Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–14

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Selective adsorption and degradation of organic pollutants over Au decorated Co doped titanate nanotubes under simulated solar light irradiation

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ARTICLE INFO

Article history:
Received 18 January 2018
Revised 25 March 2018
Accepted 3 April 2018
Available online xxx

Keywords:
Selective adsorption
Selective degradation
Photocatalysis
Water treatment
Au decorated Co doped titanate nanotubes

ABSTRACT

Au decorated Co doped titanate nanotubes (TNT) was prepared for selective removal of methylene blue (MB) dye followed by selective photocatalytic degradation under solar light in presence of another highly concentrated dyes. The adsorption capacity of Co doped TNT was found to be increased with increasing Co content due to the increase in the number of pores and thus increase in surface area. Due to the high concentration of MB, Co doped TNT was completely covered by MB molecules and become difficult for light to Path though or absorbed by the Co doped TNT catalyst. In order to provide some photocatalytic characteristics for the catalyst, the doped TNTs were calcined to enhance the crystallinity and thus enhancing the photocatalytic activity, but the degradation rate was very low. Thus, another direction was started by reducing the adsorption ability of Co doped TNT through coating its surface by poly(allylamine hydrochloride), which changed the surface charge of the tubes to be positive and facilitate the electrostatic attachment of Au nanoparticles (15 nm). The synergetic effect of plasmonic Au nanoparticles in addition to adsorption and catalytic properties of Co doped TNT make the new composite promising catalyst for degradation of organic pollutants. It shows a good selectivity for adsorption and photocatalytic degradation of MB dye from dyes mixture. The obtained results indicate that Au decorated Co doped TNT will have a great effect on the development of selective environmental water treatment technologies specifically on flow challenges confronted by the wastewater treatment area.

1. Introduction

Due to its high ability toward photocatalytic degradation, TiO_2 is considered as unique photocatalyst for degrading varieties of toxic organic compounds and pollutants [1]. Its high activity leads to complete mineralizing of the pollutants whatever their nature, but this restrict the using of it in selective catalysis. In the presence of other pollutants at high levels, it is as yet difficult to achieve selective removal and degradation of targeted pollutants due to the formed reactive species (radicals) are difficult to be controlled. When used in environmental treatment, the photocatalysis may not be effective if it is intended to get rid of all toxic pollutants independently [2]. Several ways have been used for achieving TiO_2 selectivity, such as controlling of reaction mixture pH [3,4], using larger anatase particles (10–25 nm) [5], creating molecular recognition sites on TiO_2 [6], using the less reactive rutile phase [7] or mesoporous anatase [8], and forming nano-channelled TiO_2 film with desired pore diameter [9] .

One of the best ways to boost the photocatalytic characteristics of nanomaterials is their transformation into one dimensional nanomaterials. When TiO_2 nanoparticles are transformed to the tubular form, unique photocatalytic properties could be achieved because of the one-dimensional geometry, the electron can transport faster for long-distance. Moreover, due to the nanotubular structure, it has a large specific surface area and pore volume. Furthermore, because of the high aspect ratio for one-dimensional nanotube, it can absorb and scatter light efficiently. In the last few years, titanate nanostructures (TNS), derived from TiO_2 particles at high pH [10,11], have been known as superior photocatalyst and adsorbents [12–14]. In reality, one dimensional titanate nanotubes (TNT) can be used for "non-selective" degradation of organic pollutants, like azo dyes and volatile organic pollutant [15–17]. However, it ought a chance to be noted that TNT is mainly UV-light photoactive [18–20]. Notably, one important structure property for TNT is its high cation-exchange ability [20–22]. The remaining sodium ions in TNT are not just can stabilize the tubular framework structure [22–24], but also provide the possibility of controlling the optical property by substituting with different metals into the nan-

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https://doi.org/10.1016/j.jtice.2018.04.003

otubular matrix [20,22,24,25]. As a result, TNT could be extended its light absorption to be in the visible region of light.

Improvement of highly selective methods for adsorption and photodegradation, driven by a heterogeneous catalyst, is the foreground between the biggest challenges in chemistry [26]. Different adsorbents have used for adsorption of anionic and cationic dyes selectively, depending on type of charge on the adsorbents surface and their electrostatic interactions with the dye [4,27,28]. However, selective adsorption of dyes by TNT has effective advantage in the simultaneous selective decomposition by photocatalysis. This phenomenon could be additionally extended to the tailored selection of dyes based on their affinity toward TNT.

From the photocatalytic perspective, it would be very useful if the photocatalyst has high catalytic activity and excellent adsorptive properties in addition to high selectivity. In organic pollutant with high concentration, without adsorption of part of the organic molecules, the highly concentrated dye solution cannot be effectively degraded by photocatalysis, because of the strong light absorption by the organic dye, therefore the solution become impenetrable to light. As such, the semiconductor photocatalyst in the solution cannot effectively interact with the photon energy, and this is named as the light shielding effect of colored dyes [29]. For this reason, developing efficient photocatalysts with high adsorptive ability is pivotal to enhancing degradation efficiency in highly concentrated organic dye solutions. Many researchers addressed the loading of different photocatalysts on a support materials have adsorption characteristics such as activated carbon [30,31], hydroxyapatite [32,33] and graphene [34]. Synergism between adsorption on the support materials and photoactivity of the catalysts was achieved.

