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Hydrothermally synthesized Copper Oxide (CuO) superstructures for ammonia sensing

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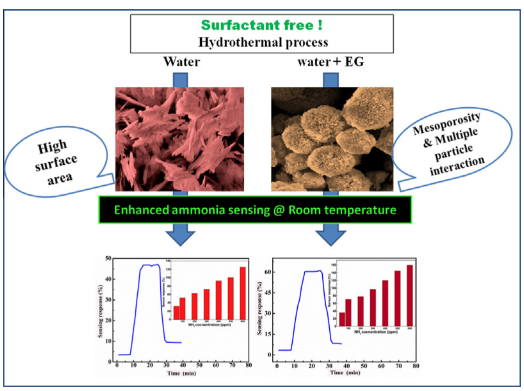
GRAPHICAL ABSTRACT



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ABSTRACT

According to environmental protection agencies (EPA), the emission threshold of NH_3 in air is 1000 kg/yr which is now about 20 Tg/yr. Hence, there is a rapid increase in need of NH_3 sensors to timely detect and control NH_3 emissions. Metal oxide nanostructures such as CuO with special features are potential candidates for NH_3 sensing. In the present study, morphology controlled 3-dimensional CuO superstructures were synthesized by surfactant-free hydrothermal method for NH_3 detection. In addition to conventional hydrothermal method where water as solvent, a modified approach using a mixture of water and ethylene glycol (EG) was used as solvent to control the growth process. Hierarchical superstructures namely, snowflake-like, flower-like, hollow-sphere-like and urchin-like feature with particle dimensions ranging from 0.3 to 1 μm were obtained by varying water/EG ratio and reaction temperature. The synthesized nanostructures exhibited morphology dependent luminescence and gas sensing properties. The surface area and pore distribution determined by BET surface analysis also largely influenced by the presence of EG in the reaction system. The average pore diameter enhanced from 6 nm to 14 nm by the addition of 10 ml EG as solvent. The room temperature ammonia sensing behavior of all samples was studied using an indigenous gas sensing set-up. It was found that hollow-sphere like CuO nanostructures showed a maximum sensitivity of 150% towards 600 ppm ammonia with a response and recovery time of 6 min. The hydrothermal synthesis strategy reported here has the advantage of producing shape controlled hierarchical materials are highly suitable for various technological applications.

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1. Introduction

Recent studies have shown an alarming increase in NH_3 emissions globally over the past few decades [1]. This is a major concern because NH_3 significantly governs the formation of atmospheric particulate matter, visibility degradation and atmospheric deposition of nitrogen to sensitive ecosystems. Thus, the increase in NH_3 emissions beyond the tolerable limits adversely affects the environment and thereby public health which has been already reflected in the recent abnormal climatic changes [2]. Hence, it is highly demanding to have novel devices which can sense NH_3 above the permissible levels. These high performance sensor devices can also help to prevent the industrial hazards from unexpected gas leakages [3]. Metal oxides such as CuO, ZnO etc are considered to be the best candidates for gas sensing applications due to their tunable physical properties, higher response to volatile gases and can be nano-engineered to design portable sensing devices.

Morphology controlled metal oxide (MOX) nanostructures have gathered enormous scientific and technological interests over the last decade owing to their superior electrical, optical, catalytic and adsorption properties [4]. There have been several reports on successful synthesis of oxide nanomaterials with peculiar shapes such as nanoparticles (0D), nanofibers & nanorods (1D) and nanosheets (2D) [5–8]. However, hierarchical assembly of these low dimensional nanostructures into three-dimensional (3D) superstructures resembling the morphological diversity of naturally occurring patterns have shown improved stability, porosity and resistance to aggregation [9–11]. Since this concept of superstructures was first proposed by Colfen and Antonietti in 2005, several attempts were reported to synthesize ordered superstructures of metal oxides in the scale of several hundred nanometers to micrometers [12]. Mali et al., synthesized 3D urchin-like TiO_2 nanoclusters for dye sensitized solar cells using a soft hydrothermal method and demonstrated a conversion efficiency of 7.16% which is 3 times higher than that reported in conventional nanoparticles [13]. Zhang et al. reported hierarchical flower-like boehmite (α-AlOOH) structures using hydrothermal method [14]. Flower-like ZnO microstructures composed of nanorod bundles were synthesized by a polyethylene glycol (PEG)-assisted hydrothermal route and used as CO sensor [15]. Stable hierarchical of SnO_2 nanospheres synthesized by several techniques showed good NO sensing properties [16].

