Proceedings of the Estonian Academy of Sciences,
2016, **65**, 2, 97–100
doi: 10.3176/proc.2016.2.06
Available online at www.eap.ee/proceedings

MATERIALS
ENGINEERING

# Homogeneous deposition of copper oxide on mesoporous 1D alumina nanofibres by combustion approach

Khachatur Kirakosyan[a,b], Marina Aghayan[a], Miguel A. Rodríguez[c], Masoud Taleb[a*], and Irina Hussainova[a,d]

[a] Tallinn University of Technology, Ehitajate tee 5, 19180 Tallinn, Estonia
[b] Institute of Chemical Physics, P. Sevak Str. 5/2, 0014 Yerevan, Armenia
[c] Instituto de Ceramica y Vidrio (ICV-CSIC), C/Kelsen 5, 28049 Madrid, Spain
[d] ITMO University, Kronverksky 49, St. Petersburg, 197101 Russian Federation

Received 9 September 2015, revised 17 November 2015, accepted 24 November 2015, available online 22 February 2016

**Abstract.** Copper oxide-doped alumina nanofibres were fabricated by the solution combustion method. The bundled alumina nanofibres were impregnated with a copper nitrate–glycine (oxidizer–fuel) solution and heat-treated in an open-air environment at 400 °C for 30 min. The microstructure and phase composition of the final product were characterized by XRD, SEM, and EDS analyses. A uniform distribution of a fine-grained CuO film on the surface of gamma-alumina nanofibres was revealed. The obtained results showed a dramatical effect of the amount of fuel, the ratios of fuel to oxidizer and fibres to Cu(II) ions in the reaction mixture on the particle size of the combustion product, its phase composition, and microstructure morphology.

**Key words:** copper oxide, alumina, nanofibres, solution combustion synthesis.

## INTRODUCTION

The synthesis and application of CuO nanostructures are of practical and fundamental importance for gas and bio-sensors [1,2], photodetectors [3], electrode material in lithium ion batteries [4], etc. due to their high theoretical capacity, hazard-safety, and environmental friendliness. Other major applications of CuO nanostructures include solar energy conversion [5], supercapacitors [6], removal of inorganic pollutants [7], heterogeneous catalysts [8–10], etc.

The CuO nanoparticles are characterized by a high surface area combined with high reactivity. Furthermore, heterogeneous catalysts can be easily separated and recycled, which is beneficial for their industrial use. Due to the versatile properties of the nanostructured CuO, it has been synthesized through solid-phase reaction method [11], sol–gel method [12], thermal decomposition process of precursor [13], electro-chemical methods [14], vapour-phase deposition [15], and many other techniques. Among these techniques the solution combustion synthesis (SCS) is a unique widely used method for the production of different types of nanomaterials [16–19] due to its versatility and simplicity as well as cost-effectiveness.

However, one-step synthesis of nano-CuO particles on a specific carrier is of special interest. For this purpose, a solution combustion synthesis method accompanied by an impregnation method was used to deposit a copper oxide nano-layer on commercially available gamma-alumina nanofibres [20]. The aim of the present work was to study the effect of glycine as a fuel, the ratios of fuel to oxidizer and alumina nanofibres (ANF) to Cu(II) ions, as well as the chemical composition and morphology of as-formed powders on the combustion behaviour.

* Corresponding author, masoud.taleb@ttu.ee

## EXPERIMENTAL

Copper nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$] (≥98%, Sigma-Aldrich) as the source of copper oxide and glycine [$C_2H_5NO_2$] (≥99%, Sigma) as the fuel were dissolved by a deionized water and mixed during 10 min by a magnetic mixer for homogenization. The obtained solution was dropped onto bundled ANF 7 nm in diameter and 50 μm in length and kept for an hour at room temperature. The wetted bundles were heat-treated at 400 °C for 30 min in a preheated muffle furnace where the combustion process takes place.

The combustion product phase identification was performed by an X-ray diffraction using a Bruker diffractometer (D8) with CuKα radiation at 40 kV and scan rate of 0.02 °/s. The morphology of the obtained product was examined by Zeiss EVO MA-15 scanning electron microscope (SEM) (Germany). An energy dispersive X-ray spectrometer (EDS) (INCA x-sight, Oxford Instruments) was used for chemical elemental analysis.

## RESULTS AND DISCUSSION

The proportions of the prepared three kinds of samples are presented in Table 1. In samples S1 and S2 the copper nitrate to glycine ratio is stoichiometric, while the ANF to copper nitrate-glycine ratio is changed. In sample S3 the amount of copper is twice larger than stoichiometric.

