



Large pore volume mesoporous copper particles and scaffold microporous carbon material obtained from an inorganic–organic nanohybrid material, copper-succinate-layered hydroxide

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ARTICLE INFO

Article history:

Received 23 April 2011

Accepted 31 May 2011

Available online 14 June 2011

Keywords:

Layered structures

Nanohybrid

Microporous carbon

Mesoporous copper

ABSTRACT

Copper-succinate-layered hydroxide (CSLH), a new nanohybrid material, was synthesized as an inorganic–organic nanohybrid, in which organic moiety was intercalated between the layers of a single cation layered material, copper hydroxide nitrate. Microporous scaffold carbon material was obtained by thermal decomposition of the nanohybrid at 500 °C under argon atmosphere followed by acid washing process. Furthermore, the heat-treated product of the nanohybrid at 600 °C was ultrafine mesoporous metallic copper particles. The results of this study confirmed the great potential of CSLH to produce the carbon material with large surface area (580 m²/g) and high pore volume copper powder (2.04 cm³/g).

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1. Introduction

Copper hydroxide nitrate (CHN) is an anionic layered material with brucite-like structure whose layers are constructed in the monoclinic lattice with its composition – Cu₂(OH)₃NO₃ (Card 15-0014). In each layer, one-fourth of the hydroxide ions are substituted by nitrate anions that are positioned between the layers and are coordinated with copper cations via one oxygen atom. This decreases the basal spacing to around 6.9 Å compared to that of other single metal layered hydroxides with the same interlayer anion such as zinc hydroxide nitrate with 9.7 Å basal spacing [1–6]. In zinc hydroxide nitrate, nitrate anions together with water molecules are free between the layers and are not coordinated to the layers. These single cation layered materials, similar to the better known layered materials, layered double hydroxides (LDHs) with at least two types of cations have a capacity to intercalate various functional anionic species into their interlayer by ion-exchange process [5,7–10]. This produces various tailor made host–guest composite materials that have frequently been used in different applications [5,7,11]. On the other hand, the layered materials and their composites have been used as precursors to produce

various upcoming products. For example, hierarchical flower-like boehmite and TiO₂/AlOOH superstructures with their enhanced photocatalytic properties were synthesized to use layered hydroxides as precursors to prepare various porous adsorbents including mesoporous alumina [12], boehmite hollow core/shell and hollow microspheres [13] and also, hierarchical spindle-like γ-Al₂O₃ materials synthesized by a non-template hydrothermal [14] were prepared for water purification with excellent performance.

Porous carbon materials have been used in various industries due to their excellent adsorption properties accompanied with good chemical stability [15–17]. Therefore, different methods, including templated syntheses (exotemplating and endotemplating) have been used to produce carbon materials with pore size capable of being tailored for specific applications [18,19]. Various carbon materials are produced by the heat-treatment of different inorganic–organic layered materials, such as, LDHs, zeolites and clays as templates [20–23]. Also, mesoporous metals that have attracted a great deal of interests due to their applications in fuel cell electrodes, electronic devices, catalysts and magnetic recording media, etc. can be produced by templated synthesis [24–26]. The synthesis contains usually either using mesoporous silica as a hard template by deposition of metals within the mesopores followed by the removal of the template or by direct-template method from lyotropic liquid crystals made up of non-ionic surfactants at high concentrations [24–26]. As a result, the type of inorganic template host and organic guest materials can play a role in determining the properties of the resultant products.

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Succinic acid, ethane-1,2-dicarboxylic acid ($C_4H_6O_4$), is a convenient and cost effective carbonaceous source with two anionic carboxylic groups that lead to its high affinity to be intercalated between the layers of anionic clays [27].

This paper reports the results obtained in the synthesis and characterization of a new nanohybrid material, copper-succinate-layered hydroxide (CSLH) and heat-treatment process of the nanohybrid at 500 °C to produce microporous carbon material and at 600 °C to obtain mesoporous metallic copper particles with large pore volume. Results from the powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), Thermogravimetric-Differential Thermal Analyzer (TG-DTA) and nitrogen adsorption-desorption studies are discussed.

2. Material and methods

All solutions were prepared using distilled de-ionized water. CHN was synthesized from aqueous solution of 0.2 M $Cu(NO_3)_2$. The solution was brought to pH = 5.5 ± 0.05 by dropwise additions of 0.5 M NaOH solution with vigorous stirring under nitrogen atmosphere. The precipitate was filtered, washed three times with water and two times with acetone and dried in an oven, overnight at 80 °C. Succinate anions (SU) were obtained by dissolving succinic acid in distilled water and neutralized with 6 M NaOH at pH ≈ 7 under nitrogen. CSLH, $(Cu_4(OH)_6C_4H_4O_4)$, was obtained by contacting 0.5 g of the pre-prepared CHN into 200 ml solution of 0.2 M SU for 6 h. The nanohybrid material, CSLH was heat-treated at 500 and 600 °C, respectively in an electric tubular furnace under argon atmospheric pressure at a flow rate of 100 ml/min for 2 h at a heating rate of 5 °C/min and then cooled down naturally under argon atmosphere. To obtain microporous carbon material, the heat-treated material was dissolved in 1 M HCl (0.5 g solid/100 ml) at 50 °C for 4 h to remove metal oxide and the carbon material obtained was labeled as C5. The heat-treated product at 600 °C was labeled as Cu6 and characterized as prepared.

