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Preparation and characterization of V-Loaded titania nanotubes for adsorption/photocatalysis of basic dye and environmental hormone contaminated wastewaters

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ABSTRACT

Titania nanotubes (TNs) with high specific surface area have been widely studied due to its excellent catalytic activities, long-term stability, nontoxicity, and low cost. Basic violet 3 (BV3) dye and perchloroethylene (PCE) environmental hormone are recognized as difficult-to-treat pollutants and are discharged by a wide variety of sources. Therefore, the main objectives of the present work were to prepare V–loaded TN photocatalysts by an impregnation method and to characterize the adsorptive/photocatalytic properties, fine structures, adsorption/photodegradation mechanisms or removal efficiencies of dye and environmental hormone pollutants in wastewaters using V–TNs. Experimentally, FE–SEM and HR–TEM microphotos showed that the length and diameter of TNs were 100–150 and 10–30 nm, respectively. XRD weak vanadia patterns observed in V–TNs indicating the V_2O_5 nanoparticles are possibly well dispersed on the surface of TNs. The BET surface area and pore volume of TNs (V–TNs) are 312 (291) m^2g^{-1} and 1.054 (0.879) cm^3g^{-1} with N_2 type IV hysteresis isotherms, respectively. The EXAFS data showed that the 5% V–TNs had Ti (V) atoms coordinated by primarily Ti—O (V—O) with bond distances of 1.95 Å (1.71 Å) and coordination numbers of 2.29 (5.35). The removal efficiencies of BV3/PCE onto 5% V–TNs were 100 and 96%, respectively and loaded V_2O_5 is the main specimen that can promote the photocatalytic efficiencies significantly under visible light irradiation. Finally, adsorption and photocatalytic mechanisms of BV3/PCE onto V–TNs were examined using DKR/pseudo-second-order equations and Langmuir-Hinshelwood model.

1. Introduction

Dye wastewaters (e.g. basic violet 3 (BV3)) are recognized as difficult-to-treat pollutants and are discharged by a wide variety of sources, such as textiles, mills, printing, plants, dyestuff manufacturing, and food plants [1–7]. The color produced by minute amounts of organic dyes in water is of great concern because the color in water is aesthetically unpleasant. Typically, chlorinated solvent such as perchloroethylene (PCE) has been commonly used as a solvent in the metal degreasing and dry cleaning industrial processes. It is also recognized as one kind of environmental hormones and has constituted major public health problems and environmental concerns [8–12]. The PCE with low aqueous solubility, high density (> 1 g cm^{-3} of water), and easy mobility, is mostly distributed in contaminated waste streams, soils, and groundwaters [9–11]. Moreover, they are also the major sources of water pollution, because BV3 basic dyes or PCE and their degradation products may be carcinogens and toxic to human beings or mammals [10–12]. These pollutants have shown an excellent stability and resistant to environmental degradation such as physical, chemical, and biological routes. Therefore, their release into ecosystems without appropriated treatment can become long-term contaminated sources to human health and environment [8–12].

Some investigations have been conducted on the physical, chemical, and biological methods for removal of the color/toxicity from dye or chlorinated-contaminated wastewaters [13–18] and it was found that physical adsorption or photocatalysis might be an efficient and economic process to remove dyes or chlorinated–contaminants from the wastes streams and also to control the biochemical oxygen demand [18–25]. Many adsorptive materials such as some natural adsorbents, certain waste materials, and some agricultural by-products (e.g. rice husks) have also been investigated as alternatives [13–17]. Moreover, mesoporous molecular sieves, such as clays [14], MCM–41 [15],

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FSM–16 [16], and MCM–22 [17] have been accepted as the appropriate adsorbents for the removal of dyes from wastewater due to their unique mesoporous pore structure, high specific surface area, and pore volume. In recent years, the application of combined adsorption/photocatalysis technology utilizing titania nanotubes (TNs) have become one of the most effective technologies for the removal of effluents of dyes [19–21]. The TNs or TiO_2–related materials derived from a hydrothermal method, possesses ion-exchange characteristics [26–32] and they may also offer a special environment for the adsorption of large cations or environmental hormones, such as BV3 basic dye and PCE. In addition, TNs with high specific surface area have been also studied due to its excellent catalytic activities, long–term stability, non-toxicity, and low cost [23–25].

Many groups have tried to analyze the characteristics of TNs, from which the synthetic mechanism was examined and the sheet folding mechanism was often assumed [26–32]. The effects of synthetic conditions on the microstructures of the TiO_2–derived nanotubes with the emphasis placed on the reaction time, synthesis temperature, and acid washing concentration were also investigated [33–39]. However, it is rare in the literature to investigate systematically the photocatalytic enhancement of metal-loaded (e.g. vanadium (V) dopant) effects on the microstructures of TNs [40–42]. Most interestingly, vanadium has been found to be the most effective in enhancing photocatalytic activity, which corresponds to the enhanced absorption in the visible light region. The V_2O_5 nanoparticles with high surface area and the improved quantum efficiency leading to improvement of photoinduced electrons (e^-) and holes (h^+) pair separation ability [40,41]. In addition, redox properties of V atoms are modified leading to an electronic interaction between TNs and VO_x species. The V–loading is a key point for the photoactivity and it has been suggested that a single redox surface site participates in the kinetically significant steps, with the formation of crystalline V_2O_5 nanoparticles being detrimental on oxidation activity [40–42].