The X-ray diffraction patterns of the synthesized combustion product (S1 and S3) containing different amounts of glycine are shown in Fig. 1. As it can be seen, mainly CuO is obtained as a result of the combustion of the stoichiometric mixture ($f = 1$) (Fig. 1, curve (a)). However, at fuel-rich composition ($f = 2$) (Fig. 1, curve (b)) the X-ray diffraction (XRD) pattern mostly contains CuO diffraction lines. Low intensity of $CuAlO_2$ and $Cu_2O$ diffraction lines can also be registered. The formation of reduced copper oxide along with CuO points to a decreasing oxygen concentration. In this case the oxygen is supplied to the system in two ways: from the decomposition of copper nitrate and from air. It is supposed that when the supply of oxygen

**Table 1.** Composition of the initial compounds

| Number of sample | Content of copper | Amount of ANF, mg | Amount of $Cu(NO_3)_2 \cdot 3H_2O$, mg | Amount of glycine, mg |
|---|---|---|---|---|
| S1 | High | 1.8 | 7.3 | 2.5 |
| S2 | Low | 1.8 | 0.73 | 0.25 |
| S3 | High | 1.8 | 7.3 | 5 |

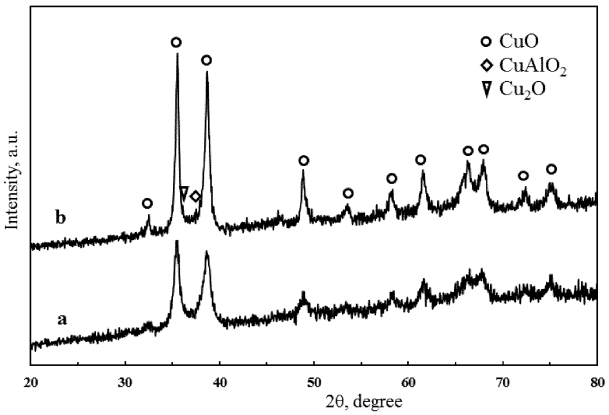


**Fig. 1.** XRD pattern of the combustion product using (curve **a**) the stoichiometric amount of fuel ($f = 1$) and (curve **b**) a fuel-rich mixture ($f = 2$).

is not sufficient in the combustion system, metals or their reduced oxides or fuel contaminations may form. When the amount of fuel was increased, only CuO phase was determined. This is caused by the smaller size of the particles, which can oxidize very fast in air after the combustion process. Pure $Al_2O_3$ is not found on the XRD pattern because of the large difference in the atomic scattering factors of copper and aluminium and low content of alumina in the combustion product.

The SEM images of the combustion product with a low and a high content of CuO are presented in Fig. 2. It is obvious that the CuO particles are developed as separate fine-sized particles in the mixtures with the low concentration of CuO (Fig. 2a and b). The CuO particle sizes can be further decreased by increasing the amount of glycine in the starting mixture at a constant content of CuO (Fig. 2b and c).

It should be noted that a high concentration of glycine results in an increase in the temperature of the combustion process. The adiabatic combustion temperature can increase up to 1890 °C as calculated by ISMAN-THERMO software [21]. A high combustion temperature could create suitable conditions for further CuO particle growth and agglomeration. On the other hand, the extra amount of glycine also results in an increase in the amount of the emitted gas due to a reaction with oxygen from the environment. As a result, the gas outflow decreases the system's energy more rapidly and hampers further particle growth and agglomeration (Fig. 2b). During the combustion process, the developed CuO nanoparticles remain separated from one another on the surface of ANFs.

As presented in Fig. 2a, CuO is present in a wide range of particle sizes starting from some nanometres up to 200 nm. The EDS analysis proved that nanoparticles located in between nanofibres were copper oxide (Fig. 2b).