This work aims to find a tunable catalytic material Possessing both adsorption and catalytic properties in addition to selectivity characteristics. To the best of our knowledge, no published report about selective adsorption and degradation of dyes using Co doped titanate nanotubes and the Au decorated. Moreover, no one reported the selective adsorption and degradation of cationic dye in mixture of highly concentrated dyes, which is one of the important targets. Here, 1D Co doped TNT and Au decorated Co doped TNT were used for selective adsorption and degradation of methylene blue (MB) dye in a highly concentrated mixture of dyes. The attached gold nanoparticles shifted the degradation to the visible light region.

2. Materials and method

2.1. Materials

TiO_2 powder and sodium hydroxide (NaOH) were purchased from Loba Chemie, Cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), tetrachloroauric acid ($HAuCl_4{\cdot}3H_2O$), sodium citrate ($Na_3C_6H_5O_7$), poly(allylamine hydrochloride) (PAH, MW: 17,500), sodium chloride (NaCl), Methylene blue (MB), Rhodamine B (RhB), Brilliant green (BG), Reactive blue (RB) and tartrazine (Tz) were from Sigma–Aldrich. All chemicals were used without further purification.

2.2. Preparation of titanate nanotubes (TNT) via a hydrothermal method

TNTs were synthesized using hydrothermal method in alkaline conditions [14]. 5 g of anatase TiO_2 powder were stirred in an aqueous solution of NaOH (10 M, 500 ml) on a magnetic stirrer for 60 min to form a milk-like suspension. The obtained suspension was placed into a Teflon-lined stainless-steel autoclave, sealed and hydrothermally treated at 160 °C for 24 h. The synthesized sodium titanate precipitates were filtered and thoroughly washed with double distilled water. The product was dried at 80 °C overnight. The final product was donated as sodium titanate powder (TNT).

2.3. Synthesis of Co-doped TNT

The synthesis of cobalt-doped TNT was performed using an ion-exchange reaction of TNT in an aqueous ammonia solution with Co^{2+}, because of the stability of TNT in a basic solution and the stabilization of substituting ion by complexation with ammonia [20,23]. The metal-ion precursors ($Co(NO_3)_2$ $6H_2O$) was dissolved in water to form Co^{2+} solution with different molar concentrations followed by adding ammonia solution (28%) drop by drop to form clear solutions at room temperature. After that, the TNT nanotubes (0.5 g) were dispersed evenly in metal-ion solution (50 mL) (the molar ratios of Co^{2+}: Ti^{4+} were adjusted to be 1:10, 1:7 and 1:5), and stirred for 20 h at 100 rpm at room temperature in order to allow a sufficient ion-exchange process. After that, the products were carefully washed with deionized water several times with the control pH 8, to avoid physical adsorption of the substituting ions on the surface of the TNT nanotubes. The as-obtained samples are denoted as Co doped TNT 1, Co doped TNT 2, and Co doped TNT 3 corresponding to 1:10, 1:7 and 1:5 Co^{2+}: Ti^{4+} molar ratios, respectively.

2.4. Attaching of gold nanoparticles on TNT surface

Au (15 nm) were prepared as described previously [35] (see the supporting materials S1). The obtained Au nanoparticles have a negative charge on its surface, the same as TNT (See Table S1). To guarantee the attachment of gold nanoparticles on the TNT surface electrostatically, the later was functionalized by PAH (see the supporting materials S2). After functionalization the net charge of TNT was changed to positive value (Table S1). 50 mg of functionalized TNT in 30 mL H_2O were dispersed well by ultrasonication followed by stirring at 400 rpm during the addition of 5.5 mL of Au nanoparticles (15 nm, 5.15×10^{-4} M). The suspension was allowed to stir for 10 min followed by centrifugation, washing with distilled water twice and dried. Due to the opposite charge on Au nanoparticles and TNT, the Au nanoparticles were attached electrostatically on TNT surface and the net charge of the new composite became negative (Table S1). Scheme 1 represents the steps of ion exchange and decoration of Co doped TNT by Au nanoparticles.

2.5. Characterization of the nanoparticles

Crystallite phases of the prepared nanomaterials were examined using X-ray diffractometer (Philips, Netherlands) using CuKα radiation (wavelength $\lambda = 1.54045$ Å) at an accelerating voltage 40 kV, current 30 mA, scan range 5–80° and scan step 0:02°. Microstructure and particle shape were examined using transmission Electron microscope (TEM, JEOL-JEM 1010, Japan) with an acceleration voltage of 100 kV and using high resolution transmission Electron microscope (HRTEM, JEOL-JEM 1010, 2100 Japan) with an acceleration voltage of 200 kV. Energy dispersive X-ray (EDX) spectroscopy and elemental mapping were conducted on STEM-EDXS (FEI Titan Themis) with an aberration-corrected transmission electron microscope operating at acceleration voltage of 200 kV. Surface area, pore volume and pore size distribution analysis were performed on surface area analyzer (TriStar II 3020, Micromeritics, USA). X-ray photoelectron spectroscopy (XPS) experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source (Aluminum Kα line of 1486.6 eV energy and 300 W). The samples were placed perpendicular to the analyzer axis and calibrated using the $3d_{5/2}$ line of Ag with a full width at half maximum (FWHM) of 1.1 eV. The selected resolution

Please cite this article as: W.M.A. El Rouby, Selective adsorption and degradation of organic pollutants over Au decorated Co doped titanate nanotubes under simulated solar light irradiation, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.04.003