



Large-scale preparation of indium-based infinite coordination polymer hierarchical nanostructures and their good capability for water treatment



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ABSTRACT

The removal of dyes in wastewater has been of much interest in the recent decades because dyes are stable, toxic and even potentially carcinogenic, and their release into environment causes serious environmental, aesthetic, and health problems. In the current work, indium-based coordination polymer particles (In-CPPs) have been fabricated via a facile solvothermal synthesis without any template or surfactant. In-CPPs are composed of hierarchical nanostructures assembled from abundant nanoplates with thickness of about 20 nm. Owing to their high BET surface area and pore volume, In-CPPs exhibit excellent adsorption capability for Congo red with a maximum capacity of 577 mg g⁻¹, which was higher than that of most materials reported to now. In-CPPs can also be outstanding adsorbents for removing other dyes such as acid chrome blue K, brilliant red GR and brilliant green. Furthermore, after calcinations in air In-CPPs can be converted to morphology-preserved porous In₂O₃ products which can detect NO_x gas in air at room temperature.

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1. Introduction

In the past few years, the efficient removal of dyestuffs from effluents has raised great concerns, because the discharge of harmful dyes into water not only pollutes water bodies, but also affects aquatic life [1–3]. There have been considerable efforts in treating wastewater based on the adsorption, photocatalysis and membrane filtration [4–9]. Of these, adsorption is one of the most convenient approaches due to its low cost, simplicity, and high efficiency as well as low secondary pollution. Recently, various materials have been extensively employed as the adsorbents for removing dyes, such as activated carbon, silicon, transition metal oxide nano-materials and so on [10–12]. Among them, it has been demonstrated that three-dimensional (3D) hierarchically nanostructured materials with high surface area exhibit enhanced properties compared to their bulk counterparts [13–15]. Though various hierarchically nanostructure materials have been used widely as potential adsorbents for the adsorption and the removal

of dyes, the adsorption capacity is quite limited. Therefore, it is still of great significance to discover new materials with hierarchically nanostructures for efficient adsorption and the removal of dyes.

Infinite coordination polymers (ICPs) or metal–organic frameworks (MOFs) are a new class of inorganic–organic hybrid materials based on metal ions coordinated by multidentate organic bridging ligands. In the recent years, ICPs or MOFs have been studied for the use in sorption-related fields, such as storage of hydrogen, capture of greenhouse gases, adsorption and removal of dyes, pharmaceuticals, alkylaromatics and sulfur-containing compounds from liquid phase, owing to their high surface area and porous nature [16–23]. Very recently, with the development of nanoscience and nanotechnology, nanoscale ICPs or MOFs have attracted more and more attention due to their variable morphologies compared with the bulk ones, as well as their unique applications in gas storage, sensing, catalysis, biomedical imaging and anticancer drug delivery [24–27]. However, to the best of our knowledge, the vast majority of the reported work concerns the synthesis of nanoscale ICPs or MOFs and their gas-sorption applications, and studies on aqueous adsorption of contaminants using nanoscale ICPs or MOFs are rather rare [28].

Therefore, in this work we report solvothermal synthesis of indium-based infinite coordination polymer hierarchical

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nanostuctures using $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ and isophthalic acid (H_2IPA) without any template or surfactant. The indium-based coordination polymer particles (In-CPPs) are found to exhibit high surface area and good adsorption capability for anionic dyes. As a result, the In-CPPs possess better adsorption characteristic than the most nanomaterials reported to now and accordingly can be considered as an excellent adsorbent for removing dyes in water treatment. This work also provides a new method to improve the dye adsorption performance of adsorbent by combining the nanoscale effect and large pore volume of ICPs or MOFs.

2. Materials and methods

2.1. Sample preparation

All chemicals are of analytical grade and were used without further purification. In a typical experiment, 0.156 g of $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ and 0.032 g of H_2IPA (H_2IPA = isophthalic acid) were dissolved in 20 mL of DMF to form solution. Then the mixture was vigorously stirred with a magnetic pulsator at room temperature for 20 min. The as-obtained solution was transferred into a Teflon-lined stainless-steel autoclave. The reaction was carried out at 140 °C for 20 h. After that, the autoclave was cooled to room temperature naturally. The colorless products were collected, washed with distilled water several times and dried in air for 6 h. After annealing treatment at 500 °C for 1 h, In-CPPs were calcinated to In_2O_3 .

2.2. Characterization

The products were characterized by powder X-ray diffraction (XRD) on a Shimadzu XRD-6000 powder X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. Transmission electron microscopy (TEM) images were obtained on a JEM-2100 high resolution transmission microscope, employing an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images and energy dispersive spectrometry (EDS) of the products were got on field emission scanning electron microanalysers (Hitachi S-4800), employing an accelerating voltage of 5 kV or 20 kV. FT-IR spectra were recorded in the range of 400–4000 cm^{-1} on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer with a heating rate of 10 °C min^{-1} . Nitrogen adsorption–desorption isotherms and surface areas of the samples were measured via N_2 adsorption at 77 K on a Belsorp-max volumetric gas sorption instrument. The zeta potential was measured with a Zetasizer Nano Z (Malvern Instruments, UK) at 25 °C. Elemental analyses (EA) for C, H, and N were performed on a Perkin-Elmer 240C Elemental Analyzer at the analysis center of Nanjing University.

