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Effect of organic acids on the physicochemical properties of titania and its photodegradation efficiency of methyl orange

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ABSTRACT

Mesoporous mixed phase titania was synthesized *via* a solvothermal method in the absence and presence of different organic acids (acetic acid, tartaric acid and citric acid) followed by calcinations at 700 °C/2 h. The synthesized product was characterized by XRD, DTA/TG, Raman, FTIR, N_2 adsorption-desorption study, FESEM, TEM and UV-DRS. The presence of anatase and rutile phase of TiO_2 was confirmed by XRD, Raman and TEM analysis. Citric acid modified TiO_2 showed highest rutile content (66%) with lowest band gap energy (2.96 eV). Microstructural study of tartaric and citric acids modified TiO_2 revealed spherical particles (1–3 μm) consisting of nanoparticle (10–40 nm) assembly. The photocatalyst prepared using tartaric acid showed the highest photocatalytic activity with rate constant 0.0079 min^{-1}, which is due to its highest BET surface area (~39 $m^2 g^{-1}$) and efficient synergistic effect between anatase and rutile phase.

1. Introduction

Titania has been extensively applied in different fields like sensor, capacitors, solar cells, photodegradation or photocatalytic reduction of pollutants, destruction of bacteria, pigment etc [1–4]. Among these, titania is majorly used as a photocatalyst because it is non-reactive, non-toxic, in-expensive and photostable. Photocatalytic activity of titania depends upon several factors like porosity, morphology, crystallinity etc., which could facilitate in creating surface active sites and mass transport properties along with inhibiting the recombination of electron-hole pair. Mesoporous TiO_2 has been extensively used as a highly active photocatalyst due to its promising diffusion rate and high access to the reactive sites on the surface [5,6]. Titania exhibits two significant polymorphs, the stable rutile and metastable anatase. Anatase and rutile TiO_2 show different properties as well as different photocatalytic performances. In recent time, the mixed phase of TiO_2 is becoming advantageous for reducing the recombination of photogenerated electron-hole pairs, which profits the photocatalytic activity [7–9]. Thus, it attracts the researchers to synthesize titania with mixed crystalline phases.

Titania nanoparticles with different morphologies like rod-shaped, wire-shaped, sphere-shaped etc. were synthesized [10,11]. Most of them are synthesized using templating method. Using a template in synthesis process, it increases the cost of the method as well as it is difficult to remove the template from the system. For the synthesis of mixed-phase titania, many researchers used inorganic additives. Yang *et al.* used ZrO_2 and Al_2O_3 as inorganic additive [12,13]. But the removal of the additives to get the pure titania is difficult. In recent time, many researchers have synthesized mixed-phase TiO_2 by varying the solvent and cosolvent [14], using different inorganic anions (e.g., NO_3^- and SO_4^{2-}) [15,16], applying advanced plasma electrolytic oxidation of pure titanium foils [17] etc.

This study deals with the synthesis of mesoporous mixed phase titania *via* a simple solvothermal method in the absence and presence of different organic acids. The role of the number of carboxylic (mono-, di- and tricarboxylic) and hydroxyl (mono-, dihydroxyl) groups present in the organic acids used on the crystallinity, spectroscopic, microstructural and textural behaviors of the samples were studied. The photocatalytic efficiency of the samples was also investigated for the degradation of methyl orange (MO) dye, an organic water pollutant which has toxic effects on human health. In this investigation the influence of different properties of mixed phase TiO_2 obtained by using different organic acids was studied toward the photocatalytic efficiency for the degradation of MO dye.

2. Experiment

2.1. Materials

Titanium isopropoxide (TIP) was purchased from Aldrich. Citric acid, tartaric acid, acetic acid, acetone and ethanol were purchased from Merck, India.

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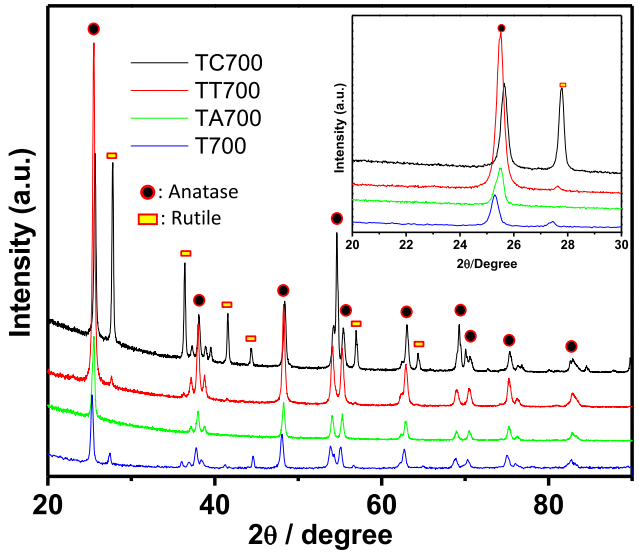

Fig. 1. XRD patterns of the samples.

Table 1
Crystallite size, anatase content and band gap energies of the calcined samples.

