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Fabrication of hierarchical bristle-grass-like $NH_4Al(OH)_2CO_3@Ni(OH)_2$ core-shell structure and its enhanced Congo red adsorption performance

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ABSTRACT

Hierarchical bristle-grass-like $NH_4Al(OH)_2CO_3@Ni(OH)_2$ core-shell structure is fabricated through a simple hydrothermal approach combined with subsequent chemical bath deposition. Electron microscopy characterization reveals that the ammonium aluminum carbonate hydroxide ($NH_4Al(OH)_2CO_3$) microfibers were uniformly covered with interconnected and vertically aligned nickel(II) hydroxide ($Ni(OH)_2$) nanosheets, forming hierarchical pore structure. The $NH_4Al(OH)_2CO_3$ microfibers not only serve as substrate for the growth of the $Ni(OH)_2$ nanosheets but also prevent the nanosheets from aggregating. The synthesized hierarchical bristle-grass-like $NH_4Al(OH)_2CO_3@Ni(OH)_2$ composite showed excellent adsorption performance toward Congo red (CR), which was superior to the aggregated $Ni(OH)_2$ microspheres and the bare $NH_4Al(OH)_2CO_3$ microfibers. The adsorption isotherm can be well described by the Langmuir model, with an estimated maximum adsorption capacity of $426\,mg\,g^{-1}$ for the $NH_4Al(OH)_2CO_3@Ni(OH)_2$ composite. The major adsorption mechanism is electrostatic interaction between the CR molecules with negative charge and the positively charged sample surface of the $Ni(OH)_2$ nanosheets at neutral pH. The as-prepared $NH_4Al(OH)_2CO_3@Ni(OH)_2$ core-shell microfibers can be expected to act as potential materials for CR removal in purification of wastewater.

1. Introduction

Synthetic dyes, which possess the advantage of abundant colors, superior stability and color fastness, have been applied in many industries, including textile, papermaking, coatings and plastics [1–3]. However, most wastewater from these industries is discharged without proper treatment. As the dyes are highly visible even at extremely low concentration, the dyes in effluents would prevent the sunlight entering the water and consequently affect the lives in water and the water ecosystem. Moreover, the dyes in effluents can be toxic to organisms and put human health at risk because of the intrinsic toxicity and carcinogenicity of some dyes [1,4,5]. Therefore, it is essential to treat the dye effluents for the considerations of both environmental and health reasons.

To eliminate the serious dye pollution in wastewater, numerous investigations have been carried out, and adsorption is regarded as an effective and easy means to extract dyes from water [6–10]. Although multifarious adsorbents have been developed to remove dyes from water, including silica [11], zeolites [12], polymer [13], bioadsorbents [14] and magnetic nanocomposites [15,16], their disadvantages such as low selectivity and adsorption capacity have limited their application. Hence the exploitation of new adsorbents for effective removal of dyestuffs from water is indispensable and imperative.

Recently, numerous efforts have been directed into the design of hierarchical porous materials, which possessed pores on different length scales, including macropores, mesopores and micropores. Due to the synergistic effect of the presence of the pores with different sizes, the hierarchically structured porous materials have wide applications in catalytic oxidation [17], supercapacitors [18,19], photocatalysis [20] and adsorption [21]. Hierarchical porous

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adsorbents possessed interconnected porous networks, thus can promote the accessibility of active sites and accelerate the diffusion of adsorbate molecules, thus leading to high adsorption efficiency. Numerous hierarchically structured adsorbents have been synthesized for dye removal and all exhibited excellent adsorption performance, e.g., flower-like γ-Al_2O_3@C composite [22], MnO_2 microspheres [23], zinc oxide microspheres [24], nickel hydroxide and nickel oxide [25–27], 3D self-assembled iron hydroxide and oxide [28], and layered double hydroxides (LDH) [29,30].

Nickel(II) hydroxide possesses two polymorphs: α-$Ni(OH)_2$ and β-$Ni(OH)_2$. Specifically, α-$Ni(OH)_2$ has layered structure, with the layers intercalated with water molecules and/or anions, while β-$Ni(OH)_2$ exhibits hexagonal close-packed brucite-like structure without any intercalation [31,32]. As a promising functional metal hydroxide, $Ni(OH)_2$ has found extensive applications in sensors [31], supercapacitor [32], and adsorption [25]. On the other hand, ammonium aluminum carbonate hydroxide ($NH_4Al(OH)_2CO_3$), which possesses a similar structure to the natural mineral dawsonite ($NaAl(OH)_2CO_3$), is constituted by $AlO_2(OH)_4$ octahedra chains, and CO_3^{2-} and NH_4^+ are linked to $AlO_2(OH)_4$ octahedra through hydrogen bonds. $NH_4Al(OH)_2CO_3$ materials with different morphologies, including microfibers [33], 3D urchin-like microspheres [34], nanoleaves [35], have been synthesized and, amongst them, fiber is the most common morphology. Moreover, on account of the low point of zero charge (PZC) of $NH_4Al(OH)_2CO_3$, the surface of the $NH_4Al(OH)_2CO_3$ is negatively charged when dispersed in alkaline solution [35]. Therefore, when the solution pH is alkaline to precipitate metal ions, metal ions with positive charge are prone to be adsorbed on $NH_4Al(OH)_2CO_3$ surface, thus making it a wonderful substrate to support metal hydroxides. Herein, we first synthesized uniform $NH_4Al(OH)_2CO_3$ microfibers by a facile hydrothermal reaction without surfactant or template, and then employed the $NH_4Al(OH)_2CO_3$ microfibers as substrate to construct hierarchical $NH_4Al(OH)_2CO_3$@$Ni(OH)_2$ core–shell microfibers through chemical bath deposition. The as-prepared $NH_4Al(OH)_2CO_3$@$Ni(OH)_2$ possesses hierarchical porous structure and exhibits excellent adsorption performance toward Congo red (CR), suggesting that it is of great promise for the elimination of dye pollution from wastewater.

