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Ambient Conditioned, Solution Processed CuO Nanoflakes Over Carbon Fabric for Supercapacitor Application: Performance Enhancement via Nanoparticle Attachment

Research Article

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Abstract. All Solid-state supercapacitors based on pure CuO nanoflakes and CuO@Au heterostructure over carbon cloth were fabricated where directly functioned nanostructure over carbon fiber acts as electrode and detour the necessity of any binder or ancillary materials. High coverage of CuO nanoflakes over entire cylindrical surface of each fiber provide decent electrochemical performance which was further uplifted after Au nanoparticle decoration. Registered electrochemical performance from CuO nanoflakes was found to be 11.77 F/g at 20 mV/s scan rate which significantly improved to 28.84 F/g at the same scan speed after nanoparticle attachment. Increase in surface area as well as increment of overall conductivity of the hybrid system due to Au nanoparticle attachment may accredit for such performance enrichment.

Keywords. Chemical synthesis; Heterostructure; Supercapacitor

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1. Introduction

Contemporary era with ever-increasing energy demand and concurrent rapid exhaustion of limited global resources witness the emergence of supercapacitors (SCs) as one of the most environmental benign, budgetary rechargeable power source for foreseeable devices which reaped mammoth attention from scientistsâ€™ for their advanced exploration. Moreover, these energy sources with flexibility and lightweight features are very significant as they become integral part of electronic devices such as roll-up display, sensor network, flexible and portable energy storage device etc. [1, 2]. Out of numerous issues, inherent features of the building materials are directly associated with device performance which has made the development of electrode material for SC an intriguing field of research [3]. A wide range of electrode material including carbonaceous material, various transition metal oxides (TMOs) and conducting polymers have been widely considered in this regard among which TMOs are the most promising where they generate capacitance from electric double-layers and offer rich redox reactions [3]. From the rich assortment of TMOs, copper oxide (CuO) is a special electrode material for supercapacitor application not only for its high theoretical capacity (670 mAh g^{-1}) also for ample abundance, low toxicity, environmental stability and desirable electrochemical properties [4]. On the other hand, carbon cloth beneficiary of its foldable feature, woven like geometry, high durability, high conductivity and large surface area behaves as good scaffold to fabricate attractive electrode materials for SCs. In this aspect, realization of CuO nanoforms over carbon fiber could be one plausible pathway to achieve improved performance [5–9].

Herein, we have fabricated CuO nanoflakes based supercapacitor where the nanostructure over carbon fiber is realized via facile, ambient conditioned wet chemical synthesis protocol. Underlying carbon cloth so chosen as it elucidates the dual purpose of scaffold and current collector. Further to uplift the performance of SC, CuO nanoflakes were decorated with gold (Au) nanoparticle. Au@CuO hybrid electrode having large surface area and higher electrical conductivity exhibits superior electrochemical performance than pristine CuO nanoflakes.

2. Experimental

All analytical grade reagents were used for experiment without any purification. Firstly, metallic copper (Cu) film was deposited on ultrasonically cleaned carbon cloth substrate via thermal evaporation. Subsequently, CuO nanoflakes were synthesized via wet chemical route. A solution was prepared by mixing each 10 mL of two separately prepared solutions of 0.04 M ammonium persulphate ($(NH_4)_2S_2O_8$) and 0.2 M sodium hydroxide (NaOH). 2 mL of aforesaid mixture solution was added with 80 mL D.I. water and metallic Cu coated substrate was dipped into it for 6h at room temperature. Thereafter the substrate was washed with copious amount of D.I. water and dried overnight. Finally, the as synthesized CuO nanoflakes were coated with gold by vacuum evaporator at base pressure of $\sim 1 \times 10^5$ Torr.

3. Characterization

Product morphology was investigated with field emission scanning electron microscope (FESEM, HITACHI S-4800) equipped with an energy dispersive X-ray attachment (EDX). Cyclic voltammetry (CV) and galvanostatic charge-discharge tests were performed using an electrochemical analyzer (CV Model FRA2 Meu Autolab Type III) with two electrode cell using H_3PO_4/polyvinyl alcohol (PVA) as the solid-state electrolyte.