Cupric oxide (CuO) is a promising p-type semiconductor suitable for variety of applications such as room temperature gas sensors [17–19], photocatalysts [20], waste water treatments [21] and charge storage devices [22]. CuO nano-particles with different morphologies and structures have been achieved by various synthesis methods like wet-chemical, hydrothermal, thermal decomposition, physical and chemical vapor deposition [23–27]. Using PEG 200 as surfactant, Seo et al. synthesized flower-like CuO which showed good catalytic properties [28]. Self-assembled CuO ellipsoids were prepared by a wet chemical approach, but their properties were not investigated [29]. Chemiresistors based on 3D urchin-like CuO superstructures exhibited improved H_2 sensing performances compared to 1D fiber-like or rod-like structure [30]. CuO superstructures based metal-organic structures are also found to be suitable for efficient electrochemical oxidation of glucose etc. [31]. Faster adsorption and higher removal capacity of toxic arsenic from drinking water using 'cotton candy-like' CuO superstructures have also been reported [32].

In all these reports, the observed physical and chemical properties of the synthesized CuO nanostructures were found to be greatly dependent on their morphology, size and crystallinity. Hence, the appropriate choice of precursors and suitable chemical synthesis methods with tuned reaction conditions are critical in obtaining novel superstructures of CuO for specific applications. Most of the reported works on the synthesis of CuO nanostructures made use of shape controlling agents such as hard templates, surfactants, or capping agents for controlling the growth, morphology and dimensions of the nanoparticles. However, the presence of surfactants tends to depreciate the surface properties such as active surface area and porosity which are crucial in applications and require adsorption of external molecules on the surface sites [33]. Hence, it is highly desirable to design chemical methods which do not require the presence of shape controlling agents for the synthesis of nanostructures. Apart from these, specific applications require CuO superstructures with specific morphologies that could not be achieved by utilizing the shape controlling agents.

Here, we report a modified surfactant-free hydrothermal method using water and ethylene glycol as solvent for the fabrication of morphology controlled CuO superstructures. The usage of water (dielectric constant at 25 °C = 78.4) has major constraints such as its lower boiling point (100 °C) and comparatively lowers reduction potential and hence the reaction times are relatively high and achieving superstructures is much tedious without shape controlling agents [34]. Hence, ethylene glycol ($C_2H_6O_2$), a commonly used polyol is a possible choice as solvent having appreciable dielectric constant (dielectric constant at 25 °C = 40.3), higher boiling point (~198 °C) and reduction potential [35]. However, faster reduction using ethylene glycol (EG) as hydrothermal solvent resulted in the formation of Cu_2O instead of anticipated CuO and hence ethylene glycol alone is not preferred. Therefore, the best strategy to enhance the reaction rate in hydrothermal process is using a mixture of both water and ethylene glycol in appropriate proportion as solvent to yield novel superstructures with much ease. Well dispersed and uniformly oriented snowflake-like, flower-like, hollow sphere-like and urchin-like 3D CuO superstructures were obtained at relatively lower temperatures and time durations. The influence of water and ethylene glycol on the evolution of morphology of the CuO nanostructures and their corresponding physical properties are studied. The synthesized CuO superstructures are subjected NH_3 sensing room temperature.

2. Materials and methods

2.1. Experimental

CuO superstructures were synthesized by hydrothermal method using water (alone) and a mixture of water (H_2O) & EG in varying proportions as solvent. Copper nitrate semipentahydrate ($CuNO_3 \cdot 2.5H_2O$, 99% purity), sodium hydroxide (NaOH, 99% purity), and ethylene glycol (EG) ($C_2H_6O_2$, 99% purity) were purchased from Alfa Aesar and used without further purification.

In the first case (water alone as solvent), 0.1 M of $CuNO_3 \cdot 2.5H_2O$ and 0.007 M of NaOH were added to 75 ml double distilled water separately (A & B) and stirred vigorously for 30 min. In second case (EG assisted synthesis), the solution ratio maintained as 10 ml EG + 65 ml water (C) and 20 ml EG + 55 ml water (D). These mixture solutions then transferred into 100 ml Teflon-lined autoclave and maintained in furnace for 12 h separately at 100 °C (A) and 200 °C (B), 6 h at 100 °C (C & D). Once the stipulated reaction time is over, the autoclaves were allowed to cool down to room temperature and the precipitate was collected, washed several times with distilled water & ethanol and dried at 60 °C for 24 h. The samples prepared are named as S1 (A), S2 (B), S3 (C) and S4 (D).

The synthesized samples were characterized by different characterizations tools. The structural and phase analysis of the samples were carried out using a Rigaku Ultima III X-ray diffractometer with Cu K_α (λ = 1.514 Å) radiation. Morphological and