reduction of Cu<sup>2+</sup> to Cu<sub>2</sub>O was accelerated according to Eq. 3, and Cu<sub>2</sub>O seeds occupied most of the active sites. As the reaction rate of Eq.3 was much higher than Eq.5, the Cu<sub>2</sub>O seeds were rapidly grew up to a certain size and then the conversion of Cu<sub>2</sub>O to Cu was inhibited similarly as that at room temperature. Without the concentration of Cu<sup>2+</sup> on Cu metal surface, the size of Cu<sub>2</sub>O octahedron could grow much larger than those prepared at room temperature, as same amount of charges were injected to the solution.

## Conclusions

In summary, we have applied an atmospheric-pressure microplasma as gaseous anode for transferring positive charges and depositing Cu and Cu<sub>2</sub>O nanocrystals on ITO cathodes. Cu and Cu<sub>2</sub>O nanocrystals have been co-deposited by using galvanostatic method and pure product could be prepared by simply changing the precursor concentration and reaction temperatures. This is a new rapid and simple method for preparing copper and cuprous nanostructures and the mechanism is different with former reports. Also it was the first report on using an atmospheric-pressure microplasma as anode for the controllably electrodepositing of Cu and Cu<sub>2</sub>O nanocrystals in aqueous solution. Our work will expand the application area of plasma electrodes in electrochemistry and nanomaterials synthesis.

## Acknowledgements

This work was supported by National Natural Science Foundation of China (21390413, 21405090, 21273128, and 91426302), Program for Changjiang Scholars and Innovative Research Team in University (IRT13026) and Tsinghua University Initiative Scientific Research Program (2014z22063).

## Notes and references

1. P. Attri, B. Arora and E. H. Choi, *RSC Adv.*, 2013, **3**, 12540-12567.
2. R. Akolkar and R. M. Sankaran, *J. Vac. Sci. Technol. A*, 2013, **31**, 050811.
3. K. Baba, T. Kaneko, R. Hatakeyama, K. Motomiya and K. Tohji, *Chem. Commun.*, 2010, **46**, 255-257.
4. T. T. Yan, X. X. Zhong, A. E. Rider, Y. Lu, S. A. Furman and K. Ostrikov, *Chem. Commun.*, 2014, **50**, 3144-3147.
5. X. Z. Huang, X. X. Zhong, Y. Lu, Y. S. Li, A. E. Rider, S. A. Furman and K. Ostrikov, *Nanotechnology*, 2013, **24**, 09504.
6. J. Patel, L. Nemcova, P. Maguire, W. G. Graham and D. Mariotti, *Nanotechnology*, 2013, **24**, 245604.
7. C. J. Liu, Y. Zhao, Y. Z. Li, D. S. Zhang, Z. Chang and X. H. Bu, *ACS Sustain. Chem. Eng.*, 2014, **2**, 3-13.
8. Z. A. Li, Q. Tan, X. D. Hou, K. L. Xu and C. B. Zheng, *Anal. Chem.*, 2014, **86**, 12093-12099.
9. M. R. Webb, F. J. Andrade and G. M. Hieftje, *Anal. Chem.*, 2007, **79**, 7807-7812.
10. M. R. Webb, F. J. Andrade and G. M. Hieftje, *Anal. Chem.*, 2007, **79**, 7899-7905.
11. X. Wang, M. Zhou and X. Jin, *Electrochim. Acta*, 2012, **83**, 501-512.
12. B. Jiang, J. Zheng, S. Qiu, M. Wu, Q. Zhang, Z. Yan and Q. Xue, *Chemical Engineering Journal*, 2014, **236**, 348-368.
13. C. Richmonds and R. M. Sankaran, *Appl. Phys. Lett.*, 2008, **93**, 131501.
14. C. Richmonds, M. Witzke, B. Bartling, S. W. Lee, J. Wainright, C. C. Liu and R. M. Sankaran, *J. Am. Chem. Soc.*, 2011, **133**, 17582-17585.
15. P. Rumbach, M. Witzke, R. M. Sankaran and D. B. Go, *J. Am. Chem. Soc.*, 2013, **135**, 16264-16267.
16. Z. H. Ren, Y. X. Lu, H. Yuan, Z. Wang, B. Yu and J. Chen, *Acta Phys. Chim. Sin.*, 2015, **31**, 1215-1218.
17. P. C. Dai, W. Li, J. Xie, Y. M. He, J. Thorne, G. McMahon, J. H. Zhan and D. W. Wang, *Angew. Chem.-Int. Edit.*, 2014, **53**, 13493-13497.
18. X. Y. Yan, X. L. Tong, Y. F. Zhang, X. D. Han, Y. Y. Wang, G. Q. Jin, Y. Qin and X. Y. Guo, *Chem. Commun.*, 2012, **48**, 1892-1894.
19. C. G. Morales-Guio, L. Liardet, M. T. Mayer, S. D. Tilley, M. Gratzel and X. Hu, *Angew. Chem.-Int. Edit.*, 2015, **54**, 664-667.
20. L. N. Guan, H. A. Pang, J. J. Wang, Q. Y. Lu, J. Z. Yin and F. Gao, *Chem. Commun.*, 2010, **46**, 7022-7024.
21. J. A. Switzer, C. J. Hung, L. Y. Huang, E. R. Switzer, D. R. Kammler, T. D. Golden and E. W. Bohannan, *J. Am. Chem. Soc.*, 1998, **120**, 3530-3531.
22. L. F. Gou and C. J. Murphy, *Nano Lett.*, 2003, **3**, 231-234.
23. Y. C. Mao, J. T. He, X. F. Sun, W. Li, X. H. Lu, J. Y. Gan, Z. Q. Liu, L. Gong, J. Chen, P. Liu and Y. X. Tong, *Electrochim. Acta*, 2012, **62**, 1-7.
24. Y. H. Lee, I. C. Leu, M. T. Wu, J. H. Yen and K. Z. Fung, *J. Alloy. Compd.*, 2007, **427**, 213-218.
25. S. Y. Ng and A. H. W. Ngan, *Electrochim. Acta*, 2011, **56**, 7686-7695.
26. B. B. Luo, X. M. Li, X. L. Li, L. P. Xue, S. Y. Li and X. L. Li, *Crytengcomm*, 2013, **15**, 5654-5659.
27. S. Y. Ng and A. H. W. Ngan, *J. Electrochem. Soc.*, 2015, **162**, D124-D128.
28. T. Ghodselahi, M.A. Vesaghi, A. Shafiekhani, A. Baghizadeh and M. Lameii, *Appl. Surf. Sci.*, 2008, **255**, 2730-2734.
29. C. Q. Zhu, A. Osherov and M. J. Panzer, *Electrochim. Acta*, 2013, **111**, 771-778.