Sample ID	Crystallite size of anatase (nm)	Crystallite size of rutile (nm)	Contents of anatase (%)	Band gap energy (eV)
T700	28.36	31.65	81	3.01
TA700	23.64	–	100	3.16
TT700	28.37	40.71	96	3.10
TC700	21.83	40.72	44	2.96

2.2. Preparation of TiO_2 microstructures

In a typical experiment, 6 mmol of organic acid each such as citric acid (tricarboxylic acid), tartaric acid (dicarboxylic acid) and acetic acid (monocarboxylic acid) was dissolved in 20 mL of ethanol followed by addition of 1 mL of TIP under stirring. After that 10 mL of formamide was added into the above mixture and stirred for 30 min. The total solution mixture was then transferred into a 50 mL autoclave and kept at 180 °C for 12 h. After the reaction, the as-prepared product was washed with acetone and dried at 60 °C for 4 h. The as-prepared gel samples were designated as T, TA, TT, TC prepared in the absence of organic acid and in the presence of acetic acid, tartaric acid and citric acid, respectively. To obtain the oxide particles, the samples were then calcined at 700 °C for 2 h with heating rate of 1 °C/min in air atmosphere. The same procedure was followed for the synthesis of the sample in the absence of any organic acid.

2.3. Characterization

For X-ray diffraction (XRD) study, Philips X'Pert Pro XRD (Model: PW 3050/60) with Ni-filtered Cu-$K_\alpha$radiation (λ = 0.15418 nm) was used operating at 40 kV and 30 mA. The characteristic vibration bands of the product were recognized by Fourier transform infrared (FTIR; Spectrum two, Perkin Elmer) with KBr pellet and 4 cm^{-1} resolution. The thermal properties of the sample were studied using TG-DTA (Netzsch STA 449C, Germany) from 30° to 1000 °C in air (heating rate of 10 °C min^{-1}). To carry out the Nitrogen adsorption-desorption study, a Quantachrome (ASIQ MP) instrument was used at 77 K. The surface area was measured by BET method with outgas temperature of 200 °C for 4 h. The total pore volume was calculated from the amount of nitrogen adsorbed at the relative pressure (p/p_o) of ca 0.99. The morphological study of the sample was conducted by FESEM (Model: Zeiss, Supra™ 35 V P, Oberkochen, Germany, accelerating voltage of 10 kV) and transmission electron microscopy (TEM) with a Tecnai G2 30 S T (FEI) instrument operating at 300 kV. UV-VIS spectrophotometer (Jasco V-730) was used to record the UV–visible spectra (200–800 nm).

2.4. Photocatalytic degradation of methyl orange (MO)

In a typical procedure, 5 mg of the sample was added into 10 mL of 5×10^{-5} M methyl orange (MO) dye solution under stirring condition for 1 h in dark to attain adsorption equilibrium, and the percentage of adsorption is calculated as $(A/A_o)*100$, where A is the absorbance after 1 h stirring and A_o is the initial absorbance. Aliquots were filtered and analyzed using UV–visible spectrophotometer. Rest of the MO dye solution was kept in a rectangular box with dimension of 36 cm × 30 cm X 44 cm. The solutions with the samples were irradiated by UV light of wavelength 365 nm at room temperature in the photo reactor. The aliquots were filtered and analyzed by UV–visible spectrophotometer after a fixed interval of irradiation. The photocatalytic degradation of the MO was observed by gradual depletion of absorption intensity at λ_{max} = 464 nm.

3. Results and discussion

The calcined samples were designated as T700, TA700, TT700 and TC700 prepared in the absence of organic acid and in the presence of acetic acid, tartaric acid and citric acid, respectively. Fig. 1 shows the X-

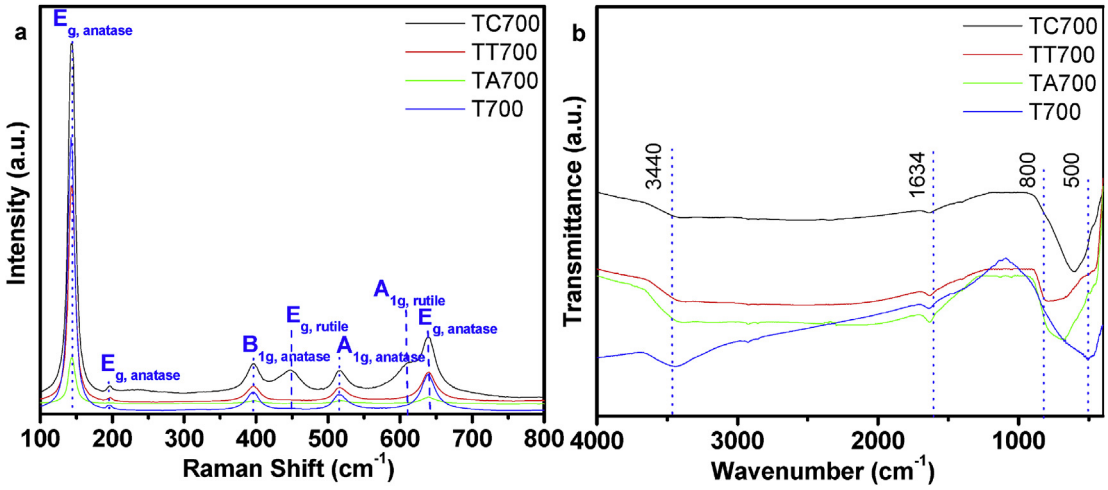

Fig. 2. (a) Raman and (b) FTIR spectra of the samples.