4. Preparation of Solid-State SCs

H_3PO_4/PVA gel electrolyte was prepared by mixing appropriate amount of PVA powder, H_3PO_4 and deionized water. Thereafter, the mixture was stirred and heated to 85° C until it became clear. This electrolyte was coated homogeneously on the synthesized samples under investigation and such two similar electrodes were assembled one by one after the gel solidified, and the solid state SC was prepared.

5. Results and Discussion

Figure 1 schematically displays the preparation procedure of CuO@Au heterostructure over carbon fiber. Starting with a bare cloth, it was first coated with metallic Cu followed by dipping in an oxidative solution and resulted in formation of CuO nanoflakes over the fiber which further deposited with Au nanoparticle via vacuum evaporation.

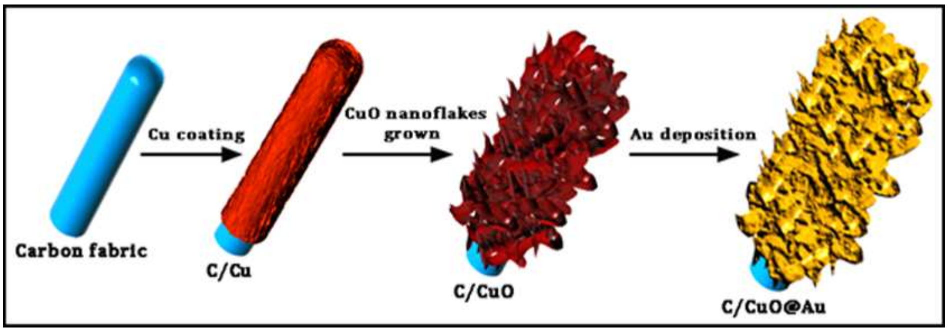

Figure 1. A schematic diagram of CuO@Au heterostructure formation on carbon cloth.

Figure 2a reveals uniform, compact coverage and radial arrangement of CuO nanoflakes over carbon fabric. Higher magnification image (Figure 2b) discloses their dimensional features. These nanoflakes have lateral dimension of ~400 nm long and a diameter that changes from ~100 to ~20 nm from the base to the top. Figure 2c shows that Au layer uniformly coated on CuO nanoflakes. After Au coating the morphology of the nanoflake becomes slightly different from the pristine where the surfaces of nanoflakes are uneven and rough. Close inspection of this hybrid illustrates the small dimension of the Au particles which are ~10 nm.

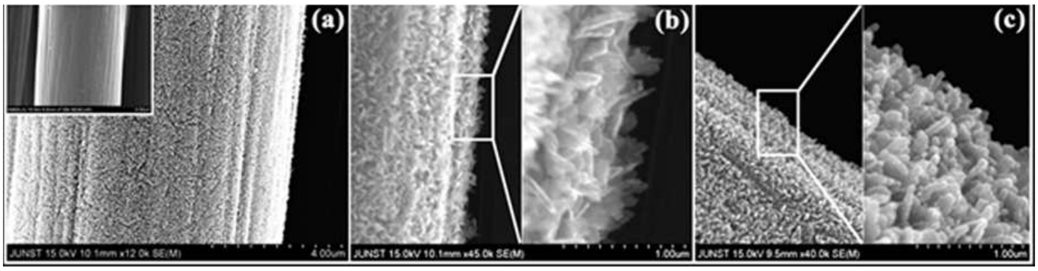

Figure 2. FESEM images of CuO nanoflakes over carbon fiber; low magnification (a), high magnification (b) and CuO@Au heterostructure (c); inset of (a) shows a single carbon fiber.

To check the elemental composition of hybrid sample, EDX analysis was carried out. The

EDX spectrum of CuO@Au heterostructure and corresponding elemental mapping (Figure 3) shows the co-existence of Cu, O, and Au and also confirm the uniform distribution of Au nanoparticle over the entire nanoflakes.

