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Original Research

Comparative Study of Rhodamine B degradation by TiO_2 nanoparticles synthesized from titanium sec butoxide and its chloroacetato derivatves

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Abstract: TiO_2 has been well recognized as a proficient photocatalyst. TiO_2 nanoparticles have been synthesized from titanium sec butoxide (1) and its monochloroacetate derived compounds. The modifications of $Ti(O^sBu)_4$ with monochloroacetic acid in 1:1 and 1:2 molar ratios afforded $Ti(O^sBu)_3(OOCCH_2Cl)$ (2) and $Ti(O^sBu)_2(OOCCH_2Cl)_2$ (3), respectively. The use of monochloroacetic acid as a modifier allows the control of both the degree of condensation and oligomerization of the precursor. The cross linking of the gel and connectivity of the molecular building blocks are lowered in these heteroleptic alkoxides which results in the formation of gels instead of crystalline precipitate. This modification of the precursors leads to the generation of new building blocks which significantly affect the properties of the resulting TiO_2. TiO_2 powders were prepared via sol-gel method from these precursors and calcined at 400°C and 600°C for 4 h. Phase and morphology of the prepared metal oxide nanoparticles were studied. XRD patterns showed TiO_2 in anatase phase. After coating with the surfactant trioctyl phosphinoxide (TOPO), TiO_2 particles were dispersed in chloroform to study the particle size and distribution. The optical properties were studied by UV-VIS drs. The photocatalytic activity was studied over the degradation of Rhodamine B under UV radiation.

Key words: Sol-gel; XRD, DLS; UV-VIS Drs; Photocatalytic activity.

Introduction

TiO_2 has got a great concern of research due to its exceptional physicochemical properties. It has been well established for several potential applications such as semiconductors, photocatalysts, gas sensors, photoluminescent materials, H_2 generation and memory devices (1-4). Though Juillet and Teichner (5), Kato et al. (6), McLintock et al. (7) and some others observed the photosensitivity of titania, it was the contribution of Fujishima and Honda (8) that popularized TiO_2 as a photocatalyst. Like other metal oxides, it is hard, thermally stable and chemically resistant. There are three well known polymorphs of TiO_2: anatase (tetragonal, density = 3.79 g/cm^3), brookite (orthorhombic, density = 4.12 g/cm^3), and rutile (tetragonal, density = 4.25 g/cm^3).

Sol-gel method is proven to be advantageous and reproducible for the synthesis of high purity metal oxide nanomaterials. The main advantages of this process lie in the low cost processing, ease of fabrication, high homogeneity, versatility of processing and low processing temperatures. Titanium (IV) alkoxides serve as one of the best precursors for sol-gel route. These are highly susceptible to hydrolysis. This hydrolytic instability can be controlled by incorporating hydroxylated nucleophilic ligands such as chlorocarboxylic acids. Small substitutions in the alkoxides by these ligands change their properties like volatility, solubility, oligomerisation and ultimately the characteristics of final nanomaterial.

Phase and morphology are the two main parameters to decide the ultimate performance of the nanocrystalline TiO_2 for various applications. Heat treatment plays key role in affecting phase transformation and morphology, and accordingly crystallinity, porosity, surface area and surface hydroxyl groups are influenced. Crystallinity increases and the surface area decreases with the increase in calcination temperature. Slow heating rates provide relatively mild conditions for phase transformation (9). Preparation methods and precursors also impart influence to the phase transformation. Anatase is the most favorable phase for solar energy conversion and photocatalysis. Metal oxide nanoparticles (NPs) serve as potential photocatalysts (10). Morphology of the metal oxide nanoparticles (surface area, porosity etc.) decides their photocatalytic activity for the degradation of organic pollutants from water.

The present work deals with the effect of temperature on phase formation and size of TiO_2 obtained by sol-gel method of chemically modified titanium sec butoxides. Titanium sec-butoxide (**1**) and its monochloroacetic acid modified compounds $Ti(O^sBu)_3(OOCCH_2Cl)$ (**2**) and $Ti(O^sBu)_2(OOCCH_2Cl)_2$ (**3**) were used as precursor alkoxides.

Materials and Methods

All the procedures before sol-gel were performed under argon atmosphere using standard Schlenk technique. Titanium sec butoxide was prepared from $TiCl_4$ (Aldrich) and 2-butanol (Aldrich) by ammonia method and purified by vacuum distillation. Monochloroacetic acid (Aldrich) was used as received. Synthesis of the precursor alkoxides are discussed elsewhere (11). Microprocessor Controlled Furnace was used for the cal-

cinations of the samples. X-ray diffraction pattern were recorded on SEIFERT XRD 3003 PTS Diffractometer System, using CuKα X rays (1.5418 Å). Particle size distribution in chloroform dispersion was recorded by Nanotrac particle analyser.

