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Morphology and crystalline phase-controllable synthesis of titania nanoparticles via acrylamide gel method and their photocatalytic properties

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ABSTRACT

Titanium dioxide nanoparticles with average particle size of about 5 nm to 60 nm were readily synthesized via a simple, fast and low cost method; polyacrylamide gel method. Furthermore, the effect of the used acid and solvent together with calcination temperature, on crystallite size, morphology, band gaps of resultant material were investigated. The products were characterized by means of thermo gravimetric and differential thermal analysis (TG-DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and UV–vis diffuse reflectance spectroscopy analysis. The XRD results show that the presence of different anions in the precursor solution leads to the formation of samples with different anatase/rutile ratios. Their photocatalytic activities were evaluated by photocatalytic degradation of Yellow GX aqueous solution under ultraviolet radiation. The results show that the photocatalyst ($TEPC_I$), containing 79% anatase exhibits the highest photocatalytic activity, which is due to a synergistic effect between anatase and rutile.

1. Introduction

TiO_2 is an important semiconductor material for use in a wide range of applications, including photocatalysis, environmental pollution control, and solar-energy conversion [1,2]. It has shown to be a powerful photocatalyst for the oxidative decomposition of numerous organic compounds under ultraviolet (UV) light illumination [3–5]. Most of the studies have shown that the photocatalytic activity of TiO_2 is influenced by its crystalline form. TiO_2 exists in three polymorphic phases: anatase (density = 3.894 g/cm^2), rutile (density = 4.25 g/cm^2) and brookite (density = 4.12 g/cm^2). Anatase and rutile belong to different space groups, but both have tetragonal crystal structure. Anatase has the space group $I4_1/amd$ [6], with four TiO_2 formula units in one-unit cell and rutile has the space group $P4_2/mnm$ [7], with two TiO_2 formula units in one-unit cell [7,8]. Anatase phase has low density due to this it is less stable and undergo the transition into rutile phase. This transformation occurs between temperatures 450 and 1200 °C [4]. The transformation is dependent on several parameters such as initial particle size, initial phase, dopant concentration and annealing temperature, etc. [9].

Many approaches have been used to obtain nano-sized titania samples with anatase phase, such as chemical vapor synthesis [10], the sol–gel method [11,12] and the hydrothermal [13,14] or solvothermal methods [15]. The polyacrylamide gel has been demonstrated to be an efficient and cost-effective tool for easy synthesis of ultra fine oxide powders [16,17]. In this method, direct pyrolysis of polymeric network without separate drying step yields ultra fine and highly dispersed powders [18]. This method is timesaving in comparison to the Pechini method

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because in this method, the formation of the gel at low temperatures is more rapid than the Pechini method [19]. This method has been successfully applied in the synthesis of a considerable number of ultra fine powders and there are few reports of the synthesis of TiO_2 nanoparticles with this method.

The main objective of the present work was the synthesis of the titania nanoparticles via polyacrylamide gel method. In addition, the effect of different condition on the synthesis process was investigated, and the obtained samples were characterized by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and UV–vis diffuse reflectance spectroscopy analysis. Finally, photocatalytic properties of the prepared samples were investigated by monitoring the degradation of Yellow GX. Yellow GX is considered as a pollutant in waste water of Boyakhsaz carpet Company (East Azarbayjan, Iran). We aimed to remove this pollutant as a model azo dye.

2. Experimental

2.1. Chemicals

Tetraethylorthotitanate, absolute ethanol, acryl amide, 2,2'-azoisobutyronitrile (AIBN) were obtained from Merck Company. Yellow-GX was obtained from the Boyakhsaz Company (Iran) and used without further purification. The structure of the dye is shown in Fig. 1.

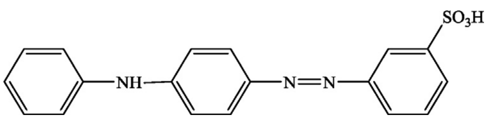

Fig. 1. Structure of Yellow GX.

2.2. Preparation of materials

2.2.1. Preparation of TE series of TiO_2 samples

In a typical synthesis, 4.5 ml of tetraethylorthotitanate and 7 ml of absolute ethanol were mixed and slightly heated until a clear solution has been obtained. Afterwards, the solution has cooled down to room temperature and stirred for another 0.5 h, followed by adjusting the pH value in the range of 3–4 by using a concentrated acid, and stirring was continued. Subsequently, the monomer of acrylamide (6 g) was added into the clear solution. The resulting solution was heated in a water bath and during the whole process, the system was continuously stirred. The solution became gradually transparent with temperature rising. When the temperature reached about 80 °C, a small amount of initiator AIBN ($C_8H_{12}N_4$) was added into the solution, and polymerization occurred quickly and the gel started swelling until it reached its equilibrium degree of swelling. Thus transparent polymeric resin was obtained without any precipitation. At last, the gel was dried at 110 °C for 12 h to yield a xerogel (as shown in Fig. 2). The obtained xerogel was homogenized using mortar and pestle and submitted to one subsequent thermal treatment. The grinded xerogel was sintered up to 450 °C, meanwhile, kept at 250 °C and 410 °C for 1 h, and at 450 °C for 5 h respectively, to gain the TiO_2 powders and also small amounts of the obtained powder samples were calcinated for 2 h at temperature of 700 °C. These products are referred to as TE series and the letter after TE is related to the kind of used acid: A, C, N, PC, S for acetic acid, hydrochloric acid, nitric acid, perchloric acid, sulfuric acid, respectively. Moreover, the inferior letter as I or II is referred to the calcination process; the inferior letter "I" was dedicated to the conventional samples which were calcined at 450 °C and also in the case of performing additional calcination at 700 °C, the letter "II" was used as subscript.

Fig. 2. The xerogel of TEN sample.

2.2.2. Preparation of TW series of TiO_2 samples

The synthesis of these materials was conducted in the exactly similar manner as reported above but instead of adding 6 g of the monomer of acrylamide, a solution of the same amount of acrylamide in 30 ml of distilled water was added. These products are referred to as TE series and the letter after TW is related to the kind of used acid: A, C, N, PC, S for acetic acid, hydrochloric acid, nitric acid, perchloric acid, sulfuric acid, respectively. Moreover, the inferior letter as I or II is referred to the calcination process; the inferior letter "I" was dedicated to the conventional samples which were calcined at 450 °C and also in the case of performing additional calcination at 700 °C, the letter "II" was used as subscript.