On the synthesis, characterization and photocatalytic applications of nanostructured TiO₂

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Abstract. Nanocrystalline semiconducting materials are attracting much attention due to their potential applications in solar energy conversion, nonlinear optics, and heterogeneous photocatalysis. In the present investigation, we have synthesized nanostructured TiO₂ photocatalysts, which have been used in the photocatalytic degradation of phenol (one of the most common water pollutants). These catalysts have been prepared through sol–gel technique using titanium tetra-isopropoxide as a raw material for synthesis. Characterization techniques such as XRD, SEM and TEM have been employed for structural/microstructural investigations. XRD results show that the as synthesized TiO₂ nanopowder exhibit anatase phase, TiO₂. The average sizes of the TiO₂ nanopowders are ~5–10 nm. The optical properties of the samples were investigated through UV-visible and fluorescence techniques. It has been observed that absorption edge corresponds to ~410 nm (band-gap, ~3.02 eV). The emission peak in the fluorescence spectrum at ~418 nm corresponds to the bandgap energy of ~2.97 eV. Concentration of phenol (initial concentration, ~100 ppm) with illumination time was monitored by measuring the absorbance of pure and illuminated phenol through UV-visible spectrophotometer. Salient feature of this study relates to the fact that the present sol–gel synthesized TiO₂ nanopowders have been found to be better photocatalysts for phenol degradation than the presently employed commercial TiO₂ (P-25, Degussa) photocatalyst. Thus, whereas phenol concentration, with the presently synthesized TiO₂ nanopowders, the concentration of phenol decreases up to ~32% but for commercial TiO₂ nanopowder (P-25, Degussa), it decreased only up to ~25%. The improved surface area is considered as an important factor for the aforesaid decrease in phenol concentration.

Keywords. Sol–gel method; nanostructured TiO₂; P-25 Degussa; photocatalytic degradation.

1. Introduction

Photocatalytic effects of the semiconductors have been of much interest from the viewpoint of solar energy utilization. They have been used to convert pollutants present in the waste streams to innocuous products (Kutal and Serpone 1993; Junge and Grange 2000; Yuan *et al* 2002; Srinivasan *et al* 2006). The fact, that among the other common water pollutants, the organic pollutants such as phenol undergoes photocatalytic degradation to produce less harmful products, indicates some potential for photocatalytic treatments of waste water utilizing semiconductor and sunlight. Phenol is a refractory and also a common compound present in the industrial wastes. The photocatalytic decomposition of phenol is one of the attractive methods which utilizes solar energy and a semiconductor photocatalyst. The decomposition process of phenol generally obeys the first order reaction kinetics (Kawaguchi and Vejima 1983). The photocatalytic decomposition of phenol has not, however, been clarified in detail yet. Photocatalytic decomposition of phenol present in water is a straightforward process for lowering the concentration of phenol to safe limit.

Titanium dioxide (TiO₂) offers a great potential as a catalyst material for its use in the industrial technology for detoxifying wastewater (Kutal and Serpone 1993) and it has been widely investigated as a key material for applications in photovoltaic cells, batteries, chemical sensing (Varghese *et al* 2003), optical emissions, photonic crystals, catalysis, photocatalysis (Livraghi *et al* 2005) and environmental purification (Homyara *et al* 2001). Anatase TiO₂ electrodes are used in solar cells, lithium batteries and electrochromic devices (Hagfeldt and Gratzel 1995; Kavan *et al* 2000; Gratzel 2001). Non-toxicity, environmental compatibility and low prices are the other practical advantages of TiO₂. As a catalyst and/or catalyst support, it is employed in the processes of photo degradation of chlorine hydrocarbons. Anatase phase of TiO₂ is important because of its higher Fermi level, lower capacity to absorb oxygen and higher degree of hydroxylation (i.e. number of hydroxy groups on the surface) (Maruska and Glesch 1978; Gerischer and Heller 1992).

Nanocrystalline materials are attracting much attention due to their increasing applications in the solar energy conversion, nonlinear optics and heterogeneous catalysis. Recently, efforts have been made to obtain nanostructured TiO₂-based materials with large specific surface area. The energy band structure and photophysical, pho-

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tochemical and surface properties for nanostructured TiO_2 are quite different than those of its bulk counterparts due to the quantum size effect.