General method of synthesis of TiO_2:

The precursor titanium alkoxide (1 mmol) was taken in 2-butanol (15 ml) and the solution was cooled to -80°C followed by dropwise addition of 10 mmol distilled water over 4 h with continuous stirring. The pH of water was adjusted at 2 by using conc. HCl. It was allowed to reach to room temperature slowly leading to the formation of a gel. The obtained gel was left at room temperature for 48 h for aging. It was dried at 90°C for 12 h to remove solvents and other volatilities to provide off white - white powder. It was calcined at 600°C for 4 h.

General method for preparation of TiO_2 dispersion in chloroform

100 mg of the TiO_2 powder was stirred with 1 g of TOPO in 5 ml chloroform for 12 h. It was then centrifuged at 1500 rpm for 10 minutes. The supernatant was collected in another vial and excess methanol was added to it until turbidity appeared and the mixture was centrifuged at 2000 rpm for 10 minutes to get the precipitate. The precipitate was re-suspended in chloroform (10 ml) and this suspension was used for analysis based on light scattering. The final value was calculated by taking mean of the three runs for each sample.

Results

XRD analysis

XRD patterns of synthesized TiO_2 powders calcined at 400°C and 600°C for 4 h. are shown in Figure 1. The peaks at 2θ values 25.3, 37.8 and 48.0 are the diffractions corresponding to (101), (004) and (200) planes of anatase form of TiO_2. This phase is stable up to 600°C heating with all the used precursors. The average crystallite size was determined by Scherer equation and the average grain sizes of TiO_2 synthesized from **1**, **2** and **3** at 600°C were found to be 10 nm, 13 nm and 15 nm, respectively.

DLS measurements

Figure 2 shows the particle size of TOPO coated TiO_2 obtained from different precursors. TOPO coated TiO_2 obtained from $Ti(OBu^s)_4$, $Ti(OBu^s)_3(OOCCH_2Cl)$ and $Ti(OBu^s)_2(OOCCH_2Cl)_2$ found to display the secondary particle sizes of 174 nm, 165 nm and 312 nm with almost uniform distribution.

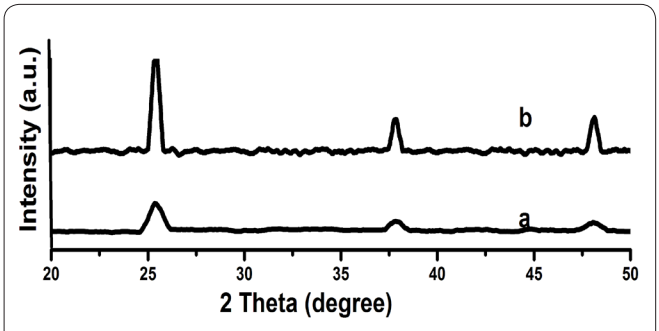

Figure 1. XRD paterns of TiO_2 synthesized from **2** calcined at (a) 400°C and (b) 600°C.

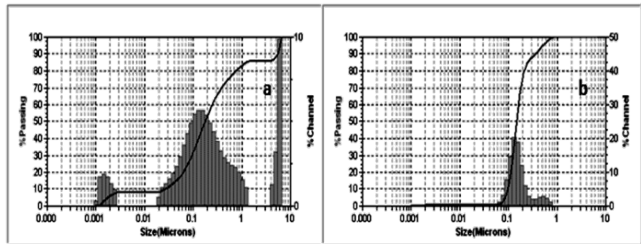

Figure 2. Size and distribution of TOPO coated TiO_2 nanoparticles in chloroform obtained from (a) 2 and (b) 3.

Optical properties

The optical property of the synthesized titanium dioxide nanoparticles were studied by UV-VIS drs. For the measurement, the nanoparticles were pressed into thick tablet, and placed at the entrance port of the integrating sphere. Figure 3 display the obtained reflectance spectrum. The synthesized TiO_2 nanoparticles exhibit the characteristic spectrum of TiO_2 with the fundamental absorbance edge at ~ 385 nm. The band gaps were found to be 3.1-3.2 eV for all prepared samples as calculated by Tauc Plot (10).

Photocatalytic activity

The photocatalytic efficiency was studied by the degradation of Rhodamine B (RhB) by TiO_2 under UV radiation. In each experiment TiO_2 was added to 50 ml water and sonicated, followed by addition of RhB and exposure to UV light (λ=365 nm) irradiation at 25°C. To attain adsorption–desorption equilibrium it was stirred in the dark for 45 min. After every 15 minutes aliquot of 3.0 ml was withdrawn and processed to determine the concentration of left over dye in the solution by the change in the intensity of absorption (Figure 4). The degradation of RhB was found to be approximately 80%, 85% and 82% with the precursors 1, 2 and 3, respectively.

