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Preparation of Al₂O₃ hollow microsphere via calcining carbon template and its adsorption application

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Abstract

Carbon microsphere was synthesized from glucose via hydrothermal method, and then alumina hollow microsphere was prepared using carbon template. At reaction time of 6 h, the carbon sphere displayed uniform diameter of 800 nm. After removal of carbon core during calcination, it obtained 600 nm of γ -Al₂O₃ hollow sphere with shell thickness of 80 nm and surface area of 186 m²/g. For adsorption of methylene blue, material exhibited adsorption capacity of 26.5±1.2 mg/g, fitting well with Langmuir isotherm. It is demonstrated that calcining carbon template was an effective and facile approach to obtain hollow sphere material.

Key words: Carbon materials; Al₂O₃ hollow microsphere; Formation mechanism; Adsorption

1. Introduction

Hollow micro/nanomaterial exhibits huge inside space and nanoscale shell, such as hollow sphere, hollow tube and hollow polyhedron [1,2]. Hollow material is widely used in adsorption, catalysis, hydrogen storage, electrology and mechanics [3]. Alumina (Al_2O_3) shows many advantages [4], such as strong mechanical strength, chemical stability, perfect electrical and thermal insulation and slight toxicity.

Generally, carbon was selected as the core with coating of metal ions on its surface, and the hollow shell would be obtained after remove the carbon template [5]. Multiple methods were applied to synthesize hollow material, like sol-gel, coprecipitation, hydrothermal method, etc. [1,3]. Due to relatively low reaction temperature, convenient procedure and various morphologies, hydrothermal method was a facile approach, although the process was difficult to observe directly. Sun et al. [6] used hydrothermal method to synthesize carbon spheres with diameter of 150–1500 nm, and then the carbon sphere was used as template to prepare nano Au, Ag, and Pt. Yin et al. [7] synthesized the carbon sphere template from glucose, and the TiO_2 hollow spheres were prepared via sol–gel method and calcination at 500 °C in air.

In present work, hydrothermal method was used for preparation carbon microsphere from green and low cost precursor of glucose. The core-shell structure was formed with carbon core and Al^{3+} shell. After removal of carbon template via calcination, the as-prepared Al_2O_3 material expressed uniform and complete hollow sphere structure. Further, the application performance of material was investigated by adsorption for typical adsorbate of methylene blue solution.

2. Materials and methods

2.1 Preparation

Typically, 8.1 g of anhydrous glucose (98%) was dissolved in 75 mL of deionized water to form 0.6 M glucose solution. Subsequently, solution was transferred to Teflon autoclave and heated at 180 °C for 3, 6 or 9 h. After washing and drying, carbon microsphere (CM) was synthesized. Then, 2.4 g of CM was immersed into 100 mL of 0.5 M $\text{Al}(\text{NO}_3)_3$ (98%) solution, with 6 g of NaOH (96%), heating at 80 °C for 12 h. After filtration and drying, the CM coating with adsorbed Al^{3+} (Al@CM) was prepared. The Al@CM was heated in N_2 at 5 °C/min up to 400 °C for 1 h, and then it was heated in air at 500 °C for 1 h. Finally, the powder of Al_2O_3 hollow microsphere (AIHM) was obtained (Fig. 1). All of chemical reagents were analytical grade.

Fig. 1. Preparation flowchart of AIHM.

2.2 Characterization

Particle size distributions were investigated using laser particle size analyzer (Mastersizer 2000, Malvern). X-ray diffraction (XRD) was measured by a Bruker

diffractometer (D8 Advance) using Cu K α radiation ($\lambda=0.154$ nm) under 40 kV. Surface functional groups were examined with the Fourier transform infrared spectroscopy (FTIR) analyzer (Nexus 670, Nicolet) using KBr tablet. Textures were determined via N₂ adsorption–desorption data at –196 °C using a Quantachrome NOVA-3000 gas sorption analyzer. Surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method, and pore size distribution was obtained from the Barrett–Joyner–Halenda (BJH) model. Surface morphology was observed by scanning electron microscope (SEM, Helios Nanolab 600i, FEI) at 5 kV and transmission electron microscope (TEM, Tecnai G2 F20, FEI) at 200 kV.

