Applied Surface Science 320 (2014) 218–224

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Preparation of flexible zinc oxide/carbon nanofiber webs for mid-temperature desulfurization

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ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form
12 September 2014
Accepted 14 September 2014
Available online 22 September 2014

Keywords:
Electrospinning
Carbon nanofibers
Zinc oxide
Hydrogen sulfide
Desulfurization

ABSTRACT

Polyacrylonitrile (PAN) derived carbon nanofiber (CNF) webs loaded with zinc oxide (ZnO) were synthesized using electrospinning and heat treatment at 600 °C. Uniformly dispersed ZnO nanoparticles, clarified by X-ray diffraction and scanning electron microscopy, were observed on the surface of the nanofiber composites containing 13.6–29.5 wt% of ZnO. The further addition of ZnO up to 34.2 wt% caused agglomeration with a size of 50–80 nm. Higher ZnO contents led the concentrated ZnO nanoparticles on the surface of the nanofibers rather than uniform dispersion along the cross-section of the fiber. The flexible composite webs were crushed and tested for hydrogen sulfide (H_2S) adsorption at 300 °C. Breakthrough experiments with the ZnO/CNF composite containing 25.7 wt% of ZnO for H_2S adsorption showed three times higher ZnO utilization efficiency compared to pure ZnO nano powders, attributed to chemisorption of the larger surface area of well dispersed ZnO particles on nanofibers and physical adsorption of CNF.

1. Introduction

Zinc oxide (ZnO) has been widely used to remove hydrogen sulfide (H_2S), which is one of toxic gases to degrade industrial facilities and pollute environment. Even though various adsorbents such as metal oxides [1], metal oxide modified alumina [2,3], and zeolites [4,5] were applied to remove H_2S at relatively high temperature range from 500 to 800 °C, ZnO is recognized to be the most effective adsorbent under hot gas stream condition [6–8]. The volatility of Zn at reducing environment over 600 °C has been known as a serious drawback so that the effort to reduce the reaction temperature using ZnO nanoparticles has been studied because they are much more reactive due to the increased surface area and enhanced gas diffusion characteristics [9–11]. However, it is known that aggregations of ZnO nanoparticles can be formed even at 300 °C due to relatively unstable characteristics of ZnO, which reduces efficient surface area for adsorption of H_2S [9]. Therefore, ZnO nanoparticles on stable supports such as Al_2O_3, silica, and carbon have been investigated to increase the thermal durability of ZnO nanoparticles [10–14]. Desulphurization takes place on ZnO as following well-known reaction [6].

$$ZnO(s) + H_2S(g) \rightarrow ZnS(s) + H_2O(g) \quad (1)$$

Fang et al. reported activated carbon (AC) supported metal oxides as H_2S adsorbents [15]. Metal precursors (1 wt%) were impregnated into commercial AC in solution, and heat treatment at 300–450 °C for 4 h led to the adsorbents, showing as high as 125 min in breakthrough time. Even though similar *ex situ* loadings of metal oxides on carbon materials were studied, there was a limitation on uniform dispersion of a large amount of metal nanoparticles, which is critical to minimize the fixed cost on facilities [16,17]. Previously, we reported well dispersed ZnO nanoparticles, loaded on reduced graphene oxide, showing significantly high breakthrough time in H_2S adsorption test at 300 °C without any aggregation of ZnO nanoparticles [9].

In this study, we report *in situ* preparation of ZnO nanoparticles dispersed on nanofibers using simple and fast electrospinning for

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http://dx.doi.org/10.1016/j.apsusc.2014.09.093
0169-4332/

