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Synthesis, characterization and DFT studies of zinc-doped copper oxide nanocrystals for gas sensing applications†

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Due to their unique properties, p-type copper oxide nanostructures have demonstrated promising potential for various applications, especially for the detection of ethanol vapour and other volatile organic compounds (VOCs). In this work a simple and cost-effective synthesis from chemical solutions (SCS) at low temperatures (≤80 °C) and rapid thermal annealing (RTA) process were used to grow zinc-doped copper oxide ($Zn_xCu_{1-x}O_y$) nanostructures. The structural, morphological, vibrational, chemical, electronic and sensorial characteristics of $Zn_xCu_{1-x}O_y$ nanocrystallite layers obtained by using such an efficient approach based on both, the SCS and RTA processes, have been studied. The investigations demonstrated the possibility to tune sensitivity from VOC to H_2, as well as an improved response and high selectivity with respect to hydrogen gas for $Zn_xCu_{1-x}O_y$ nano-crystalline thin films with $x = 0.03$. Density functional theory calculations showed that the charge transfer together with changes in the Fermi level facilitate H_2 gas sensing, which is further enhanced by Zn doping. Hydrogen gas sensing with a high response and selectivity using p-type hybrid semiconductor nanostructures has been reported. An improved stability in humid air was observed by exposure of doped samples to rapid thermal annealing process for the first time. The experimental and calculation results provide an alternative to sensitive and selective detection of ethanol and hydrogen gases, which would be of particular benefit in the area of public security, industrial and environmental applications.

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Introduction

Hydrogen is widely used in industries, as a power source in aerospace, for metal sintering and annealing, in research laboratories, biomedical systems, automotive and transportation equipment, *etc.*[1–8] Therefore, the reliable, selective and fast detection of hydrogen gas leaks appears to be the strict necessity for preventing the accumulation of hydrogen in air (4% H_2).[6] In this context nano- and microstructures of p-type materials and especially the n-type semiconducting oxides have been intensively investigated over the past few decades due to their remarkable gas sensing properties, and importance for fundamental research and applied technologies.[9–12] Due to their unique properties and specific gas sensing mechanism, p-type copper oxide nanostructures have demonstrated promising potentials in various gas sensing applications, especially in detection of ethanol vapour and other volatile organic compounds (VOCs), like benzene, acetone and toluene, *etc.*[13–17] Copper oxide semiconductors and their derivatives are excellent candidates for the fabrication of low-cost p-type nanosensors due to high abundance of copper in nature,[18] simple synthesis and nanointegration methods.[19]

However, most of the reported studies on gas sensing properties of copper oxides with different types of morphologies have demonstrated selective ethanol or acetone vapour sensing[14,20,21] and only a few reports reveal the selectivity and response with respect to hydrogen gas.[17,22–24] In this context, the change of chemical and physical properties by doping of foreign elements is an important and efficient way to further control the gas sensing characteristics of semiconducting oxides such as sensitivity, response and recovery times, as well as selectivity.[16] From the existing literature, it is difficult to find any study which demonstrates the p-type nanomaterials based hydrogen gas sensing with high response/selectivity characteristics.

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