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Impact of mesoporous pore distribution on adsorption of methylene blue onto titania nanotubes in aqueous solution

Chien-Te Hsieh *, Wen-Syuan Fan, Wei-Yu Chen

Department of Chemical Engineering and Materials Science, Yuan Ze Fuel Cell Center, Yuan Ze University, Taoyuan 320, Taiwan

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ABSTRACT

This study investigates the liquid-phase adsorption behavior of methylene blue (MB) dye onto titania nanotubes, prepared by hydrothermal method, at different temperatures ranging from 30 °C to 50 °C. The nanotubes are mainly mesoporous, and their pore sizes were found to increase with calcination temperature. The maximum of MB adsorption capacity was found to be *ca.* 290 mg/g at 30 °C. The isosteric heat (q_{st}) of adsorption was obtained from the adsorption isotherm measurements. The heat of adsorption at low coverage is in the range ~10.1–13.5 kJ/mol, while at the monolayer completion, the value of q_{st} displays a minima within 4.6–6.2 kJ/mol. The magnitude of q_{st} confirms that the adsorption mechanism is physisorption. The variation of isosteric heat with surface coverage reflects that the titania nanotubes have a surface heterogeneity for adsorption of MB in liquid phase. The heat of adsorption of MB on the nanotubes is the decreasing function of the tubular size of the nanotubes. The difference of q_{st} value can be attributed to two concepts: (i) in narrow pores, the concave pore walls would provide overlapping potentials at low coverage; (ii) at high coverage, capillary process easily takes place in the smaller pore. This result supports the usefulness of open-ended titania nanotubes for dye adsorption in liquid phase.

1. Introduction

Nanocrystalline metal-oxide semiconductors have been extensively used in photocatalytic or photoelectrochemical systems due to their large surface area of the solid-solution interface, where the interactions between the photo-induced charge carriers and the active species in the solution occur [1,2]. Among these semiconductors, titanium dioxide (or called titania) has received a deal of attention, and many researchers have devoted to investigating the synthesis of nanosized TiO_2 [3–7]. These abilities to fabricate various nanoarchitectures are expected to positively impact realistic applicability. To our knowledge, raising the available surface area in various photochemical electrodes is still a necessary concern. It is believed that the crucial points are the active surface area and the adsorption potential.

Promising techniques such as hydrothermal treatment [1–4], soft-chemical synthesis [6], and self-organization combined with electrochemical method [5,7] have been developed in synthesis of TiO_2 nanostructures. Among these syntheses, hydrothermal treatment is capable of preparing TiO_2 particles in the form of nanotubes, thus efficiently increasing the active surface area. Early work has reported a simple hydrothermal treatment of crystalline titania to produce high-purity titania-based nanotubes with an average diameter of *ca.* 10 nm [1–4]. This kind of tubular structure is of mesoporosity, and it is credited that titania-based nanotubes would appear to be excellent candidates for use in photocatalytic (e.g., de-NO_x catalyst) [8] and photoelectrochemical (e.g., electrodes of dye-sensitized solar cell) systems [9].

To explore the activity of a catalyst, it is important to examine the nature of interactions between adsorbate molecules and the catalyst surface. It is generally recognized that adsorption potential is significantly affected by pore size of porous media. Dubinin and Plavnik have used the small-angle X-ray scattering technique to study carbon adsorbents with different microporous structures [10]. Their analysis of experimental data revealed an inverse proportionality between the slit-pore half width and the characteristic adsorption energy for the standard vapor benzene at 20 °C. However, the fact that the tubular size of titania nanotubes affects the adsorption behavior have not yet been clearly elucidated and requires a deeper investigation.

In the present work, we intend to correlate the adsorption potentials of different titania nanotubes with their structural and morphological details. One of the polynuclear aromatic complexes, methylene blue (MB, MW = 320), was employed as adsorbate to explore the adsorption behavior of nanotubes. Its molecular size (*ca.* 130 $Å^2$) [11] is close to the dimension of polymeric electrolyte. Liquid-phase adsorption of MB is an indication of evaluating adsorption capability of supramolecule in solution, which is useful for development of novel electronic nanodevices, e.g., photovoltaic

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* Corresponding author. Tel.: +886 3 4638800x2577; fax: +886 3 4559373.
E-mail address: cthsieh@staurn.yzu.edu.tw (C.-T. Hsieh).

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cells [12]. Specifically, we synthesized titania nanotube with various tubular sizes, using hydrothermal treatment operated at different temperatures. This effort is devoted to examining the MB adsorption isotherms at different temperatures and the isosteric heat of adsorption. The dependence of these quantities on the surface coverage is also reported.

2. Experimental

2.1. Preparation of titania nanotubes

Titania-based nanotubes synthesized by hydrothermal synthesis have been reported elsewhere [1,2,4]. The TiO_2 precursor used for nanotube production was a commercially available TiO_2 nanopowder (P25, Degussa AG) that consists of *ca.* 30% rutile and *ca.* 70% anatase in crystalline phase. In nanotube preparation, 2 g of the TiO_2 powder was mixed with 100 mL of 10 N NaOH solution, followed by thermal treatment of the mixture at 135 °C in Teflon-lined autoclave for 24 h. After that, we subjected the precipitate from filtration to pH-value regulation by mixing it with 1 L of 0.1 N HCl solutions. The final products were obtained by filtration with subsequent drying at 110 °C overnight. Early study has pointed out that the pore structure of nanotubes was controlled by different operating conditions such as pH value, post treatment and calcination temperature [2]. In the present work, different tubular sizes of titania nanotubes were prepared by treating them at various calcination temperatures, ranging from 300 °C to 600 °C.