Powder X-ray diffraction patterns were collected on a Unisantis XMD300 powder diffractometer unit using $CuK\alpha$ ($\lambda = 1.54 \text{ \AA}$) at 45 kV and 0.8 mA. FTIR spectra were recorded using a BRUKER (VECTOR 33) spectrophotometer in the range of 400–4000 cm^{-1} . Inductively coupled plasma-atomic emission spectrophotometer (ICP-AES), a Labtest Equipment Co. Model 710 Plasmascan, was used to determine the copper amount in the precursor, CHN and in the resulting nanohybrid, CSLH. CHNS instrument (Leco, USA) was used to determine the elemental contents in CHN, CSLH and the obtained microporous carbon, C5. Thermal analysis (simultaneous thermal analyzer instrument, Polymer Laboratories PL-STA 1640) was carried out to study the thermal behaviors of the as-prepared nanohybrid. In the STA study, heating was conducted in argon atmosphere (Ar flow rate = 50 ml/min) with temperatures ranging from 25 °C to 1000 °C at a rate of 5 °C/min. The surface area was determined with a BELSORP measuring instruments (BELSORP-mini, JAPAN, INC) using nitrogen gas adsorption-desorption technique at 77 K. The carbon material and metallic copper powder morphologies were characterized by a SEM (Vega 2 Tescan, Czech Republic).

3. Results and discussion

3.1. PXRD of CHN and the nanohybrid, CSLH

PXRD patterns for the as-prepared CHN and its resulting nanohybrid with SU, CSLH are shown in Fig. 1. As shown in the figure, CHN has a brucite-like structure with high crystallinity evidenced by the narrow width and intense reflection of the basal spacing peak around 6.9 Å [2,3,6]. Also, Fig. 1 shows PXRD pattern for the

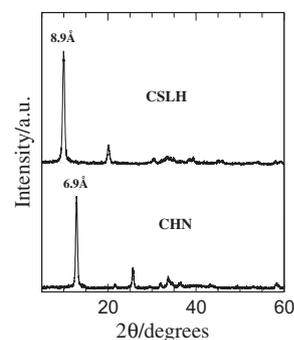


Fig. 1. PXRD patterns for CHN and its resulting nanohybrid with SU, CSLH.

nanohybrid, CSLH with the presence of a new sharp peak around 8.9 Å and the lack of the peak at 6.9 Å due to the parent material, CHN. That is, the ion-exchange technique was found to be effective for the intercalation process in the formation of the nanohybrid, in which nitrate was replaced by bigger size succinate anions in the interlayer of the CHN and SU has expanded the basal spacing from 6.9 Å in the CHN to 8.9 Å in the nanohybrid.

3.2. FTIR study and CHNS analysis

Fig. 2 shows FTIR spectra for CHN, succinic acid and the organic-inorganic nanohybrid, CSLH. In the CHN sample, lattice vibrations of metal-oxygen bonds Cu-O and Cu-OH are observed at 427 and 507 cm^{-1} [3,4,6]. The band at 675 cm^{-1} can be attributed to the δ -mode of the O-H groups [4,28]. The bands at 877 and 1383 cm^{-1} show the ν_2 and ν_3 vibrational modes of the interlayer anion, nitrate in CHN [3,4]. At 1623 cm^{-1} water-bending vibrations (δ_{H_2O}) of the adsorbed water molecule is observed [3,4]. The band at 1045 cm^{-1} is due to the bending vibration of Cu-O-H [3,29]. The intense band at 1421 cm^{-1} is a characteristic of well crystallized copper hydroxide nitrate [3]. The broad band about 3435 cm^{-1} is ascribed to the presence of the hydroxyl groups within the layers of CHN and/or physically adsorbed water molecule stretching [3,4,28]. This broadness can indicate the existence of the hydrogen bonding between the layers [4,6].

The FTIR spectrum of succinic acid (Fig. 2b) shows two bands at 918 and 1417 cm^{-1} , which are due to C-O-H out of plane and in plane bending vibrations, respectively [29]. The band at 1202 cm^{-1} is due to C-O stretching vibration of acidic groups [8,29]. As expected, the presence of carboxylic group of C=O stretching vibration would be described by the observation of two bands at 1687 cm^{-1} asymmetric and at 1314 cm^{-1} symmetric vibrations [8,11,29]. Few bands around 2934 cm^{-1} are attributed to C-H and O-H stretching vibrations [29].

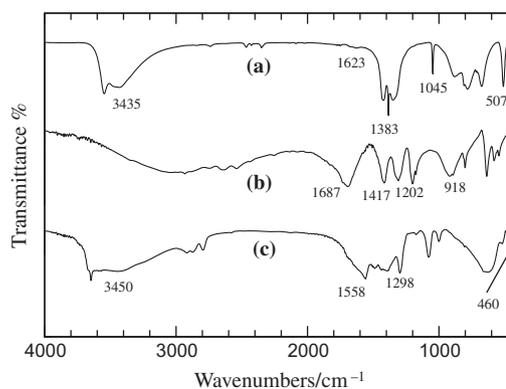


Fig. 2. FTIR spectra for the as-prepared CHN (a), succinic acid (b) and the nanohybrid, CSLH (c).

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