2.3 Adsorption

As a typical dye, methylene blue (MB) was usually used as adsorbate in liquid adsorption to investigate mesopores and micropores. During continuous stirring adsorption at 25 ± 1 °C, 0.1 g of AIHM powder were added into 100 mL of MB (97%) solution, with MB concentrations of 5, 10, 20, 50, 100 and 200 mg/L, respectively. After 8 h for adsorption equilibrium, the MB concentration was determined using an UV1800 ultraviolet spectrophotometer (Shanghai AUCY) at 660 nm. Adsorption capacity q_e (mg/g) of MB was calculated using the following [Eq. 1](#):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where C_0 and C_e are initial and equilibrium concentrations of MB (mg/L), respectively; V is volume of solution (L) and m is mass of AIHM sample (g).

For kinetic studies, the linear pseudo first-order model [Eq. 2](#) and pseudo second-order model [Eq. 3](#) were presented as [\[8\]](#):

$$\ln(q_{e1} - q_t) = \ln q_{e1} - K_1 \cdot t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_{e2}^2} + \frac{t}{q_{e2}} \quad (3)$$

where q_{e1} (mg/g) and q_{e2} (mg/g) are equilibrium capacities of corresponding kinetic models, q_t (mg/g) is adsorption capacity at certain time; K_1 (mg/(g·h)) and K_2 (mg/(g·h)) are corresponding speed constants; t (h) is adsorption time. Further, the fitting results were investigated using correlation coefficient of R^2 .

For classic Langmuir (homogenous monolayer adsorption, Eq. 4) and Freundlich (heterogeneous multilayer adsorption, Eq. 5) isotherms, the equations were expressed as followings [8]:

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (5)$$

where q_m (mg/g) is monolayer adsorption capacity for Langmuir equation; n is dimensionless heterogeneity factor for Freundlich equation; K_L (L/mg) and K_F (mg/g)(mg/L) ^{n} are constants of Langmuir and Freundlich equations, respectively.

3. Results and discussion

3.1. Morphology

Microstructures of samples are shown in Fig. 2. The CM 3h (Fig. 2a) displayed an aggregated spherical structure, with average diameter of ~500 nm. Under longer hydrothermal time of 6 h in Fig. 2b, microspheres became relatively uniform and individual sphere. In illustration, the CM 6h showed smooth surface with larger size of ~800 nm [7]. For CM 9h in Fig. 2c, the microspheres grew larger and expressed wide

particle size distribution, with size of 800–1500 nm. Besides, several microspheres became cracked. As shown in Fig. 2d for AlHM from CM 6h, it still maintained the spherical structure, while the surface became pleated and squamous structure after calcination [7]. Due to the thermal shrinkage at 500 °C [9], its diameter was reduced from ~800 nm (CM template) to ~600 nm. For TEM image in Fig. 2e, there was uniform sphere structure for CM 6h. After calcination for AlHM 6h in Fig. 2f, it exhibited apparent hollow structure with shell thickness of ~80 nm. Fig. 2g and h display mapping of Al@CM 6h and corresponding AlHM. There were uniform distributions of C, O and Al elements on surface of Al@CM. After calcination, Al³⁺ layer changed to Al₂O₃ shell and CM pyrolyzed [10], leaving Al and O elements.

Fig. 2. SEM images of (a) CM 3h, (b) CM 6h, (c) CM 9h, (d) AlHM 6h, TEM images of (e) CM 6h, (f) AlHM 6h; (g,h) mapping of Al@CM and AlHM 6h.

3.2 Physical properties

Particle size distributions of CM 3–9h and AlHM are shown in Fig. 3a. Under short reaction time of 3h, the CM expressed relatively small size, with average diameter of 520 nm. With prolonging time to 6h, the CM grew larger and distributed uniformly [10], locating around 810 nm. At hydrothermal time of 9h, the CM presented wide size distribution, with peak value size of ~1100 nm. Due to relatively uniform size and smooth surface, the CM 6h was selected as template for preparing Al@CM. For AlHM from, it still remained relatively narrow size distribution, and its diameter was reduced to 630 nm due to thermal shrinkage during calcination [9].