2.2. Nanotube characterization

The as-grown TiO_2 nanotubes were characterized by using high-resolution transmission electron microscope (HR-TEM, JEOL JEM-6500F). The crystalline structure of the synthesized titania samples was characterized by X-ray diffraction (XRD) with Cu Kα radiation using an automated X-ray diffractometer (Shimazu Labx XRD-6000). Specific surface areas and pore volumes of the derived nanotubes were determined by gas adsorption. An automated adsorption apparatus (Micromeritics, ASAP 2000) was employed for these measurements. Adsorption of N_2, as a probe gas, was performed at −196 °C. Nitrogen surface areas and micropore volumes of the samples were determined from Brunauer–Emmett–Teller (BET) and Dubinin–Radushkevich (D–R) equations, respectively. The amount of N_2 adsorbed at relative pressures near unity ($P/P_0 = 0.98$ in this work) has been employed to determine the total pore volume, which corresponds to the sum of the micropore and mesopore volumes. The peak pore diameter of nanotubes can be estimated according to pore size distribution, determined from Barret–Joyner–Halenda (BJH) method.

2.3. Liquid-phase adsorption

Adsorption experiments of MB were conducted by placing a certain amount of TiO_2 adsorber and 100 cm^3 of the prepared aqueous solution into a glass-stoppered flask. The flask was put in a constant-temperature shaker bath, with a shaker speed of 100 rpm. The adsorption temperatures employed here were 30 °C, 40 °C, and 50 °C, respectively. Preliminary experiments had shown the adsorption process attained equilibrium in 5 h for all TiO_2 samples used in the present study.

Upon equilibration, all samples were filtered through Nylon filters prior to analysis, in order to minimize interference of the TiO_2 nanotubes with the analysis. The concentrations of MB in the residual solutions were analyzed by an UV/visible spectrophotometer (Shimadzu UV-2550) at appropriate wavelengths, i.e., $\lambda = 665$ nm. Concentrations were measured by comparing the light absorbance of the sample solutions against a standardization curve prepared for each compound. The amount of MB captured by the TiO_2 adsorbers was determined as follows:

$$Q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

where Qe is the amount of adsorbate on the TiO2 nanotubes at equilibrium, in units of (mg adsorbate/g adsorber), Ci is the initial concentration of adsorbate in the aqueous solution, Ce is the equilibrium concentration, V is the volume of the aqueous solution, and M is the amount of the adsorber used in the adsorption.

3. Results and discussion

3.1. Textural characteristics of titania nanotubes

HR-TEM image of TiO_2 samples clearly reveals the nanotubular structure of the material, as shown in Fig. 1a and b. This titania sample was prepared by the hydrothermal treatment at 135 °C (without any heat treatment). The nanotubes are hollow with an outer diameter of 10–12 nm, inner diameter between 5 and 10 nm, and lengths of several hundred nanometers. Since they have the uniform tubular size, we stress that the as-grown nanotubes are homogeneous. This growth mechanism has been reported elsewhere; some Ti–O bonds of the TiO_2 precursor is

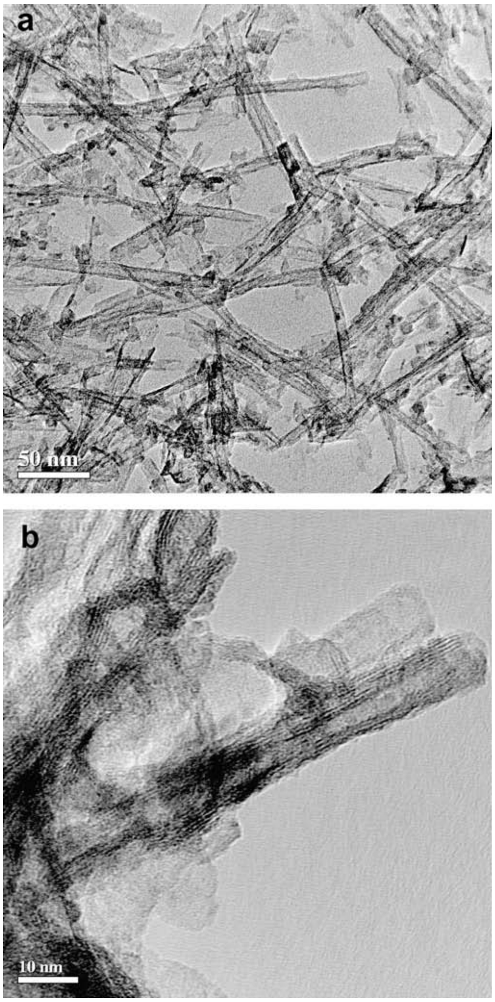

Fig. 1. Typical HR-TEM photographs at (a) low and (b) magnification for titania nanotubes (TNT-A sample) prepared by hydrothermal treatment.