

Solution Synthesis of Bimetallic Copper–Based Nitrides Cu₃M_xN (M = Pd, Ag, Zn, Ni)

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Extended Abstract

Copper(I) nitride (Cu₃N) is a semiconductor with an *anti*-ReO₃ cubic crystal structure, that has attracted considerable interest due to its optical and electrical properties and potential applications in optical data storage, and integrated circuits [1]. The defect tolerance of the Cu₃N structure also makes it suitable for energy conversion and storage, e.g. for solar cells and batteries [2]. A significant area of study is focused on the electrocatalytic activity of Cu₃N in various redox reactions, e.g. electrochemical reduction reaction of carbon dioxide (CO₂RR) [3] and oxygen reduction reaction (ORR) [4].

The cubic crystal structure of Cu₃N allows for the intercalation of other metal atoms into the unit cell, which can significantly change the material properties. There are numerous reports on the synthesis of Cu₃M_xN structures, where M is a transition metal atom, e.g. Sc, Cr, Zn, Pd; however, they are limited to physical deposition methods, such as magnetron sputtering [5].

This study attempted to synthesize Cu₃M_xN structures with palladium, silver, zinc, and nickel. The chemical solution method was applied using long-chain primary amine as a reducing agent. Different reaction conditions were studied, e.g. heating technique, time, and temperature of the reaction, and type of metal precursors. As a result, homogenous Ag- and Pd-doped Cu₃N nanocrystals with diameters < 20 nm were successfully obtained [5]. Doping with zinc resulted in a mixture of Cu₃N/ZnO due to the low reduction potential of zinc(II). Syntheses with nickel led to mixtures of copper nitride, metallic copper, and copper and nickel oxides. The crystal structure, chemical composition, and morphology were studied using high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), IR, and Raman spectroscopy. The obtained materials were also tested for their electrochemical properties using voltammetric techniques. Ag-doped Cu₃N nanostructures revealed electrocatalytic activity in ORR higher than binary Cu₃N, comparable to a commercial Pt/C electrode [5]. Pd-doped Cu₃N NCs also showed activity in CO₂RR, higher than binary Cu₃N.

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References

- [1] A. Ścigala, E. Szłyk, L. Dobrzańska, D. H. Gregory, R. Szczyński, “From binary to multinary copper based nitrides—unlocking the potential of new applications”, *Coord. Chem. Rev.*, vol. 436, no. 213791, 2021.
- [2] A. Zakutayev, C. M. Caskey, A. N. Fioretti, D. S. Ginley, J. Vidal, V. Stevanovic, E. Tea, S. Lany, “Defect Tolerant Semiconductors for Solar Energy Conversion”. *J. Phys. Chem. Lett.*, vol. 5, no. 7, pp. 1117–1125, 2014.
- [3] Z. Yin, C. Yu, Z. Zhao, X. Guo, M. Shen, N. Li, M. Muzzio, J. Li, H. Liu, H. Lin, J. Yin, G. Lu, D. Su, S. Sun, “Cu₃N Nanocubes for Selective Electrochemical Reduction of CO₂ to Ethylene”, *Nano Lett.*, vol. 19, pp. 8658–8663, 2019.
- [4] H. Wu., W. Chen, “Copper Nitride Nanocubes: Size-Controlled Synthesis and Application as Cathode Catalyst in Alkaline Fuel Cells”, *J. Am. Chem. Soc.*, vol. 133, no. 39, pp. 15236–15239, 2011.
- [5] A. Ścigala, R. Szczyński, P. Kamedulski, M. Trzcinski, E. Szłyk, “Copper nitride/silver nanostructures synthesized via wet chemical reduction method for the oxygen reduction reaction”, *J. Nanopart. Res.*, vol. 25, no. 28, 2023.