2.3. Water treatment experiment

In the adsorption kinetics experiment, 20 mg of the as-prepared In-CPPs powder was mixed with 40 mL of aqueous solution of Congo red with a concentration of 50 mg L^{-1} in a flask reactor (capacity ca. 100 mL). The suspension was stirred at room temperature. At different time intervals, 4 mL of the solution was pipetted and analyzed after centrifugation. Ultra-violet-visible (UV–vis) absorption spectra were obtained using a UV–vis spectrophotometer (Shimadzu, UV-3600). In order to evaluate the adsorption capacity, the initial concentrations of the Congo red solutions were scaled in the range of 50–600 mg L^{-1} , and the dosage of In-CPPs was kept at 20 mg. The mixtures were stirred at room temperature for 30 min, and the concentrations of the final Congo red solutions were obtained using UV–vis spectroscopy after centrifugation.

The concentration of Congo red was determined using a linear calibration curve over 575 mg L^{-1} based on the absorbance value at 497 nm.

After the first time it was used, the adsorbent was washed thoroughly using ethanol by ultrasonication and centrifugation several times and then dried in vacuum at 80 °C for 10 h. The dried In-CPPs were reused for adsorption with a Congo red concentration of 50 mg L^{-1} for 30 min. After each run, the concentration of Congo red is determined using UV–vis spectroscopy.

In addition, the adsorption kinetics experiments for removing other dyes were tested by the same procedure except that acid chrome blue K, brilliant red GR and brilliant green were used instead of Congo red, respectively.

2.4. Gas sense experiment

In_2O_3 (5 mg) was evenly dispersed in 10 mL of EtOH solution to obtain a suspension. A small quantity ($\sim 0.05 \text{ mL}$) of suspension was dropped onto the interdigitated Au electrode ($7 \times 5 \times 0.38 \text{ mm}$) and then dried at 60 °C for 2 h under vacuum to obtain In_2O_3 film gas sensor. On the top side, two gold electrodes with a gap of $\sim 50 \text{ mm}$ were used for the measurements. These sensors were exposed to NO_x gas (10–300 ppm in air) in a gas chamber of 1030 mL volume. To analyze the resistance vs gas concentration and exposure time, the sensors were probed with a constant voltage (5 V) while the electrical current through the In_2O_3 films was monitored. Sensor recovery was done after each measurement, depending on the previous gas exposure, recovery of the sensors varied from 5 to 10 min.

3. Results and discussion

3.1. Characterization of In-CPPs

The morphology of the resulting product was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The low-magnification SEM image (Fig. 1a) reveals that the products are comprised of a great deal of honeycomb-like nanostructures with a mean size of about 1.5 μm . A high-magnification SEM image is shown in Fig. 1b, from which honeycomb-like nanostructures made of abundant nanoplates with thickness of $\sim 20 \text{ nm}$ can be clearly seen. Fig. 1c shows a representative TEM image of the product. There are a great amount of nanoplates, which further confirms the result of SEM observation.

The composition and structure of indium-based infinite coordination polymer particles (In-CPPs) were characterized by XRD, EA, EDS and FT-IR. The XRD pattern of In-CPPs shows a sharp peak at 7° with several weak ones at higher 2θ degree (Fig. 2a), which is difficult to be indexed to a known indium crystal structures. However, the elemental analysis of the as-synthesized product suggests a chemical formula of $[\text{In}_2(\text{IPA})_{1.5}(\text{OH})_3] \cdot \text{DMF} \cdot 1.5\text{H}_2\text{O}$ (calcd. C 28.74, H 3.05, N 2.23; found C 29.03, H 3.32, N, 2.32). The chemical composition of these particles was measured by EDS, which confirmed that they contain In, N, C, and O (Fig. 2b). The weak Al peak should be contributed to the aluminum support. Furthermore, the formation of In-CPPs was verified by IR spectral data (Fig. 3). The FT-IR spectrum of In-CPPs shows that the carboxylate groups of the organic building blocks are coordinated to In(III) ions, as evidenced by a shift of C=O stretching frequency from 1694 to 1613 cm^{-1} . Additionally, the FT-IR spectrum of the In-CPPs shows that the ν_{OH} bands at about 3432 cm^{-1} and peaks at 2900 and 1662 cm^{-1} corresponding to the vibrations of N–C and C=O bonds of the free DMF molecules. Although there are inherent difficulties in determining the exact structure of In-CPPs, it is reasonable to

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