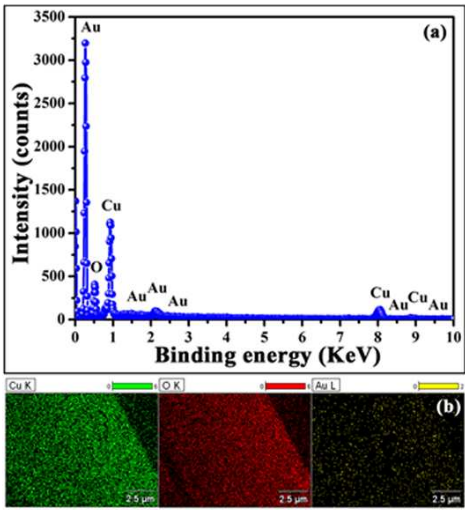

Figure 3. (a) EDX spectrum of the CuO@Au heterostructure and (b) corresponding elemental mapping showing the homogeneous distribution of the constituent element over entire nanostructure.

To investigate the electrochemical performance of 3D hybrid nanostructures, the Brunauer-Emmett-Teller (BET) surface area measurements were first carried out via nitrogen (N_2) sorption and the corresponding adsorption-desorption isotherms of the samples prior and after Au particle attachment are presented in Figure 4. The CuO@Au heterostructure possess a surface area of 12.26 m^2/g, which is higher than pure CuO nanoflakes (9.50 m^2/g).

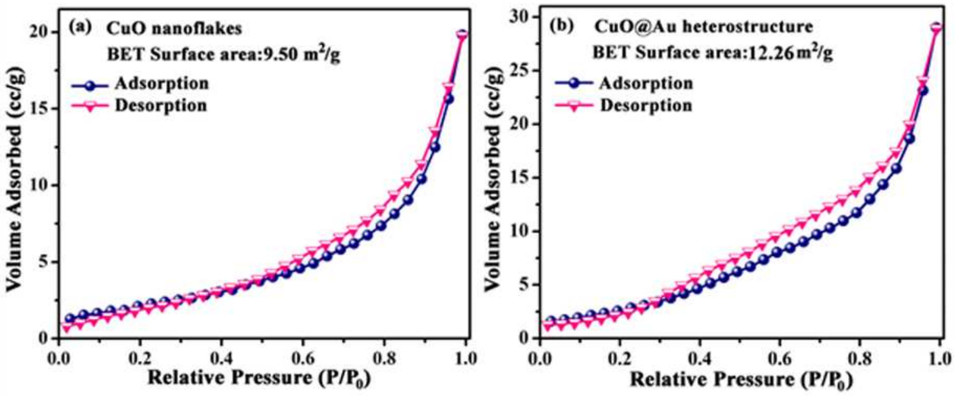

Figure 4. N_2 adsorption-desorption isotherms of (a) CuO nanoflakes, (b) CuO@Au heterostructure.

6. Electrochemical Property

To demonstrate the high electrochemical performance of flexible CuO@Au heterostructure as solid state supercapacitor, cyclic voltammetry (CV) measurements including galvanometric charge-discharge and electronic impedance spectroscopy were performed using the H_3PO_4/PVA gel electrolyte in two-cell electrode set up. For comparison, CV measurements of pure CuO nanostructures and bare carbon fabric electrodes were also investigated which reveal the superior electrochemical performance of CuO@Au heterostructure among all (Figure 5a). Figure 5b shows the CV curves of pure CuO nanoflakes electrode at different scan rates where the same for CuO@Au heterostructure are presented in Figure 5c. It is very obvious from Figure 5(b,c) that the composite electrode possess enhanced CV curve area along with prominent redox peaks compares to the pristine CuO nanoform during all cycles. The calculated specific capacitance values for the nanostructures are obtained as 11.77, 9.56, 8.12 and 7.0 F/g at scan rates of 20, 50, 100 and 150 mV/s and the same for heterostructure composite are 28.84, 21.02, 14.35 and 12.65 F/g respectively.

