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Controlled synthesis and humidity sensing properties of CdS/polyaniline composite based on CdAl layered double hydroxide

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ABSTRACT

CdS/polyaniline (CdS/PANI) composite with sandwich structure has been prepared by vulcanization process of polyaniline and sodium dodecyl sulfonate (SDS) co-intercalated CdAl layered double hydroxide (CdAl-LDH/PANI), which has been obtained by traditional method of hydrothermal synthesis. CdAl-LDH/PANI precursor and CdS/PANI composite have been characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS). The preparation process applies the framework of layered double hydroxide to prepare CdS nanoparticles and combines the intercalation of PANI to fabricate the sandwich structure of CdS/PANI composite. A humidity sensor based on the CdS/PANI composite has been further fabricated and tested. It indicates that the CdS/PANI composite with the sandwich structure shows excellent humidity properties with a good linearity between the logarithmic resistance and the relative humidity above 35% RH, fast response–recovery time and good repeatability compared with the pure PANI and CdS and the simple mixture of PANI and CdS.

1. Introduction

Humidity sensors play an important role in industrial productions and daily life, such as food storage, agricultural planting, livestock breeding, medical care, air conditioning control and laundry dryer control, etc. [1–5]. The basic humidity sensors are composed of electrodes, humidity-sensitive materials, and the test circuit. The most important factor which influences the performance of humidity sensors is the choice of humidity-sensitive materials. Nowadays, plenty of materials such as metal oxides [6], graphene [7], divinylbenzene [8], and cellulose [9] have been employed to fabricate humidity-sensitive materials. And those humidity sensing materials normally have been separated into inorganic semiconductor materials and organic polymer materials. However, there is no single material can fulfil all the requirements of humidity sensor, such as a preferably wide range of operating temperature, good linearity, high sensitivity, low hysteresis, fast response and recovery time, easy reproducibility and stability. Hence, recently, more and more researches on humidity sensitive materials have focused on hybrid composites [10–12] of inorganic semiconductor materials and organic polymer materials, particularly, which can combine their respective advantage and make up for their deficiency reciprocally.

Remarkably, as a member of conjugated conducting polymer, polyaniline (PANI) has been utilized for humidity sensing, and exhibits good conductivity and electrochemical reversibility. However, PANI shows intrinsic shortcomings of instability at high humidity and large hysteresis [13]. To solve this problem, many references have reported the humidity properties of modified PANI composites [14–17]. Comparing with the unmodified PANI, the modified PANI composites show better sensing performance in terms of response time, sensitivity and repeatability [18–20]. The commonly used modifying methods include doping with semiconductor metal oxides, forming nanofibres, and depositing ultrathin film [21–24], etc.

Recently, as an II–VI compound semiconductor, Cadmium sulfide (CdS) has been intensively studied for many years. It indicates that CdS has a strong absorptive and dehydrated capacity which has fast response and small hysteresis error in low humidity range [25–29]. In addition, there are evidences to prove that sensors based on nanostructures exhibit better sensing properties than bulk or thin film counterparts due to their huge surface-to-volume ratio [30]. Up to now, various CdS nanostructures have been successfully

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synthesized and their sensing properties are intensively investigated [31–33].

Therefore, it is promising to fabricate PANI and nanosturctured CdS for humidity sensing applications. In this work, a special sandwich structured CdS/polyaniline composite containing polyaniline as the organic part and CdS as the inorganic part has been used for studying humidity sensing properties, which has been obtained by the sulfuration of PANI and sodium dodecyl sulfonate co-intercalated Cd, Al layered double hydroxides (CdAl-LDH). The structure of hydrotalcite-like layered double hydroxides (LDHs) is composed of divalent and trivalent cations coordinated by six OH groups (hydroxide), forming octahedral sheets in a layered environment [34,35]. The interlayer space is occupied by anions (e.g., carbonate anions) and water molecules. Therefore, in our system, the anionic sodium dodecyl sulfonate assists the intercalation of neutral PANI into the interlayer of the LDH. In our work, PANI and the sodium dodecyl sulfonate co-intercalated LDH is named as CdAl-LDH/PANI. The resulting CdS/PANI composite has been obtained by in-situ sulfuration process of CdAl-LDH/PANI, forming the orderly sandwich structure. To the best of our knowledge, this is the first ever attempt made to study this sandwich structured composite of PANI/CdS as humidity sensor. The CdS/PANI composite has shown high sensitivity, quick response to humidity and good stability compared with the pure PANI part and CdS part. In-situ sulfuration process makes the CdS/PANI composite keep the sheeting structure, which exhibits the following advantages: first, the polyaniline chains intercalated into the interlayer could enhance the interaction between the composite and water molecules in high humidity conditions and hence the impedance of the humidity sensor decreases markedly with an increase in RH (relative humidity); second, CdAl-LDH/PANI has been utilized as a precursor for fabrication of CdS nanoparticles through an in-situ sulfuration process, and in this way, CdS nanocrystals with diameters in the range 3–6 nm have been implanted in the LDH matrix, which helps the sensing behavior; third, the sandwich structure provides polymer molecules with a confined and stable environment, which improves humidity and thermal stability.

