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The effect of ZIF-8 on the phase structure and morphology of bead-like $CuMn_2O_4$/ZnO photocatalytic electrospun nanofibers

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ABSTRACT

Uniform bead-like $CuMn_2O_4$/ZnO nanofibers were successfully fabricated via a facile electrospinning technology. The current new findings can be emphasized on the introduction of ZIF-8 into Cu-based precursor solution that had a great significance for controlling phase structure and morphology of $CuMn_2O_4$/ZnO composites. Compared with hollow $CuMn_2O_4$ nanofibers and $CuMn_2O_4$/$ZnMn_2O_4$ irregular rod-like materials, $CuMn_2O_4$/ZnO nanofibers can display the enhanced photocatalytic efficiency of 86% as the irradiation time increasing to 50 min and the good photocatalytic cycle stability to methylene blue (MB). The influence of adding amount of ZIF-8 on the morphological evolution and photocatalytic property of $CuMn_2O_4$/ZnO nanofibers and the relevant photocatalytic mechanism were investigated. The synthesis approach of $CuMn_2O_4$/ZnO nanofibers is expected for fabricating other 1D semiconductor composites with novel morphologies and advanced properties in photocatalysis, gas sensing, and electrochemical applications.

1. Introduction

As a typical mixed transition metal oxide with spinel structure, Copper manganese oxides ($CuMn_2O_4$) with various morphological features mainly referring to spherical and granular characteristics can be employed as catalysts because of the large reserves, high catalytic activity, and good stability. There has been fascinating and sustained focus on fabricating $CuMn_2O_4$-based nanofibers with different constructions for photocatalytic application in recent years due to their good electron transport capacity, large specific surface area, and excellent chemical inertness [1]. Zeolitic imidazolate frameworks (ZIFs) have been attractive as high-profile porous materials displaying unique and highly desirable properties such as massive surface active sites, high porosity, and good hydrothermal stability [2]. Structural regulation by depositing ZIFs on the surface of oxide photocatalysts was considered as a promising approach for improving photocatalytic properties. For example, Zeng et al. presented the sonochemical method to fabricate ZIF-8 nanoparticles on the surface of TiO_2 nanofibers with the enhanced photocatalytic activity for Rhodamine B degradation [3]. However, composite modification do not engender a lot of attentions on introducing ZIF-8 into the mixed transition metal oxide electrospun nanofibers by embedding ZIF-8 into the polymeric precursor solution, which is an emerging strategy for constructing novel 1D nanocomposites by solving a series of blockages, including dispersion, solubility, dimensional matching, and chemical reaction [4].

In this work, highly-dispersed and uniform hollow $CuMn_2O_4$ and bead-like $CuMn_2O_4$/ZnO nanofibers have been synthesized by adjusting the adding amounts of ZIF-8 nanoparticles in the electrospinning process. The effect of ZIF-8 on the phase structure and morphology of nanocomposites was investigated as well as the enhanced photocatalytic properties.

2. Experimental section

$CuMn_2O_4$/ZnO nanofibers were prepared by the modified electrospinning technology. Different amounts of ZIF-8 were added into the precursor solution containing $Mn(CH_3COO)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, and PVP. The obtained precursor fibers were heated at 600 °C for gaining the products. The detailed experimental procedures, characterization, and photocatalytic tests were described in supplementary information.

3. Results and discussion

As shown in Fig. 1a–h, the morphology of $CuMn_2O_4$-based 1D materials can be gradually transformed from uniform hollow nanofibers into regular bead-like structures without any