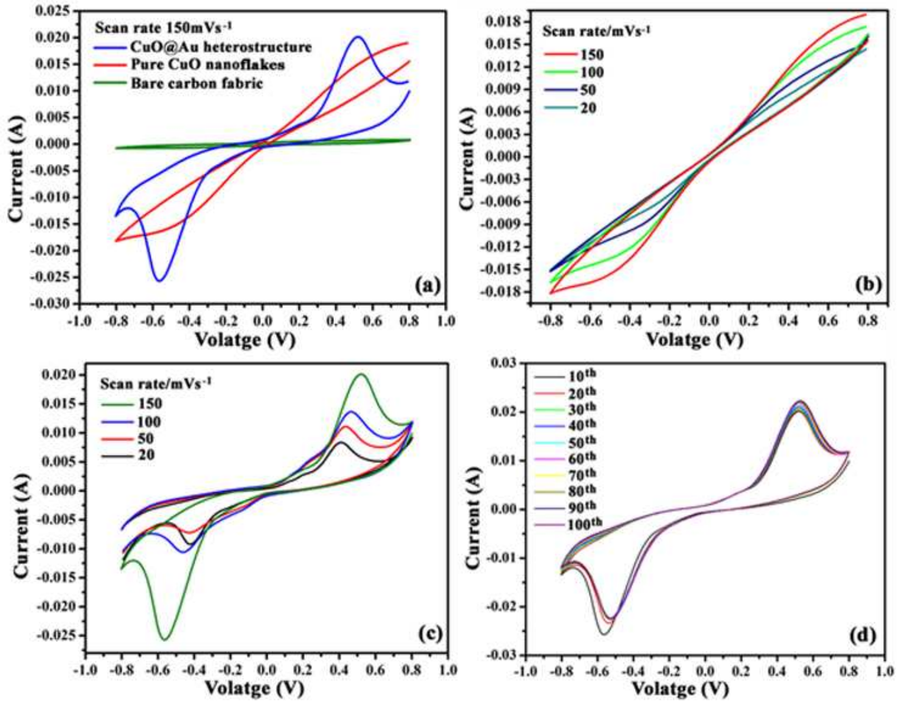

Figure 5. CV curves for (a) all samples at a scan rate of 150 mV $\sec^{-1}$; (b) CuO nanoflakes and (c) CuO@Au heterostructure electrodes at different scan rates ranging from 20 to 150 mV $\sec^{-1}$; (d) Cycle performance of CuO@Au heterostructure during 100 cycles at a scan rate of 150 mV $\sec^{-1}$.

Increase in specific capacitance at same speed can be ascribed to the enhanced conductivity of the composite nanostructure after being coated with the Au layer. Further, the heterostructure composites possessing larger surface area compare to pure CuO nanoform provides more active sites and large interface between the electrolyte and electroactive materials. The long-term cycle stability of CuO@Au heterostructure was assessed by repeating the CV test at a scan speed of 150 mV $\sec^{-1}$ for 100 cycles. The CV curves as a function of cycle number are presented in Figure 5d for heterostructure. Very similar nature and very close overlapping of the CV curves indicate good cycling stability of the heterostructure.

Figure 6a shows the Galvanostatic charge-discharge curves of CuO@Au heterostructure at current density of 0.5 A/g within the voltage range of 0 to 0.8 V. Further to obtain more insight into the enhanced electrochemical behaviour, electrochemical impedance spectroscopy

(EIS) measurement was also carried out. Figure 6b shows Nyquist plots of CuO nanoflakes and CuO@Au heterostructure along with bare carbon fabric where the ESR (equivalent series resistance) values were found to be much lower for heterostructure (3.09 Ω) than the pristine nanostructure (5.18 Ω) and cloth (21.07 Ω).