Fig. 3b expresses the XRD patterns of samples. One broad peak at approximately $2\theta=22^\circ$ was observed and was ascribed to the (002) plane of carbon, presenting typical amorphous structure of CM [11]. After immersed in $\text{Al}(\text{NO}_3)_3$ solution, the Al@CM pattern became flat and three new peaks occurred at $2\theta=18, 20$ and 40° , assigning to reflection of the (001), (100) and (-1-10) planes of $\beta\text{-Al}(\text{OH})_3$ (JCPDS 77-0114) [12]. The reason was that Al^{3+} were adsorbed on surface of CM, and subsequently formed $\text{Al}(\text{OH})_3$ with NaOH. After calcination under N_2 and air, several new peaks located at $2\theta=38^\circ, 46^\circ$ and 67° , ascribing to the (440), (400) and (311) planes of $\gamma\text{-Al}_2\text{O}_3$ (JCPDS 80-1385) [12]. The presence of Al_2O_3 originated from the pyrolysis of $\text{Al}(\text{OH})_3$ during calcination [10].

The FTIR spectra of materials are presented in Fig. 3c. A wide peak around 3400 cm^{-1} was assigned to stretching vibration of $-\text{OH}$ bond. Peaks of 1720 and 1630 cm^{-1} were stretching vibration of $\text{C}=\text{O}$ and $\text{C}=\text{C}$, respectively [13]. While for AlHM, these two peaks almost disappeared, signifying the removal of CM template. A new peak at 1390 cm^{-1} in Al@CM spectrum could be attributed to stretching vibration of NO_3^- in adsorbed $\text{Al}(\text{NO}_3)_3$ [14]. Similarly, a weak peak around 1080 cm^{-1} was bending

vibration of Al–OH [14]. In AlHM spectrum, several significant peaks located at 600–800 cm^{-1} were attributed to vibrations of Al–O bond in $[\text{AlO}_6]$ octahedra [10].

Fig. 3d expresses the N_2 adsorption-desorption isotherms for AlHM. According to IUPAC classification, sample presented the type IV isotherm with hysteresis loop for mesopores [9]. Using the BET method, AlHM 6h displayed moderate surface area of $186 \text{ m}^2/\text{g}$. Total pore volume was given as $0.302 \text{ cm}^3 \text{ g}^{-1}$, deriving from relative pressure P/P_0 of ~ 0.99 . As seen from BJH pore size distribution, the sample exhibited hybrid pore structure of micropores and mesopores, with a peak value of $\sim 4 \text{ nm}$. The S_{BET} values of AlHM prepared from CM 3h and CM 9h were 142 and $165 \text{ m}^2/\text{g}$, respectively.

Fig. 3. (a) particle size distribution of CM and AlHM, (b) XRD patterns of CM,

Al@CM and AlHM, (c) FTIR spectra of CM, Al@CM and AlHM, (d)

adsorption-desorption isotherms of N_2 for AlHM.

3.3. Formation mechanism

The formation process of AlHM is explained in Fig. 4. Based on carbon source of glucose, the CM was synthesized via hydrothermal method. Then, CM was immersed into $\text{Al}(\text{NO}_3)_3$ solution, and Al^{3+} could be adsorbed on its surface. With effect of NaOH, the Al^{3+} became form of $\text{Al}(\text{OH})_3$ (Eq. 6) and formed the $\text{Al}(\text{OH})_3$ coating of $\text{Al}@\text{CM}$. When heating in N_2 at 400 °C, the $\text{Al}(\text{OH})_3$ would be pyrolyzed and turn into the Al_2O_3 (Eq. 7), while CM template was maintained at this time. During subsequent calcination in air at 500 °C, the CM was oxidized to CO_2 , leaving the Al_2O_3 shell of AlHM [10]. In adsorption experiment, the MB molecule could enter into pores of porous AlHM.

Fig. 4. Formation mechanism of AlHM.