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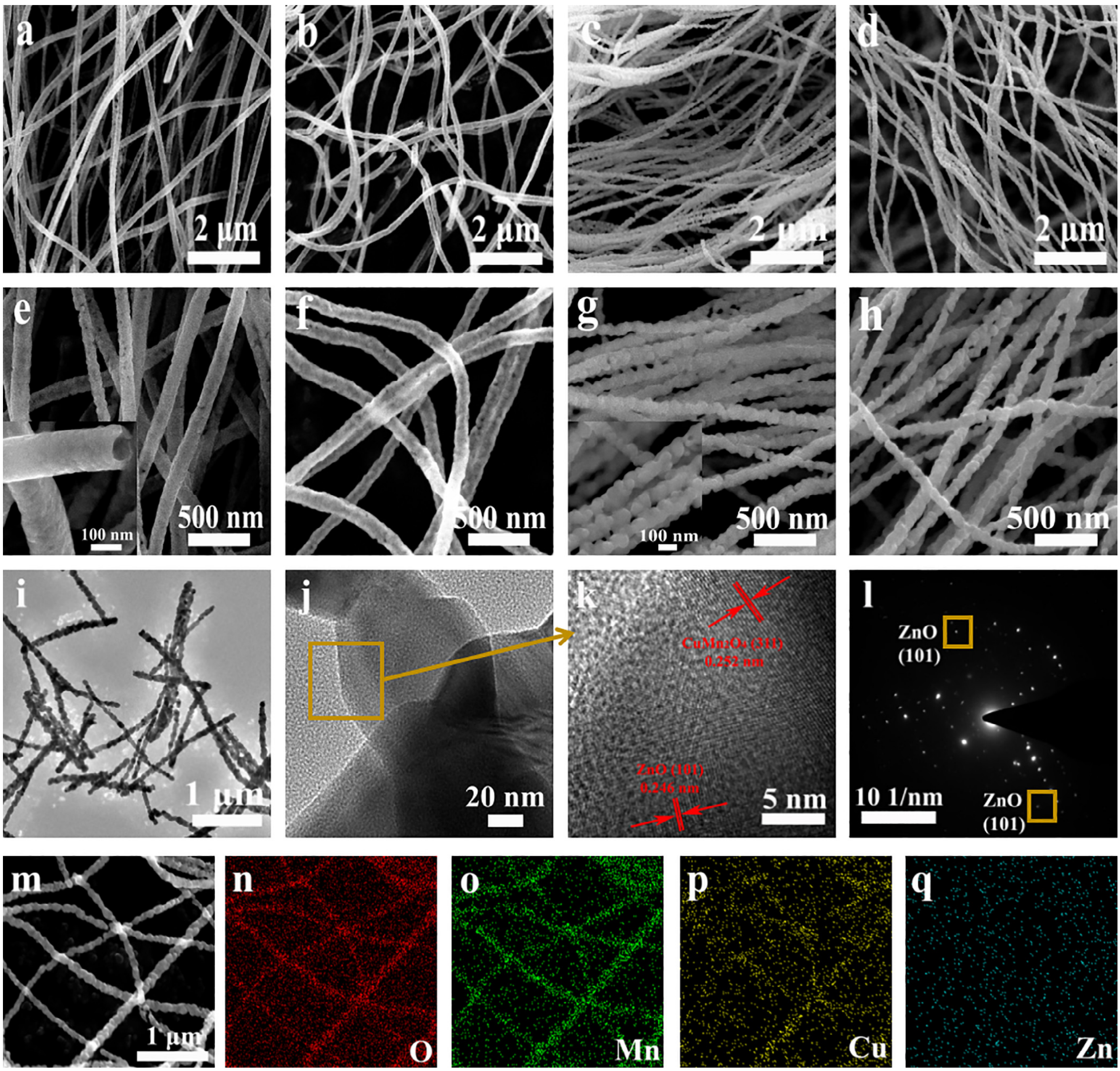

Fig. 1. SEM images of Sample 1 (a and e), Sample 2 (b and f), Sample 3 (c and g), and Sample 4 (d and h); the insets of e and g corresponding to hollow and bead-like structures of Sample 1 and 3, respectively; TEM and HRTEM images (i–k), SAED pattern (l), and element mappings (m–q) of Sample 3.

agglomerations as the adding amounts of ZIF-8 with the average diameter of 35 nm (Fig. S1) increasing from 0 to 10 mol%, along with fiber average diameter decreasing from 120 to 80 nm. The obvious evolution is ascribed to the presence of well-dispersed ZIF-8 nanoparticles in the precursor solution, in favor of modulating the migration of Cu^{2+} and Mn^{2+} and the crystal growth of $CuMn_2O_4$ and ZnO phases during the pyrolysis process. Fig. 1i–k can not only reveal the successful formation of uniform and smooth bead-like nanofibers composed of tunable particle sizes after annealing in air, but also confirm two lattice planes with interplanar distances of 2.52 and 2.46 A corresponding to the typical (3 1 1) plane of $CuMn_2O_4$ and (1 0 1) plane of ZnO, respectively. Additionally, Fig. 1 l shows the array of clear diffraction spots of ZnO in Sample 3, further verifying the phase composition of $CuMn_2O_4$ and ZnO components. EDS spectrum (Fig. S2) and elemental mappings (Fig. 1 m–q) demonstrate the existence of Cu, Mn, Zn, and O elements with good dispersion in bead-like structures, suggesting that the introduction of ZIF-8 plays a significant role in tuning the fine microstructure of $CuMn_2O_4$/ZnO nanofibers.

Fig. 2a and b show that XRD diffraction peaks of Sample 1 are well-indexed to the spinel $CuMn_2O_4$ phase (JCPDS 34-1400), and one weak shoulder peak around 36–37° that belongs to ZnO phase (JCPDS 36-1451) is clearly observed for Sample 2–4, indicating the formation of $CuMn_2O_4$/ZnO composites. Compared with Sample 1, two additional Raman absorption peaks at 380 and 320 cm^{-1} of Sample 3 are detected in Fig. 2c, which can be attributed to the first and second-order phonon frequencies of ZnO, respectively [5]. Four different XPS peaks of Cu 2p are observed in Fig. 2d for denoting Cu^{2+} of $CuMn_2O_4$, in which the peaks at 930.8 and 933.8 eV are ascribed to Cu $2p_{3/2}$, and the ones at 950.8 and 953.1 eV for Cu $2p_{1/2}$, respectively [6]. Mn 2p XPS spectrum (Fig. 2e) presents the energy gap of 11.8 eV between two peaks at 641.6 (Mn $2p_{3/2}$)