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Regulation of the adsorption affinity of metal-organic framework MIL-101 via a TiO_2 coating strategy for high capacity adsorption and efficient photocatalysis

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A B S T R A C T

TiO_2-MIL-101 nano-composite was synthesized through the growth of TiO_2 crystals on MIL-101 substrate under solvothermal conditions, and was applied into the adsorption and photocatalytic degradation of methylene blue (MB), rhodamine B (RhB) and crystal violet (CV). The fabricated TiO_2-MIL-101 nano-composite was characterized by thermogravimetric analysis (TGA), X-ray diffractometry (XRD), fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray analysis (EDAX), scanning electron microscope (SEM), transmission electron microscopy (TEM) and N_2 adsorption experiments. As a result, we found that TiO_2-MIL-101 nano-composite remained good porosity because of the MIL-101 substrate, and the TiO_2 crystals were coated on the surface of MIL-101 without agglomeration. Furthermore, on basis of experiments, remarkable enhancement of adsorption affinity of TiO_2-MIL-101 towards MB, RhB and CV could be mainly attributed to the regulation of the surface charge compared to original MIL-101 materials after coated by TiO_2 crystals. Meanwhile, the fabricated TiO_2-MIL-101 exhibited excellent photocatalytic activity for the degradation of MB, RhB and CV based on the TiO_2 coatings.

1. Introduction

Metal-organic frameworks (MOFs) are an emerging class of crystalline porous materials [1,2], the structure of which is composed of inorganic metal-oxide units and the organic linkers. Owing to numerous structures, tunable pore size and ultrahigh porosity, MOFs have gained growing attention as advanced porous materials in diverse adsorption-based applications, such as gas storage [3,4], separation [5,6], drug delivery [7] and catalysis [8,9]. However, in spite of the incredibly high surface area, post-synthetic modification of the skeleton, introduction of functional groups, molecules or nanoparticles, are also crucial to tune and optimize the adsorption performance in order to achieve better adsorption affinity and capacity [10]. Meanwhile, with the regular pore structures, MOFs are also expected to be the competent stabilizing matrix for loading of nanoparticles, such as noble metal [11,12], and metal oxide [13,14].

With the ability to excite electrons to the conduction band or to generate holes in the valence band, metal oxide semiconductor nanomaterials are applicable to perform photocatalytic reactions. Semiconductor photocatalysis is an important technique for various energy [15,16] and environmental applications [17,18]. Several metal oxide nanoparticles, such as TiO_2 [19–22], ZnO [23,24], Fe_2O_3 [25,26], are extensively studied for this purpose, and large band gap metal oxide such as TiO_2 nanoparticles which have suitable band position are found to be better one due to its stability, low cost, low toxicity, and appropriate photophysical properties in ambient to harsh conditions [26]. However, tendency to agglomeration in suspension systems as a result of the small particle size and the poor adsorption capacity by virtue of the non-porous structure make their utilization difficult. To defeat these restrictions, much effort has been devoted to treatment of the photocatalysts with porous supporting materials, such as MOFs [27–31] or zeolites [32,33].

As a demonstration, we report a simple solvothermal method for preparation of TiO_2-MOF nano-composite by using MIL-101 as the supporting adsorptive porous material, TiO_2 as the coating photoactive material, and endeavor to investigate the synergism of TiO_2-MIL-101 nano-composite for the ultrahigh efficiency adsorption and photocatalysis decomposition of methylene blue (MB) in aqueous solution. In this work, TiO_2 nanocrystals are coated and loaded onto the surface of MIL-101 without agglomeration, and the resulted TiO_2-MIL-101 nano-

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composite possesses high surface area because of the MIL-101 substrate which facilitates the photocatalytic process. Furthermore, the fabricated TiO_2-MIL-101 nano-composite exhibits higher adsorption affinity towards MB compared to MIL-101 as a result of the regulation of surface charge by the coating TiO_2 crystals.

2. Materials and methods

2.1. Chemicals and materials

All chemicals and reagents were at least of analytical grade. Ultrapure water (18.2 MΩ cm) was obtained from a WaterPro water purification system (Labconco Corp., Kansas City, MO). $Cr(NO_3)_3·9H_2O$, terephthalic acid (BDC) and hydrofluoric acid were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Titanium butoxide (TBOT) was purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Ethanol was purchased from Tianjin Concord Technology Corporation (Tianjin, China).

Ethanol was pre-treated before use to remove trace water. Typically, appropriate amount of sodium ethoxide and 500 ml ethanol were poured into a flask, and the suspension was refluxed under magnetic stirring in a solvent distillation device for 5 h. The distilled ethanol was then evaporated and collected in a solvent distillation head. The resulted anhydrous ethanol was sealed and kept in a vacuum dryer.

2.2. Synthesis of MIL-101

MIL-101 was synthesized under hydrothermal conditions. Typically, $Cr(NO_3)_3.9H_2O$ (800 mg), terephthalic acid (332 mg) and hydrofluoric acid (0.15 ml, 40%) were mixed with ultrapure water (9.5 ml). The obtained mixture was transferred to a Teflon-lined bomb, sealed, and heated at 220 °C for 8 h. After cooling down, the green crystals of as-synthesized MIL-101 was washed three times by ultrapure water and ethanol, and then dried at 50 °C for 24 h.

