

Degradation of organic pollutants by bio-inspired rectangular and hexagonal titanium dioxide nanostructures



T.V.M. Sreekanth, Jae-Jin Shim, Yong Rok Lee *

Department of Chemical Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea

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ABSTRACT

Dyes are used in textile, printing, leather, pharmaceutical, food and cosmetic industries. Dyes add color and pattern to materials. The presence of even very low concentration of dyes/dyes degradation products in effluent is highly toxic to humans and aquatic organisms. It is important to remove these dye degradation pollutants from the industrial effluents before their disposal. In recent years nanoparticles have been used for the removal of dyes from industrial waste water. Titanium dioxide nanostructures (TiO₂ NS) were synthesized via a one-step facile green process. The formation of TiO₂ NS was confirmed by Fourier transform infrared (FTIR) and Raman spectroscopy. Anatase (~76%) and rutile (~24%) phases were present, as determined by X-ray diffraction (XRD) analysis. X-ray photoelectron spectroscopy (XPS) was used to study the surface oxidation states of the TiO₂ NS. High resolution transmission electron microscopy (HR-TEM) images revealed that the samples had hexagonal and rectangular morphologies, with diameters of ~24–32 nm. The TiO₂ NS were used to evaluate the photocatalytic activities of methylene blue (MB) and malachite green (MG) dyes under UV light and in dark conditions. After 60 min of UV irradiation, nearly 71% of the MB and 78% of the MG was decolorized in the presence of as-synthesized TiO₂ NPs.

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1. Introduction

Because of Earth's growing human population, in recent years the levels of organic dye contamination have increased in both surface and ground water. Synthetic organic dyes are used in the textile, dyeing, paper, drug, cosmetic, plastic, photographic, and food processing industries [1,2]. The resulting industrial effluents contain substances which are harmful to living organisms and the environment [3]. Methylene blue (MB; C₁₆H₁₈N₃SCl) is a tricyclic phenothiazine dye, with a molecular weight (MW) of 319.85 g/mol [4]. MB exhibits various harmful effects in humans, such as heart attacks, vomiting, jaundice, quadriplegia, and tissue necrosis [5,6]. Malachite green (MG; C₂₃H₂₅N₂Cl) is a cationic triphenyl methane dye, with a MW of 364.911 g/mol. It has been widely used in the cotton, wool, silk, paper, and jute industries. MG is an effective antibacterial, antiseptic, and antiprotozoal agent. However, oral consumption of MG is hazardous, as it exhibits carcinogenic, mutagenic, genotoxic, and respiratory toxicity because of the nitrogen moieties [7]. Therefore, the removal of these harmful organic dyes from industrial effluents is necessary before discharge into the environment. The use of photocatalysts to degrade organic compounds in contaminated air or water, or to convert them into harmless chemicals,

to decrease the damage caused by organic dye pollutants to humans and the environment has been reported previously [8–10].

Various methods have been used for dye removal, including membrane filtration [11], adsorption [12], coagulation/flocculation [13], electrocoagulation/electroflotation [14], and anaerobic and aerobic biological degradation [15]. However, these treatment methods suffer from high costs, disposal problems, and transfer pollutants between phases but do not eliminate them [16]. Waste water treatment using photocatalytic degradation by nanoparticles (NPs) has several advantages over conventional methods, such as rapid oxidation, no formation of sludge, polycyclic products, and the oxidation of pollutants [17].

Recently, various metal oxides have been studied for use in the photodegradation of dyes. In particular, TiO₂ NPs have received a great deal of interest for use as semiconductor photocatalysts, because of their high catalytic activity, high photo-, optical, and chemical stabilities, low cost, facile synthesis, and biological compatibility [18–20]. However, because of their wide band gap (3.2 and 3.0 eV for the anatase and rutile phases, respectively), they only respond to UV radiation, which comprises less than 5% of sunlight [21]. Moreover, the rapid recombination of their photogenerated electron hole pairs and slow hot carrier diffusion hinder the performance of TiO₂ and limit its efficiency and practical application as a photocatalytic material [22].

The objectives of the present study were as follows: (i) to develop a bio-inspired green synthesis of TiO₂ NS using *Coptidis Rhizoma*, (ii) to evaluate the different phases of TiO₂ NS using analytical techniques

* Corresponding author.

E-mail address: yrlee@yu.ac.kr (Y.R. Lee).

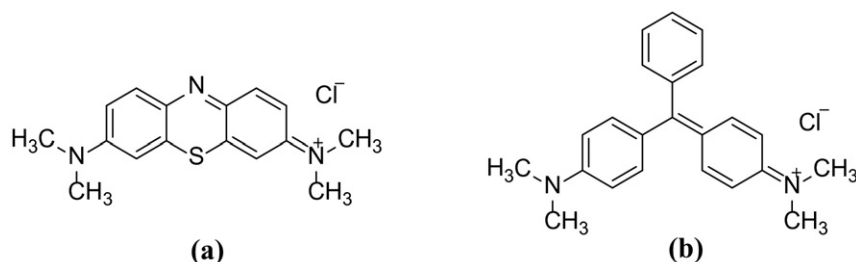


Fig. 1. Structures of cationic dyes used in this study. (a) Methylene blue and (b) malachite green.

such as X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HR-TEM), and (iii) to determine the photocatalytic activity of the TiO₂ NS with MB and MG dyes.

2. Materials and Methods

2.1. Reagents

Titanium tetrachloride (TiCl₄), methylene blue, and malachite green were purchased from Sigma-Aldrich, South Korea, and used as received. Coptis root (*Rhizoma Coptidis*) was purchased from an herbal medicine shop in Gyeongsan, South Korea.