2. Experimental

2.1. Materials

The chemicals, including aluminum nitrate nonahydrate ($Al(NO_3)_2 \cdot 9H_2O$), nickel acetate tetrahydrate ($Ni(Ac)_2 \cdot 4H_2O$), urea ($CO(NH_2)_2$), hexamethylenetetramine (HMT), and trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), were analytical grade and supplied by Shanghai Chemical Industrial Company. The chemicals were used without further refinement. Deionized water was used in all experimental processes.

2.2. Synthesis of $NH_4Al(OH)_2CO_3$ microfibers

$NH_4Al(OH)_2CO_3$ microfibers were synthesized by a facile hydrothermal method. Typically, 8 g of $Al(NO_3)_3 \cdot 9H_2O$ and 20 g of urea were added in 70 mL of deionized water to form a homogeneous solution. Then the mixed solution was transferred into a 100 mL Teflon-lined autoclave and heated to 120 °C for 24 h. After the hydrothermal reaction, the white precipitate was separated through centrifugation and washed by deionized water and anhydrous ethanol. Then, the white product was dried at 60 °C for 6 h in a vacuum oven to obtain $NH_4Al(OH)_2CO_3$ microfibers.

2.3. Preparation of $NH_4Al(OH)_2CO_3$@$Ni(OH)_2$ core–shell structures

The growth of $Ni(OH)_2$ nanosheets over the $NH_4Al(OH)_2CO_3$ nanofibers was achieved through a simple precipitation process. Ten milligram of $NH_4Al(OH)_2CO_3$ was added in 60 mL of deionized water and dispersed through sonication. Then, 0.5 mmol $Ni(Ac)_2 \cdot 4H_2O$, 0.5 mmol HMT and 0.05 mmol $Na_3C_6H_5O_7 \cdot 2H_2O$ were added into the suspension. After the complete dissolution of the reagents, the suspensions were heated at 90 °C for 8 h with continual mild stirring and then cooled down. The light green products were separated by centrifugation and rinsed with deionized water and anhydrous ethanol. Finally, the $NH_4Al(OH)_2CO_3$@$Ni(OH)_2$ products were collected after being dried at 55 °C for 8 h in a vacuum oven. For comparison, a $Ni(OH)_2$ sample was synthesized by the similar procedure in the absence of $NH_4Al(OH)_2CO_3$ fibers.

2.4. Characterization

X-ray diffraction (XRD) measurements were performed on a HZG41B-PC X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). The morphology and microstructures of the samples were characterized by a JSM-7500 F field emission scanning electron microscope (FESEM, Hitachi, Japan) and a JEM-2100 F electron microscope (TEM, JEOL, Japan). The elemental analysis of $NH_4Al(OH)_2CO_3$@$Ni(OH)_2$ was conducted on an X-Max 50 energy-dispersive X-ray spectrometer (EDS, Oxford Instruments, Britain) attached to the FESEM microscope with a 15 kV accelerating voltage. The nitrogen (N_2) adsorption and desorption isotherms of the samples were collected on an ASAP 2020 nitrogen adsorption apparatus (Micromeritics Instruments, USA). The pore size distribution of the samples was determined by the Barrett–Joyner–Halenda (BJH) method by assuming a cylindrical pore model. Fourier-transform infrared (FTIR) spectra were recorded using a Shimadzu IR Affinity-1 FTIR spectrometer (Shimadzu, Japan). X-ray photoelectron spectra (XPS) were excited by Al Kα radiation and collected by an ESCALAB250Xi electron spectrometer (Thermo Fisher, USA). The zeta potentials were analyzed on a Nano ZS90 Zetasizer (Malvern, UK) at 298 K.

2.5. Adsorption equilibrium and kinetic studies

The adsorption isotherm experiments were performed as follows: 10 mg of the as-prepared samples were introduced into a set of 250 mL conical flasks filled with 100 mL of CR ($C_{32}H_{22}N_6Na_2O_6S_2$) solutions at various concentrations (10–80 mg L^{-1}). The flasks were sealed and placed in a thermostatic shaker (150 rpm, 30 °C) for 12 h. After the equilibria were reached, the flasks were taken out from the shaker and the residual liquid-phase concentration of CR was evaluated by the maximum absorption of CR (at 496 nm wavelength) with a UV/mini 1240 spectrophotometer (Shimadzu, Japan). The adsorption quantity of CR at equilibrium on the samples can be calculated according to equation (1) listed in Table 1.

Similarly, the adsorption kinetics experiments were performed by adding 10 mg of the as-prepared adsorbents into the CR solution, whose initial concentration was fixed at 50 mg L^{-1}. Afterward, the CR concentrations at different time intervals were assayed as described above and the amount of dye adsorbed on the samples at time t, q_t (mg g^{-1}), was calculated according to equation (2) shown in Table 1.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the three synthesized samples are