2. Experimental

2.1. Materials

All reagents were analytical reagent (AR) grade. The starting materials were $Cd(NO_3)_2{\cdot}4H_2O$ (99.0% purity from Guangfu Chemical Co., Ltd.), $Al(NO_3)_3{\cdot}9H_2O$ (98.5% purity from Guangfu Chemical Co., Ltd.), Polyaniline (emeraldine salt, average Mw >15000, powder (infusible), 3–100 μm particle size, purchased from Sigma Aldrich), sodium dodecyl sulfonate (SDS) (85% purity from Xilong Chemical Co., Ltd.), N-Methyl-2-pyrrolidinone (NMP), $Na_2S{\cdot}9H_2O$ (98% purity from Guangfu Chemical Co., Ltd.), H_3PO_4 (99% purity from Guangfu Chemical Co., Ltd.), NaOH (96.0% purity from Beijing chemical plant).

2.2. Synthesis of CdAl-LDH/PANI

CdAl-LDH/PANI precursor was synthesized using a co-precipitation method with a hydrothermal process. Typically, for the synthesis of CdAl-LDH/PANI with Cd/Al molar ratio of 1/2, a solution of 0.01 mol of $Cd(NO_3)_2{\cdot}4H_2O$, and 0.02 mol of $Al(NO_3)_3{\cdot}9H_2O$ in 16 mL of deionized water were mixed with a solution of SDS surfactant (0.02 mol of SDS sodium salt in 85 mL of deionized water) in a 250 mL four-necked flask. With vigorous stirring, a solution of 2 mol/L NaOH was added slowly to maintain the pH at 9.0. The resulting slurry was further added with a solution of N-Methyl-2-pyrrolidinone (NMP) containing 0.1 g PANI under vigorous stirring at 60 °C. The mixed solution was stirred constantly for 5 h before being transferred into teflon-lined autoclaves and crystallized at 100 °C for 12 h. The resulting gel was then centrifuged and washed 3 times with ethanol before being dried in vacuum at 60 °C for 12 h.

2.3. Preparation of CdS/PANI

CdS/PANI composite was prepared using an in-situ sulfuration process. Certain CdAl-LDH/PANI was weighed and placed in an evacuated and sealed glass reaction chamber. An excess of H_2S gas was injected into the chamber at room temperature. H_2S is produced by the reaction between H_3PO_4 and $Na_2S{\cdot}9H_2O$.

2.4. Characterization

The crystalline phase of materials was examined using X-ray diffraction (XRD) characterizations on a Rigaku XRD-6000 diffractmeter using Cu K_α radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 mA in the 2θ range of 3–70°. The morphologies of the composites were observed using a Zeiss SUPRA 55 at 20 kV, with the surface coated with a thin platinum layer in order to avoid the charging effect. The lattice fringes and crystal boundaries of the composites were recorded by High-resolution transmission electron microscope (HRTEM) on a JEOL J-2100. The Fourier transform infrared (FTIR) spectra were recorded on Bruker Vector-22 Fourier transform infrared spectrometer in the range of 4000–400 cm^{-1}. All FTIR spectra were obtained from compressed KBr pellets in which the samples powders were evenly dispersed (1 mg of sample in 100 mg of KBr). And the surface's valence states of elements were performed using Thereto VGESCALAB 250 X-ray photoelectron spectroscopy (XPS), and all of the binding energy were corrected by contaminant carbon (C 1s = 284.6 eV).

2.5. Humidity sensing measurements

The prepared composite and deionized water were mixed to form a paste. Then the paste was dip-coated on Ag-Pd interdigitated electrodes with ceramic as substrate (6 mm × 3 mm, 0.5 mm thick) to form a film. And then the film was dried in air at about 25 °C for 24 h. The humidity sensitive properties of the samples were investigated at 1.25 V AC under different relative humidity (RH) on the measuring system of Chemical Humidity Sensing-1 (CHS-1) at room temperature (25 °C) (Beijing Elite Tech. Co., Ltd., China). Various Relative Humidity (RH) levels from 11% to 95% RH were produced by diverse saturated salt solutions embracing LiCl for 11% RH, $MgCl_2$ for 33% RH, $Mg(NO_3)_2$ for 54% RH, NaCl for 75% RH, KCl for 85% RH, and KNO_3 for 95% RH. The saturated salt atmosphere was homogeneous and stable.

3. Results and discussions

3.1. Characterizations

The X-ray diffraction (XRD) patterns of CdAl-LDH/PANI and CdS/PANI are exhibited in Fig. 1. The X-ray diffraction (XRD) pattern of CdAl-LDH/PANI keeps the characteristic reflections of a well-ordered layer structure of LDH, with a series of (00l) peaks appearing as narrow lines at low angle 2θ and weak non-basal reflections at high angles. The interlayer spacing can be calculated by averaging the positions of the three harmonics: $c = (1/3)(d_{003} + 2d_{006} + 3d_{009})$ [36,37]. Hence, the interlayer spacing of CdAl-LDH/PANI is calculated as 2.4 nm. Compared with CdAl-LDH from the reference [38], the sum of the calculated length of the SDS molecule (2.13 nm) and the layer thickness (about 0.48 nm) is