2.2. Synthesis

The synthesis of TiO₂ NS has been reported previously [23]. A similar procedure was used, with slight modifications, for the preparation of TiO₂ NPs. In brief, 2 ml of TiCl₄ solution was added to 98 ml of 5% plant extract at room temperature, stirred for 1 h, and then a few drops of ammonia were added. The mixture was heated to 80 °C and stirred for 4 h. The mixture was then cooled to room temperature and the resulting gel was centrifuged, washed with ethanol, then air dried at 80 °C for 6 h. Finally, the product was calcined at 500 °C for 5 h and stored at room temperature prior to analysis.

2.3. Characterization

The surface properties of TiO₂ NS were determined qualitatively by Fourier transform infrared spectroscopy (FTIR; Perkin-Elmer Spectrum Two) and Raman spectroscopy using a confocal Raman microscope (XploRA PLUS, Horiba, Japan), and quantitatively by XPS (Thermo Scientific K-Alpha) with an Al K_α X-ray source (1486.6 eV). Low and high resolution XPS scans were recorded at source energies of 160 and 30 eV, with resolutions of 1 and 0.1 eV, respectively. The poly-crystalline nature of TiO₂ NS was determined by XRD (PANalytical X'Pert³ PRO, USA) using Cu K_α radiation (λ = 1.54 Å). The data were recorded from 10 to 90° at 40 kV and 30 mA. HR-TEM (Tecnai G2 F20 S-Twin, USA), with an acceleration voltage of 200 kV, a point resolution of 0.24 nm, and a Cs of 1.2 mm, was used to investigate the morphology of the TiO₂ NS. The TEM grid was prepared according to the report of Dillip et al. [24].

2.4. Photocatalytic Activity

Aqueous phase photodegradation of methylene blue and malachite green was carried out under UV light irradiation. The structures of the dyes are shown in Fig. 1. First, 10 ppm stock solutions of MB and MG were prepared. In a typical experiment, 25 mg of catalyst was suspended in 100 ml of 10 ppm dye solution by ultrasonication for 5 min. To determine the adsorption and desorption equilibria of the dye on the catalyst, the mixture was stirred in the dark for 30 min. Subsequently, the solution was exposed to UV irradiation (40 W; Philips) at

ambient conditions with constant stirring. The distance between the lamp and beaker was maintained at 12 cm. At a given time interval, a 1.5 ml sample was taken from the beaker and centrifuged to separate the catalyst. The absorption of the sample was recorded using a spectrophotometer (Optizen, 3220UV double beam UV/Vis spectrophotometer, Mecasys Co., Ltd., South Korea). The experiment was repeated without a catalyst to determine the self-degradation of the dyes under UV irradiation.

3. Results and Discussion

Fig. 2(a) shows the FTIR spectrum of TiO₂ NPs. The strong peaks between 400 and 800 cm⁻¹ were attributed to the Ti—O and O—Ti—O flexion vibrations [25]. A broad peak around 3400 cm⁻¹ was assigned to the OH⁻ groups. The Raman spectrum of TiO₂ NS is shown in Fig. 2(b). The peaks centered at 148.6 cm⁻¹ (E_g), 198.9 cm⁻¹ (E_g), 399.8 cm⁻¹ (B_{1g}), 520.8 cm⁻¹ (A_{1g} + B_{1g}), and 640.9 cm⁻¹ (E_g) correspond to the anatase phase of TiO₂ [26,27]. This conclusion is supported by the XRD data (Fig. 3).

The XRD pattern of TiO₂ NS is depicted in Fig. 3. The TiO₂ NS consist of a mixture of anatase and rutile phases, indicated in the figure by '*' and '#', respectively. These results are in good agreement with the standard XRD data obtained from the Joint Committee on Powder Diffraction Standards (anatase: 01-084-1285; rutile: 010-089-8303). However, the anatase phase is more prevalent than the rutile phase. The peaks at 25.33° (101) and 27.44° (110) are the highest intensity peaks of the anatase and rutile phases, respectively. These two peaks were used to estimate the weight fraction of anatase (F_A) in the mixed anatase-rutile phase using the empirical formula given by Robert and

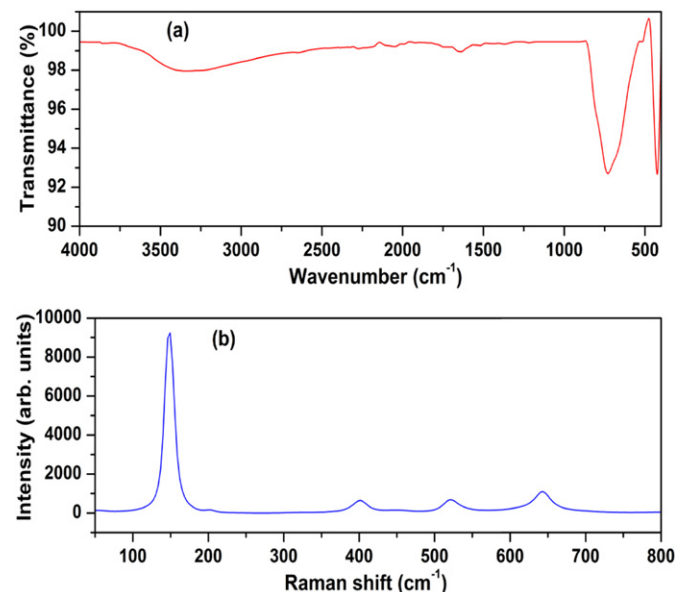


Fig. 2. (a) FTIR and (b) Raman spectra of TiO₂ NS.

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