The X–ray absorption near edge structure/extended X–ray absorption fine structure (XANES/EXAFS) spectra can provide the oxidation states and fine structures of Ti/V atoms in TNs contributing to an advanced study the removal of the basic dye BV3 or environmental hormone PCE from wastewaters [43–45]. However, the fine structures and photocatalysis of V-loaded TNs are still not clear and confirmed. Therefore, the main objectives of the present study were to investigate the effects of V–loading on the morphology, phase or pore structures, and photocatalysis of BV3/PCE pollutants under the visible–ranged light of TNs. The variation of morphology, crystal phase structure, and pore structure of V–loaded TNs were thus characterized with field emission–scanning electron microscopy/energy dispersive spectroscopy (FE–SEM/EDS), high-resolution transmission electron microscope (HR–TEM), X–ray diffraction (XRD), N_2 BET isotherms, and XANES/EXAFS. Moreover, the adsorption ability, mechanisms, kinetics, and photocatalytic efficiencies of BV3/PCE onto TNs were also examined with the aid of model analyses of the adsorption equilibrium and kinetic data.

2. Materials and methods

2.1. Preparation of TNs and V–TNs

Titania nanotubes was prepared using a hydrothermal process and washed by 0.1–0.01 M HCl solution [5,6,27]. The TiO_2 source was the as–synthesized anatase TiO_2 nanopowder and the particle size ranged of 30–50 nm. 1–3 g of the TiO_2 nanopowder was mixed with 60–90 mL of 10 M NaOH solution followed by hydrothermal treatment of the mixture at 150 °C in a 250 mL teflon–lined autoclave for 24 h. After hydrothermal reaction, the titanate nanotube precipitate was separated by filtration and washed with a 1 M HCl solution > 24 h and distilled water until pH = 7. It indicates that Na^+ of the titanate nanotube is replaced with H^+ to form hydrogen titanium oxide or hydrogen titanium oxide hydrate during the increasing concentration of acid washing treatment. The formation of TN structure is much more stable after a 24 h HCl solution washing process [19,30]. The washed samples were dried in a vacuum oven at 110 °C for 8 h and stored in glass bottles until used. In order to compare the influence of metal–loading on the photocatalytic activity, V–loaded TNs catalysts were prepared by an impregnation method [41,42]. One gram TNs support (anatase, c.a. 312 $m^2\,g^{-1}$) was impregnated with different concentrations of ammonium metavanadate aqueous solution (NH_4VO_3) (> 99.99%, ACS grade) and stirring for 24 h. The mixtures were subsequently dried at 150 °C overnight and pulverized to powder. Finally, the obtained V–TN powders (designated as x wt%V–TNs, x = 1–10) were calcined at 673 K in a flow of air for 4 h.

2.2. Characterization of TNs and V–TNs

The pore volume and surface area of TNs/V–TNs were obtained by N_2 BET adsorption (Micromeritics, ASAP 2020 with the accuracy of surface area deviation within 1%). The average metal concentrations of TNs/V–TNs were measured by ICP/MS (PE–SCIEX ELAN 6100 DRC). Crystalline structures of TNs/V–TNs were measured by XRD scanned from 5 to 80° (2θ) with a scan rate of 4° (2θ) min^{-1} and monochromatic CuK_α radiation (MAC Science, MXP18) at 30 kV and 20 mA and further identified by a computer database system (JCPDS). The morphology, particle size distribution, and microstructure of TNs/V–TNs were also determined using FE–SEM (Hitachi S–4700 II) with a resolution of 0.1 nm. In addition, TN samples were dispersed on a carbon film supported by a copper grid for TEM observation (Model Zeiss 10C) at 100 kV. The optical absorbance spectra of dyes solution samples over a range of 200–800 nm were recorded on a UV–visible spectrometer (Hitachi Instruments Inc., U–3310). The Hitachi U–3310 was equipped with both a deuterium and a tungsten iodide lamp, allowing for a scanning range from 190–900 nm with a 0.3 nm resolution at a controlled temperature. Band passes are selectable from 0.1–5 nm. The software is capable of absorbance, transmittance, and concentration modes. Experimentally, The UV–vis absorbance edges of as-synthesized TNs and 5 wt% V–TNs are 380 and 538 nm, respectively. It means that the absorption edge of 5 wt% V–TNs shifted to visible light region significantly.

XANES/EXAFS spectra were collected at the Wiggler beam line 16A1 at the NSRRC of Taiwan. The electron storage ring were operated with energy of 1.5 GeV and a current of 100–200 mA. The double crystal monochromators employing at either beamline selected X–rays with energy resolving power (E/ΔE) better than 7000, sufficient for most XAS measurements. Data were collected in fluorescence or transmission mode with a Lytle detector [43] in the regions of the Ti and V K edges at room temperature. The spectra were measured with a step size equivalent to less than 0.5 eV in the near–edge and with a count time weighted to be proportional to k^3 at high energy. Data were normalized using the program Athena (vi) with a linear pre-edge and polynomial post–edge background subtracted from the raw $\ln(I_t/I_0)$ data, and then analysed using the Artemis (vi) software, which makes use of the FFEF code–8 (Ravel and Newville 2005). The spectra were first energy–calibrated by simultaneous measurements of the transmission spectra of a Ti or V foil in Athena (vi), where the energy of the first inflection point for the reference samples absorption edges were defined as Ti (4966 eV) and V (5465 eV). After calibration, the samples were then background corrected using a linear pre–edge region and a polynomial for the post–edge region, and the samples were normalized. The EXAFS energy spectra were then converted to wavevector k space. The resulting scatter curve was weighed by k^3 (k–range = 2.5–12.5 Å^{-1}, where k is the photoelectron wave number) to enhance dampened scattering oscillations. This curve was followed by Fourier transformation (FT) to yield the radial structure function. These data directly reflect the average local environment around the absorption atoms. Spectra were analyzed using the software package