2.3. Preparation of TiO_2-MIL-101

To prepare the TiO_2-MIL-101 nanocomposites, MIL-101 power (100 mg) was dispersed in the mixed solution of titanium butoxide (2 ml) and ethanol (16 ml). The above mixture was ultrasonically treated for 10 min in order to form uniform suspension, before 0.8 mL ultrapure water was added into the suspension. The suspension was then transferred to a Teflon-lined bomb. The bomb was then sealed, placed in an oven and heated at 220 °C for 3 h, and cooled down to room temperature. The obtained TiO_2-MIL-101 was dried at 50 °C for 24 h.

2.4. Determination of equilibrium time for adsorption of methylene blue (MB)

The batch adsorption experiment method was applied to examine adsorption of MB. Adsorption kinetic curve and adsorption isotherm were made to characterize the adsorption of MB based on pure MIL-101 and TiO_2-MIL-101.

To determine the equilibrium time for the adsorption of MB on TiO_2-MIL-101, 55 mg TiO_2-MIL-101 and 10 ml MB (60 mg L^{-1}) were added into 20 ml vial, and maintained at the temperature of 30 °C in dark. After adsorption for a pre-determined time, the suspension was centrifuged at 9000 r/min for 3 min. The concentration of MB in the supernatant was determined by UV-vis spectrometer at 665 nm, which was the maximum absorption wavelength of MB. The adsorption of MB based on pure MIL-101 followed the same procedure for comparison, except for the amount of pure MIL-101 changed to 10 mg for each vial.

2.5. Determination of the maximum adsorption capacity of MB

To determination the maximum adsorption capacity of MB on TiO_2-MIL-101, eight concentrations of MB (30 mg L^{-1}, 40 mg L^{-1}, 50 mg L^{-1}, 60 mg L^{-1}, 70 mg L^{-1}, 80 mg L^{-1}, 90 mg L^{-1} and 100 mg L^{-1}) were prepared. Typically, 55 mg TiO_2-MIL-101 and 10 ml MB were mixed in a 20 mL vial at the temperature of 30 °C for 4 h in dark. Then, the suspension was centrifuged, and the concentration of MB in supernatant was determined by UV-vis analysis. The adsorption of MB based on pure MIL-101 followed the same procedure for comparison, except for the amount of pure MIL-101 changed to 10 mg for each vial.

2.6. Determination of the adsorption isotherms and its Langmuir equation

To evaluate the difference in maximum adsorption capacities of MB on MIL-101 and TiO_2-MIL-101, the adsorption isotherms were fitted with the Langmuir equation in the concentration range of 30–100 mg L^{-1} at 30 °C (eq (1)) [34].

$$\frac{Ce}{qe} = \frac{Ce}{Q0} + \frac{1}{Q0b} \tag{1}$$

where C_e (mg L^{-1}) is the equilibrium concentration of MB, q_e (mg g^{-1}) is the equilibrium adsorption capacity of MB, Q_0 is the maximum adsorption capacity (mg g^{-1}), and b is the Langmuir constant (L mol^{-1}).

2.7. Evaluation of the adsorption and photocatalysis ability of TiO_2-MIL-101

100 mg TiO_2-MIL-101 was dispersed in 100 mL MB solution (20 mg L^{-1}) under stirring. After adsorption for a pre-determined time in dark, a sample suspension was collected and centrifuged, and the concentration of MB was determined by a UV-vis spectrometer. Then, photocatalytic experiments for degradation of MB in aqueous solution were performed under a UV-light reactor. At regular time intervals of illumination, another sample suspension was collected and centrifuged at 8000 rpm for 3 min, and the concentration of MB in the supernatant was determined by a UV-vis spectrometer.

2.8. Characterization

The thermogravimetric analysis (TGA) experiments were performed on a DTG-60 thermal gravimetric analyzer (Shimadzu, Japan) from room temperature to 800 °C at a ramp rate of 10 °C min^{-1}. The X-ray diffraction (XRD) patterns were recorded with a D/max-2500 diffractometer (Rigaku, Japan) using Cu Kα radiation ($\lambda = 1.5418$ Å). Fourier transform infrared spectroscopy (FT-IR) analysis was carried out on a FTIR-650 spectrophotometer. Powder samples were prepared using the KBr wafer method and the measurements were performed in a diffuse reflectance module. The scanning electron microscopy (SEM) micrographs were recorded on a Phenom G2 scanning electron microscope at 15.0 kV. Transmission electron microscopy (TEM) images were obtained using Hitachi H-7650 equipment. An Autosorb-IQ surface area and pore size analyzer (Quantachrome, Florida, FL, USA) was used to measure the Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution of the synthesized materials at 77 K in the range $0.02 \le P/P_0 \le 0.20$. The Zeta potentials were measured using a Zetasizer (Zetaplus90). UV-vis adsorption spectrum was measured using a UV-visible spectrophotometer (Thermo Fisher, Evolution 201, USA). UV-vis diffuse reflectance spectra (UV-vis DRS) were measured using a Shimadzu UV-2700 spectrophotometer equipped with a integrating sphere using $BaSO_4$ as the reflectance sample.

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