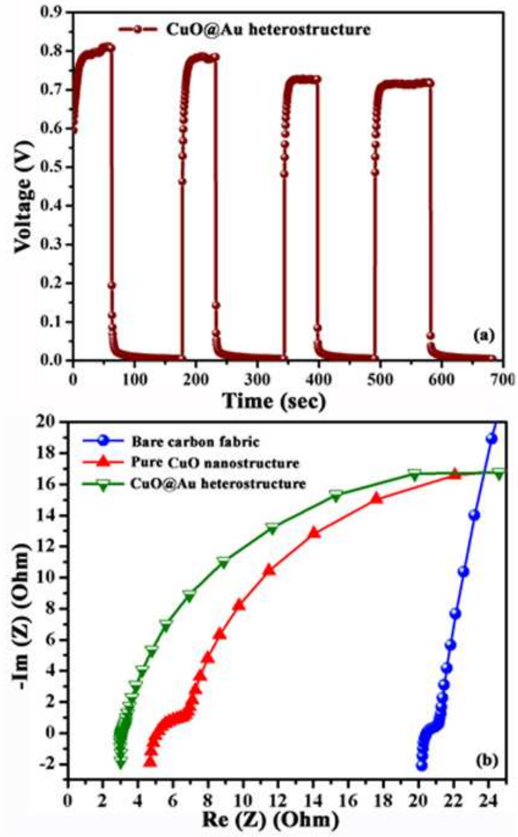

Figure 6. (a) Galvanostatic charge-discharge curve of CuO@Au heterostructure; (b) electrochemical impedance spectra (EIS) of the electrodes.

The CuO@Au sample with highly conductive Au coating decreases overall internal resistance, facilitates easier charge transfer at electrode/electrolyte interface and increases of power density (which is inversely proportional to the resistance of the cell), thereby indicates its utility in practical applications.

7. Conclusion

In summary, we have successfully synthesized CuO nanoflakes over carbon cloth via ambient conditioned wet chemical route and designed solid-state supercapacitors based on these nanoforms. Further, to attain improved electrochemical performance, CuO@Au hybrid has been realized where Au nanoparticles were uniformly decorated over entire CuO nanoflakes via evaporation. These binder-free, self-supported, 3D heterostructure-carbon textile electrodes induce good conductivity along with a large surface area than pure nanostructure. The efficient contact between the Au nanoparticles and CuO nanoflakes as well the enhancement in overall surface area provides enhanced electrochemical properties than the pristine CuO nanoflakes. We believe this work will motivate researchers to fabricate more unique solid state supercapacitor as it greatly desired for modern day portable and wearable consumer electronics.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

[1] P. Simon and Y. Gogotsi, *Nat. Mater.* **7** (2008), 845–854.

[2] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P. L. Taberna and P. Simon, *Nat. Nanotechnol.* **5** (2010), 651–654.

[3] Y.-H. Wang, C.-C. Wang, W.-Y. Cheng and S.-Y. Lu, *Carbon* **69** (2014), 287–293.

[4] K. Krishnamoorthy and S.-J. Kim, *Mater. Res. Bull.* **48** (2013), 3136–3139.

[5] L. Hu, W. Chen, X. Xie, N. Liu, Y. Yang, H. Wu, Y. Yao, M. Pasta, H.N. Alshareef and Y. Cui, *ACS Nano* **5** (2011), 8904–8913.

[6] G. Yu, L. Hu, M. Vosgueritchian, H. Wang, X. Xie, J. R. McDonough, X. Cui, Y. Cui and Z. Bao, *Nano Lett.* **11** (2011), 2905–2911.

[7] X. Lu, G. Wang, T. Zhai, M. Yu, S. Xie, Y. Ling, C. Liang, Y. Tong and Y. Li, *Nano Lett.* **12** (2012), 5376–5381.

[8] X. Lu, T. Zhai, X. Zhang, Y. Shen, L. Yuan, B. Hu, L. Gong, J. Chen, Y. Gao, J. Zhou, *Adv. Mater.* **24** (2012), 938–944.

[9] Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya and L.-C. Qin, *J. Phys. Chem. C* **115** (2011), 23584–23590.

[10] U. N. Maiti, S. Maiti and K. K. Chattopadhyay, *Cryst. Eng. Comm.* **14** (2012), 640–647.

[11] Y. L. Wang, J. J. Xu, H. Wu, M. Xu, Z. Peng and G. F. Zheng, *J. Mater. Chem.* **22** (2012), 21923–21927.