3.4. Adsorption performance

Fig. 5a exhibits the adsorption capacity of MB onto AlHM 6h during prolonged time. With the increasement of MB concentration, the adsorption capacity q_t was also increased. During the initial 0.5 h, the adsorption behavior was fast and q_t values

increased rapidly; while during subsequent time, the adsorption speed became slow and q_t values increased gently. It could be considered that at time of 4 h, the adsorption process was closed to equilibrium status [15].

Kinetic and isotherm were used to investigate the MB adsorption onto AlHM. The parameters of kinetic equations are listed in Table 1. The pseudo second-order model expressed better fitting results with R^2 of 0.999 than pseudo first-order model. Fig. 5b displays linear pseudo second-order model of MB adsorption onto AlHM 6h. Due to large R^2 , the pseudo second-order model showed good accuracy with experimental data. This fact suggested that the adsorption speed was mainly dependent on adsorption sites of AlHM rather than the MB concentration in solution [15].

Plots of two isotherms for MB adsorption onto AlHM 6h are expresses in Fig. 5c. With the increasement of equilibrium concentration C_e , the adsorption capacity q_e was increased rapidly and then became almost stable. Under the initial concentration of 200 mg/L, the maximum q_e value of MB was reached as 26.5 ± 1.2 mg/g, larger than 8.38 mg/g of Al_2O_3 hollow sphere in previous report [15]. For the Langmuir model, it presented better R^2 of 0.997 than 0.939 of Freundlich model, implying the type of monolayer adsorption [13]. Table 2 lists the parameters of these two isotherms.

At MB concentration of 200 mg/L, the q_e values of AlHM 3h and 9h were recorded as 20.1 ± 0.9 and 23.2 ± 1.1 mg/g, respectively. The adsorption performances of MB were also investigated using other typical adsorption materials, such as 180 mg/g for graphene aerogel [13], 423 mg/g for activated carbon [16], and 95 mg/g for porous TiO_2 [17]. Fig. 5d presents the relationship between surface area S_{BET} and adsorption capacity q_e from this work and literatures. It could be found that the surface area displayed significant positive correlation for adsorption capacity, with high R^2 of 0.922.

Fig. 5. MB adsorption onto AIHM 6h: (a) adsorption capacity during prolonged time; (b) pseudo second-order fitting; (c) two adsorption isotherms with error bar; (d) relationship between surface area and adsorption capacity.

Table 1 Parameters of kinetics equations for MB adsorption onto AIHM 6h.

C_0 of MB (mg/L)	Pseudo first-order model			Pseudo second-order model		
	q_{e1} (mg/g)	K_1 (h^{-1})	R^2	q_{e2} (mg/g)	K_1 (g/(mgh))	R^2
5	2.3	0.708	0.945	4.6	0.796	0.999
10	3.6	0.731	0.936	7.4	0.543	0.999
20	5.4	0.712	0.917	11.9	0.385	0.999
50	7.5	0.535	0.919	20.4	0.312	0.999

100	8.0	0.562	0.918	24.9	0.301	0.998
200	8.2	0.625	0.860	26.3	0.371	0.998

Table 2 Coefficients of isotherm models for MB adsorption.

Isotherms	Parameters		R^2
Langmuir	$K_L=0.133$ L/mg	$q_m=27.6$ mg/g	0.997
Freundlich	$K_F=5.70$ (mg/g)(mg/L) ⁿ	$n=3.03$	0.939

4. Conclusion

The CM was synthesized by hydrothermal method under time of 3–9 h using glucose, and then it was selected as template to form core–shell structure of Al@CM. At hydrothermal time of 6 h, the CM displayed relatively uniform particle size distribution with diameter of ~800 nm. After calcination in N₂ and air, the CM core was shrank and volatilized, leaving γ -Al₂O₃ shell (AlHM) with diameter of ~600 nm and shell thickness of 80 nm. Due to the high S_{BET} value of 186 m²/g, the AlHM exhibited large adsorption capacity of 26.5±1.2 mg/g for MB solution. It could be believed that this study will provide an effective and low cost approach to prepare some metal oxides with hollow sphere structure.

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Conflicts of interest

Declarations of interest: none.

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