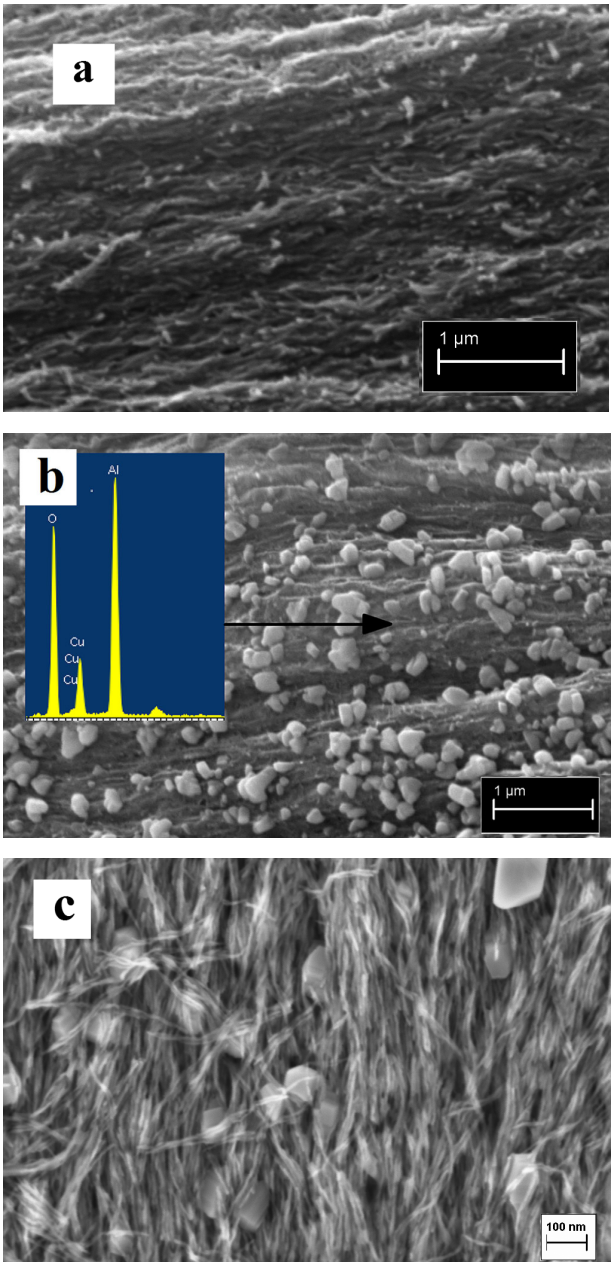


**Fig. 2.** SEM and EDS analyses of combustion products with (a) a low content of copper ($f = 1$), (b) a high content of copper ($f = 1$), and (c) a high content of copper ($f = 2$).

## CONCLUSIONS

It was the first time that in situ preparation of alumina nanofibres doped with CuO by the SCS method was realized and studied. The obtained results show that the composition of CuO/ANF can be developed due to the high exothermic interaction of copper nitrate and the glycine system. The particle size of CuO can be controlled by the concentration of copper nitrate and the copper nitrate to glycine ratio.

## ACKNOWLEDGEMENTS

This research was supported by the European Social Fund's Doctoral Studies and Internationalization Programme DoRa carried out by the Archimedes Foundation under activity 5-15 and by PUT1093 (to I. Hussainova) of the Estonian Research Council.

## REFERENCES

1. Li, D., Hu, J., Wu, R., and Lu, J. G. Conductometric chemical sensor based on individual CuO nanowires. *Nanotechnology*, 2010, **21**(48), 485502–485508.
2. Rahman, M. M., Ahammad, A., Jin, J.-H., Ahn, S. J., and Lee, J.-J. A comprehensive review of glucose biosensors based on nanostructured metal-oxides. *Sensors*, 2010, **10**(5), 4855–4886.
3. Wang, S., Hsiao, C., Chang, S., Lam, K., Wen, K., Hung, S., et al. A CuO nanowire infrared photodetector. *Sensor. Actuat. A-Phys.*, 2011, **171**(2), 207–211.
4. Venkatachalam, S., Zhu, H., Masarapu, C., Hung, K., Liu, Z., Suenaga, K., and Wei, B. In-situ formation of sandwiched structures of nanotube/$Cu_xO_y$/Cu composites for lithium battery applications. *ACS Nano*, 2009, **3**(8), 2177–2184.
5. Xu, Y., Chen, D., and Jiao, X. Fabrication of CuO pricky microspheres with tunable size by a simple solution route. *J. Phys. Chem. B*, 2005, **109**(28), 13561–13566.
6. Zhang, X., Shi, W., Zhu, J., Kharistal, D. J., Zhao, W., Lalia, B. S., et al. High-power and high-energy-density flexible pseudocapacitor electrodes made from porous CuO nanobelts and single-walled carbon nanotubes. *ACS Nano*, 2011, **5**(3), 2013–2019.
7. Yu, X.-Y., Xu, R.-X., Gao, C., Luo, T., Jia, Y., Liu, J.-H., and Huang, X.-J. Novel 3D hierarchical cotton-candy-like CuO: surfactant-free solvothermal synthesis and application in As(III) removal. *ACS Appl. Mater. Interfaces*, 2012, **4**(4), 1954–1962.
8. Zhou, K., Wang, R., Xu, B., and Li, Y. Synthesis, characterization and catalytic properties of CuO nano-crystals with various shapes. *Nanotechnology*, 2006, **17**(15), 3939.
9. Xu, L., Sithambaram, S., Zhang, Y., Chen, C.-H., Jin, L., Joesten, R., and Suib, S. L. Novel urchin-like CuO synthesized by a facile reflux method with efficient olefin epoxidation catalytic performance. *Chem. Mater.*, 2009, **21**(7), 1253–1259.
10. Zhou, K. and Li, Y. Catalysis based on nanocrystals with well-defined facets. *Angew. Chem. Int. Ed.*, 2012, **51**(3), 602–613.
11. Xu, J., Ji, W., Shen, Z., Tang, S., Ye, X., Jia, D., and Xin, X. Preparation and characterization of CuO nano-crystals. *J. Solid State Chem.*, 1999, **147**(2), 516–519.
12. Zhang, Q., Li, Y., Xu, D., and Gu, Z. Preparation of silver nanowire arrays in anodic aluminum oxide templates. *J. Mater. Sci. Lett.*, 2001, **20**(10), 925–927.
13. Xu, C., Liu, Y., Xu, G., and Wang, G. Preparation and characterization of CuO nanorods by thermal decomposition of $CuC_2O_4$ precursor. *Mater. Res. Bull.*, 2002, **37**(14), 2365–2372.