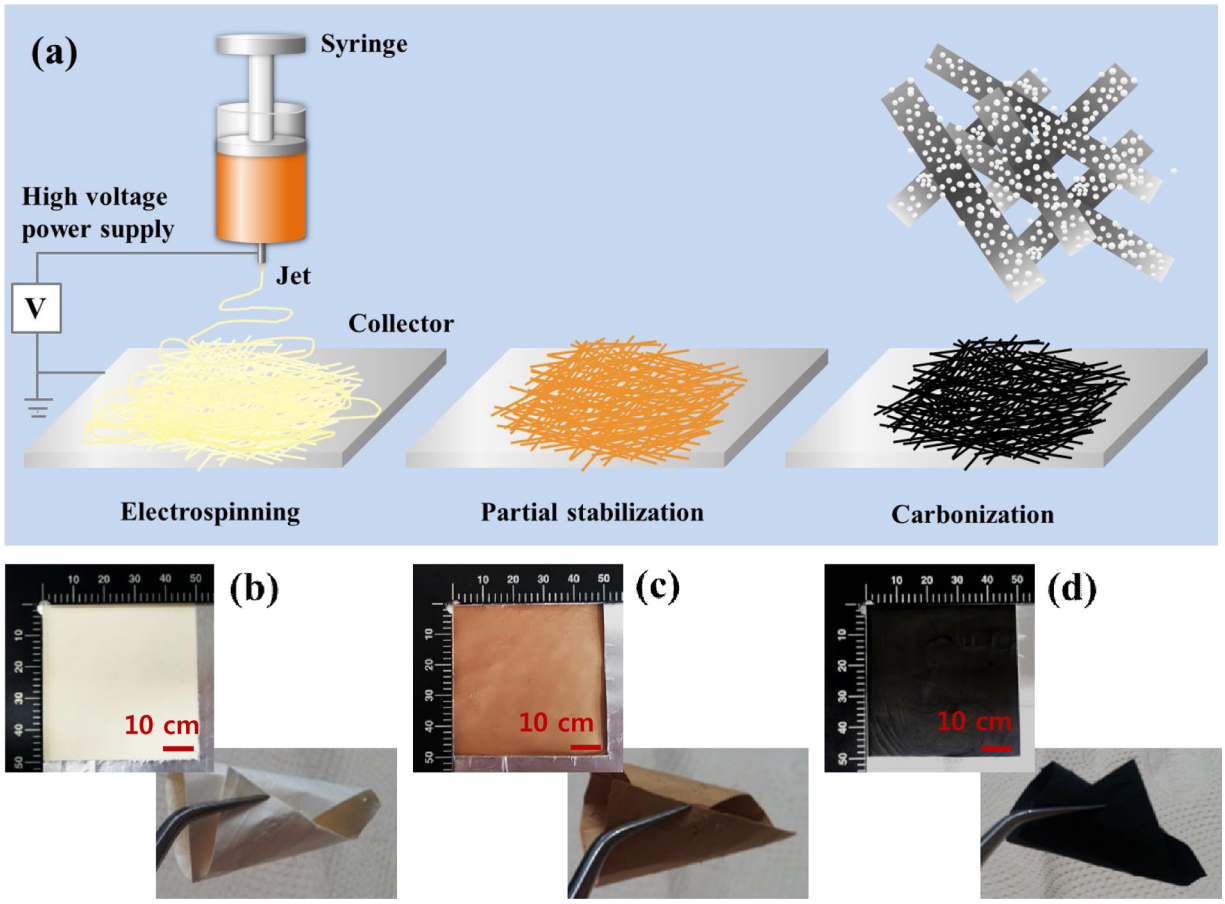

Fig. 1. (a) A schematic of preparing ZnO/CNF webs. Photographs of (b) eletrospun nanofibers containing Zn precursors, (c) stabilized and (d) carbonized resulting webs.

the application on H_2S adsorption. The mixtures of Zn precursors and polyacrylonitrile (PAN) in solvent were electrospun, and following heat treatment at 600 °C rendered ZnO/PAN nanofiber webs, which can be utilized as flexible adsorbents in various industrial applications. Recently, nanofibrous Zn–Ti–O based sorbents have been reported using electrospinning of polyvinylpyrrolidone and metal precursor solutions [18]. Electrospun nanofibers were calcined at 600 °C to remove organic components and Zn–Ti–O nanofibers with grains ranged from 70 to 90 nm were obtained. However, H_2S absorption test was conducted at 500–600 °C. H_2S adsorbent as flexible web enables fabrication of replaceable H_2S adsorbent cartridge with monolith structure that provide lower pressure drop compared to fixed bed type module. Morphology and structure of ZnO nanoparticles were investigated by transmission and scanning electron microscopes (TEM and SEM), and breakthrough time performance was carried out to determine efficiency of H_2S adsorption.

2. Experimental

2.1. Materials

PAN (MW = 150,000), zinc acetate dihydrate ($Zn(OAc)_2{\cdot}2H_2O$) as a zinc precursor, and dimethylformamide (DMF) were obtained from Sigma–Aldrich. PAN and various amounts of zinc precursors were dissolved in DMF and stirred for 24 h at 60 °C to prepare four different mixing solutions containing 8 wt% of PAN and 23.1, 32.2, 40.3, 47.4, or 53.6 wt% of zinc precursors. As a reference, pure PAN solution was also prepared.

2.2. Preparation of PAN/ZnO carbon nanofibers and ZnO powder

Pure PAN and its composite nanofibers with $Zn(OAc)_2{\cdot}2H_2O$ were electrospun by electrostatically repulsive force and an electric field occurred between positive and negative electrodes. High voltage was provided through a tip of a needle from 14.0 kV to 15.0 kV. The distance between the tip of the needle and the collector was fixed as 15 cm. Heat treatment of pure PAN and its nanofiber composites was carried out at 250 and 200 °C for 2 h in air to induce the evaporation of solvent and the partial stabilization of PAN [19]. A further heat treatment at 600 °C in N_2 resulted in pure CNF and ZnO/CNF nanofiber webs. The prepared ZnO/CNF nanofibers were designated as ZnCNF attached with numbers that indicate weight % of contained ZnO; for example, ZnCNF13.6 is the carbon nanofiber containing 13.6 wt% of ZnO. The samples prepared as webs was crushed and ground to fine powder to be loaded in the reactor for H_2S breakthrough test. For comparison, pure ZnO powders were also prepared using hydrothermal preparation method. $Zn(OAc)_2{\cdot}2H_2O$ were dissolved in deionized water and the solution was aged at 60 °C for 4 h with stirring. Then, 0.1 M solution of NaOH was added into the above solution. When the further precipitation was not observed, the resulting slurry was filtered and washed with deionized water until pH of the filtrate water dropped to ~7. Then, the filter cake was dried overnight in a forced convective oven at 100 °C followed by calcination at 500 °C for 3 h.

2.3. Characterizations

X-ray diffraction analysis (XRD, Smart Lab, Rigaku) was performed with Cu Kα radiation and 2θ ranged from 10° to 80°. The