SCIENCE CHINA Materials

ARTICLES

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Published online 12 March 2018 | https://doi.org/10.1007/s40843-017-9224-x

Cu_xO self-assembled mesoporous microspheres with effective surface oxygen vacancy and their room temperature NO_2 gas sensing performance

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ABSTRACT **A series of Cu_xO self-assembled mesoporous microspheres (SMMs), with different and controlled morphology (virus-like, urchin-like, spherical), were synthesized by facile liquid phase approach. The morphology of the as-prepared Cu_xO SMMs was evolved from spherical to virus-like shape by controlling the ratio of DI water in solution. It can also realize the transformation from loose assembly to dense assembly by extending the reaction time. These Cu_xO SMMs exhibited good response to NO_2 gas at room temperature, benefiting from their 3D self-assembly structure. Among these the resulting virus-like Cu_xO SNMMs-based sensor exhibits largely enhanced response to 1 ppm NO_2 gas at room temperature. The enhanced response of the virus-like Cu_2O SMMs-based sensor can be ascribed to the high surface area, hierarchical 3D nanostructures, micropores for effective gas diffusion, the heterojunctions formed between CuO and Cu_2O, and the existence of abundant surface oxygen vacancies.**

Keywords: self-assembly, mesoporous, Cu_xO, oxygen vacancy, NO_2 gas sensing

INTRODUCTION

The assembly of nanoparticles has emerged as an alternative approach to utilize and exploit nanomaterials in a scalable manner [1]. These nanostructures from assembly of nanoparticles represent a new class of potential building blocks for making functional materials, because they have additional collective properties induced by coupling between their constituents as well as the chemical and physical properties inherited from their constituent nanoparticles [2,3]. Numerous two-dimensional (2D) and three-dimensional (3D) super-nanostructures based on assembled nanoparticles have been fabricated for applications in sensing, photonics, optoelectronics, photovoltaics and electronic devices [4–6]. For example, the assemblies of metal nanoparticles have advantages in molecular detection by surface-enhanced Raman scattering in comparison to the individual nanoparticles [7]. 3D multilayer superlattices film has a much higher rate of photocurrent generation han that of its disordered-assembled counterpart [8]. Mesoporous colloidal superparticles made of platinum-group nanocrystals show significantly improved catalytic activity and recyclability in catalyzing solution-phase electron-transfer reactions in comparison with the well-dispersed small Pt nanocrystals [9]. Therefore, the assembly of inorganic nano-building blocks into complex 3D superstructures with well-controlled porosity, morphologies and surface defect states is still an incipient area and in strong demand.

Detection of polluted air is important for environmental monitoring, personal safety protection, and industrial manufacturing nowadays. Nitrogen dioxide (NO_2) is a notorious gas mainly released from vehicle exhausts and fossil fuel combustion, which threatens the environment and causes respiratory problems in human beings [10]. However, traditional NO_2 gas sensors are usually operated between 200 and 400°C, since closely packed metal oxides have high resistance at room temperature [11–14]. Various efforts have been devoted to decreasing the operation temperature, such as tuning the morphology of the nanostructures, surface modification, and fabrication of hybrid or composite nanostructures. For example, tungsten oxide (WO_3) hollow spheres exhibited good response to 100 ppb NO_2 at 140°C due to their hierarchical self-assembled structure [15]. The sensors based on concave Cu_2O octahedral nanostructure

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had good sensing response to NO_2 at 50°C due to their unique concave octahedral-shape [16]. Nickel oxide (NiO) hexagonal nanosheets with micropores present good sensitivity to NO_2 at room temperature due to the abundant nickel vacancies formed in NiO [17]. Tin oxide (SnO_2) nanoflower-based sensor exhibited high response toward 200 ppb NO_2 at room temperature due to the oxygen vacancies [18]. Also Cu_2O nanocrystals/graphene composites exhibited an excellent sensitivity toward NO_2 at room temperature [19,20]. The good room temperature sensing performance was attributed to the improved conductivity and effective gas diffusion. Therefore, the metal-oxide-based gas sensors could realize room temperature gas sensing if the sensing materials are elaborately designed with well-controlled porosity, nanoscale structure and surface defect states.