Discussion

In XRD (JCPDS card no. 21-1272), the peak broadening decreases with the increase in calcination tempe-

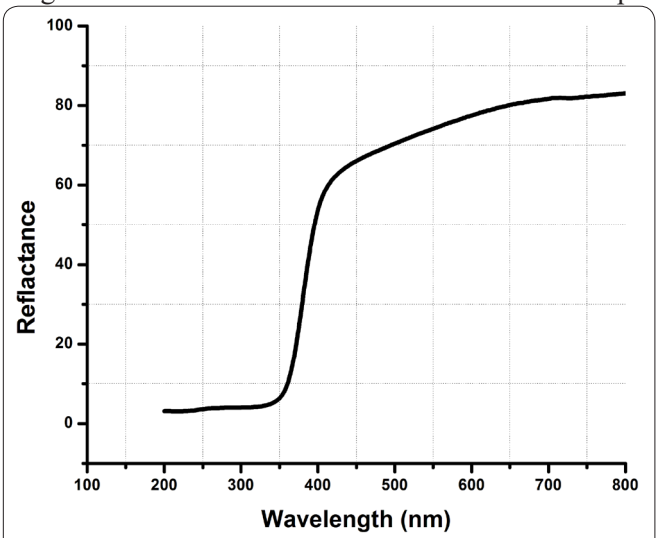

Figure 3. Solid state UV VIS reflectance spectrum of TiO_2 nanoparticles.

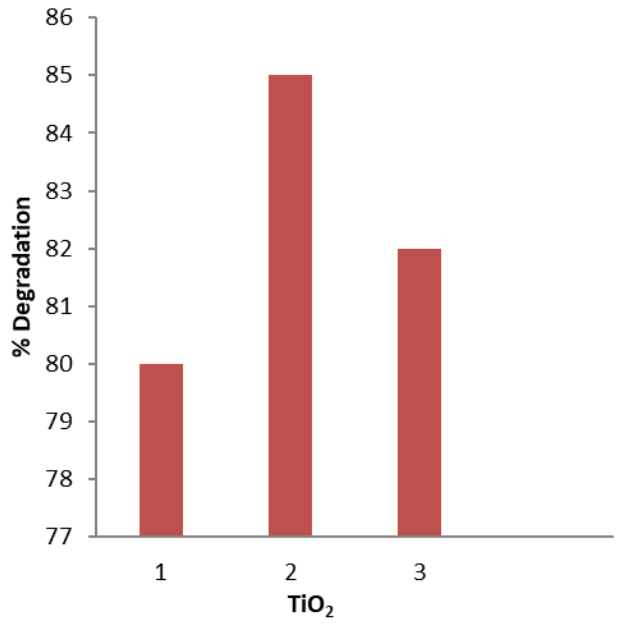

Figure 4. Degradation (%) of Rhodamine B under UV irradiation by TiO_2 nanoparticles.

rature. Notably the particle size increases with the increase in calcination temperature and with the increase in number of carboxylate groups in modified precursors. This result points towards a kind of structure –property relationship between the precursor and the final oxide in the sol-gel process.

TiO_2 nanoparticles were suspended in chloroform after coating with TOPO and characterized by particle size analyzer based on light scattering. To make stable dispersion of TiO_2 nanoparticles in chloroform, surfactant trioctyl phosphinoxide (TOPO) is used. It can be seen that the chloroform dispersions of TOPO coated TiO_2 particles derived from different precursors exhibit different particle sizes. Notably, the size of TiO_2 particles obtained from the parent precursor **1** was different than those obtained from the modified alkoxides. This clearly shows the chemical modification of the precursor has effect on the properties on the resulting metal oxides both as solid powders and suspensions. Figure 2 shows the comparison of particle sizes of TOPO coated TiO_2 obtained from **1**, **2** and **3**. Evidently, with increase in the number of the carboxylic groups in the precursor size of the resulting TOPO coated particles decreases. The distribution of particles in chloroform is more or less uniform. Distribution of particles becomes more uniform with the increasing percent of chloroacetate ligand in the precursor alkoxides.

The semiconductor nanoparticles degraded dye by a series of photochemical reactions. When the semiconductor absorbs photon of energy equal to or more than its band gap, an electron-hole pair is generated in the valence band and conducting band. These charge carriers are responsible for the photocatalytic effect. The concentration of remaining dye in solution is detected by the change in absorption intensity in the UV-Vis absorption spectra. It is found that the degradation reaction follows pseudo-first order reaction.

It may be concluded that TiO_2 nanoparticles are synthesized from sol-gel method from the titanium sec butoxide and its monochloroacetato derivatives. It is seen that the sol gel derived particles are in anatase phse and the aggregation of nanoparticles in chloroform dispersions can be tailored by modifying the titanium sec butoxide with monochloroacetate group. The photocatalytic activity of TiO_2 nanoparticles was examined by the degradation of Rhodamine B under UV irradiation.

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