14. Yin, A., Li, J., Jian, W., Bennett, A., and Xu, J. Fabrication of highly ordered metallic nanowire arrays by electrodeposition. *Appl. Phys. Lett.*, 2001, **79**(7), 1039–1041.
15. Okuyama, K., Lenggoro, W., and Iwaki, T. Nanoparticle preparation and its application – a nanotechnology particle project in Japan. In *International Conference on MEMS, NANO and Smart Systems, 2004*. IEEE, 2004, 369–372.
16. Mukasyan, A. S., Epstein, P., and Dinka, P. Solution combustion synthesis of nanomaterials. *P. Combust. Inst.*, 2007, **31**(2), 1789–1795.
17. Aruna, S. T. and Mukasyan, A. S. Combustion synthesis and nanomaterials. *Curr. Opin. Solid St. M.*, 2008, **12**(3), 44–50.
18. Patil, K. C., Hegde, M., Rattan, T., and Aruna, S. *Chemistry of Nanocrystalline Oxide Materials-Combustion Synthesis, Properties and Applications*. World Scientific, New Jersey, 2008.
19. Aghayan, M., Voltsihhin, N., Rodríguez, M. A., Rubio-Marcos, F., Dong, M., and Hussainova, I. Functionalization of gamma-alumina nanofibers by alpha-alumina via solution combustion synthesis. *Ceram. Int.*, 2014, **40**(8), 12603–12607.
20. Aghayan, M., Hussainova, I., Gasik, M., Kutuzov, M., and Friman, M. Coupled thermal analysis of novel alumina nanofibers with ultrahigh aspect ratio. *Thermochim. Acta*, 2013, **574**, 140–144.
21. Zeldovich, Ya. B., Barenblatt, G. I., Librovich, V. B., and Makhviladze, G. M. *The Mathematical Theory of Combustion and Explosions*. Consultants Bureau, New York, 1985, 22–26.

## Vaskoksiidi homogeenne sadestamine mesopoorsetele 1D alumiiniumnanokiududele

Khachatur Kirakosyan, Marina Aghayan, Miguel A. Rodríguez, Masoud Taleb ja Irina Hussainova

On vaadeldud alumiiniumnanokiududele (ANF) vaskoksiidi sadestamist lahustipõletusmeetodil. Alumiiniumnanokiudude kimp immutati vasenitraat-glütsiinlahusega (oksüdeerija-kütus) ja termotöödeldi õhu käes temperatuuril 400 °C 30 min. Lõpp-produkti mikrostruktuuri ja koostise iseloomustamiseks kasutati XRD-, SEM- ning EDS-analüüsi, mille tulemusena selgitati välja peeneteralise CuO kile ühtlane jagunemine gamma-alumiiniumoksiidist nanokiududel. Saadud tulemused näitasid, et põletusprodukti osakeste suurus, faasiline koostis ja mikrostruktuuri morfoloogia on dramaatiliselt mõjutatud kütuse hulgast, kütuse ja oksüdeerija kui ka alumiiniumnanokiudude ning Cu(II) ioonide vahekorrast reageerivas segus.