In the present study, a series of Cu_xO self-assembled mesoporous microspheres (SMMs), with different and controlled morphology (virus-like, urchin-like, spherical), were synthesized by a facile liquid method. The morphological and 3D self-assembly structural properties of the as-prepared Cu_xO SMMs were studied in detail. Their surface area, porosity, and surface oxygen vacancies have been analyzed by the nitrogen adsorption-desorption isotherm curves, electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) spectra. These Cu_xO SMMs are shown to perform effectively as sensing material for NO_2 gas at room temperature. Furthermore, the underlying gas sensing mechanism for the enhanced response characteristics due to the 3D self-assembled Cu_xO SMMs is also discussed.

EXPERIMENTAL SECTION

Materials

All reagents were of analysis grade and were used without further treatment. The Cu_2O SNMMs were prepared following an approach by Zhang *et al.* [21] with a minor modification of reactant content. 0.4 g copper acetate ($(CH_3COO)_2Cu{\cdot}H_2O$) (Sinopharm) was dissolved in 30 mL *N*,*N*-dimethylformamide (DMF) (Beijing chemical reagent factory, containing ~0.1% water), followed by the addition of poly(vinyl pyrrolidone) (PVP, 0.165 g, molecular weight = 30,000) (Sinopharm), and 0–0.5 mL deionized (DI) water. After stirring for several minutes, 40 mg $NaBH_4$ (Tianjin Fuchen Chemical reagent factory) was added. The mixture was heated to 80°C for 2–6 min. Drastic changes in the liquid color were observed during reduction of Cu^{2+} to Cu^{+} (blue to green to light yellow) quickly. Once the color of the mixture changed to light yellow, the mixture was dipped into the water bath to cool down. The precipitate was centrifuged, washed with ethanol several times.

Material characterizations

The morphologies of the as-synthesized samples were examined on SIRION 200 field emission scanning electron microscope (FESEM), and JEOL JEM-1200EX transmission electron microscope (TEM) (Hitachi H-7650B) at 100.0 kV. High resolution TEM was recorded on Tecnai G2 F20 S-Twin, operating at 200.0 kV. X-ray diffraction (XRD) patterns of the as-obtained product were recorded on a Bruker D8 Advance powder X-ray diffractometer at a scanning rate of 2° min^{-1}, using Cu-Kα radiation (λ=1.5406 Å). X-ray photoelectron spectroscopy (XPS) spectra were obtained with a PHI Quantera II XPS system using Al Kα non-monochromatic radiation. The measurement parameters were: light spot size: 100 μm; power: 100 W; voltage: 20 kV. Measurements of Brunauer-Emmett-Teller (BET) surface area and porosity were carried out at 77 K with a Quantachrome Instrument ASiQMVH002-5 system. Electron paramagnetic resonance (EPR) experiments were performed on a Bruker EMX X-band spectrometer and microwave frequency=9.40 GHz at room temperature.

NO_2 gas sensing performance evaluation

First, the gas sensor was fabricated by putting slurry of as-prepared Cu_xO SMMs on the cleaned alumina substrates which were attached with a pair of interdigital Pt electrodes and followed by a thermal treatment at 200°C for 2 h in order to burn out the organic solvent used in the preparation of coating slurry and to enhance the adherence of the sensing film to the sensor substrate. The target gas concentration was controlled by injecting volume of the target gas [22]. For recovery of the sensor resistance, the testing chamber was open in air. The changes of the sensor resistance in air or target gas were monitored by a gas sensing testing system (WS-30A, Winsen, China). The gas responses ($S=R_a/R_g$ for oxidizing gas or R_g/R_a for reducing gas, R_a: resistance in the atmospheric air, R_g: resistance in the target gas) to NO_2, SO_2, C_2H_5OH, $C_6H_5CH_3$, $(CH_3)_2CO$, CH_3OH, C_3H_7NO were measured at room temperature (25°C, humidity 26%).

RESULTS AND DISCUSSION

Fig. 1 and Fig. S1 (see Supplementary information) show the FESEM images of the resulting Cu_xO SMMs with different morphologies synthesized by the liquid phase