A variety of methods have been developed so far for the synthesis of TiO_2 nanoparticle, for example, d.c. magnetron sputtering (Loebl *et al* 1994), hydrothermal (Wu *et al* 2002; Cozzoli *et al* 2003), solvothermal method (Kim *et al* 2003) and emulsion precipitation. In addition, an attractive method for the preparation of nanostructured TiO_2 , is sol-gel method (Wilke and Breuer 1999; Francisco and Mastelaro 2002; Frindell *et al* 2002). It is known that the efficiency of TiO_2 as a catalyst is higher when it consists of a single phase in the anatase form (Francisco and Mastelaro 2002; Diebold 2003).

Keeping the above aspects in view, we report in this paper the synthesis of a single phase, ultra fine nanostructured TiO_2 photocatalyst through cost effective sol-gel technique using titanium tetra-isopropoxide as a precursor material. The composition and crystallinity of these structures have been determined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The optical absorption spectra of the as synthesized TiO_2 powders have been investigated through UV-visible and photoluminescence techniques. The photocatalytic degradation of phenol has been studied with both the photocatalyst in the reactor fabricated with a quartz tube with a fused silica tube inlet for purging oxygen during illumination (light intensity being $\sim 85 \text{ mW cm}^{-2}$) and an outlet for the collection of phenol solution. The concentration of phenol before and after illumination has been monitored by measuring the absorbance of phenol solution through UV-visible spectrophotometer (Varian, Make USA).

2. Experimental

2.1 Preparation of TiO_2 photocatalyst

The sol (nearly transparent) of TiO_2 was prepared by mixing titanium iso-propoxide, $\text{Ti}[\text{OC}_3\text{H}_7]_4$ in iso-propanol (solvent). Water (H_2O) and acetic acid (CH_3COOH) were added to the above solution for hydrolysis polycondensation reaction, where the acetic acid was used as a chelating agent. The composition for the synthesis of TiO_2 sol (stock solution) was $\text{Ti}[\text{OC}_3\text{H}_7]_4/\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ —12 : 10 : 150 : 5 in volumetric ratio. The above solution was heated at $\sim 80^\circ\text{C}$ for ~ 5 h with vigorous stirring. When the solution becomes semi-transparent, nearly 1 mL of $\sim 70\%$ HNO_3 was added to the above solution in order to prevent the agglomeration of the particles present in the sol. The stirring was continued for ~ 2 h and a transparent solution was obtained. This solution was then concentrated in vacuum until a viscous sol was obtained. This sol was dried in the oven at $\sim 100^\circ\text{C}$ for ~ 12 h. The powder was derived by drying the above

viscous sol at $\sim 100^\circ\text{C}$ for nearly 5 h. This powder was then calcined at $\sim 450^\circ\text{C}$ for ~ 2 h in order to improve the crystallinity of the powder samples.

It should be pointed out that the synthesis of pure TiO_2 in the present investigation was focused on preparation of suitable TiO_2 nanopowder for use in phenol degradation. There have been other studies on the synthesis of doped TiO_2 nanopowders aimed at preparation and characterization of their doped versions (Francisco and Mastelaro 2002; Frindell *et al* 2002).

2.2 Photocatalytic measurements

The photocatalytic measurements were carried out in a reactor consisting of a quartz tube having its diameter, ~ 3 cm, with an inlet tube for oxygen purging during photocatalysis and another outlet for the collection of samples from the reactor at different time intervals. Initially ~ 2.5 g of as synthesized nanostructured and the same amount of commercial TiO_2 (P-25, Degussa) photocatalyst in ~ 400 cc of ~ 100 ppm phenol solution was taken. Phenol solution (~ 400 ml by volume) was prepared by dissolving phenol crystals in double distilled water. During illumination, oxygen gas was purged into the solution with the help of porous fused silica tube by an external cylinder. Oxygen was bubbled through this solution at a rate of ~ 200 cc/min. During the reaction, solution was maintained at 25°C and ~ 3 cc of the samples was collected at given time intervals e.g. 10 min. After being sampled, the suspension was centrifuged and the centrifugates were subjected to further analysis. The schematic diagram of the fabricated photocatalytic reactor along with the other related accessories are given in figure 1.

3. Results and discussion

3.1 Structural and microstructural characterizations

Figure 2 represents the XRD pattern of TiO_2 powders obtained through sol-gel method. The XRD (X-Pert PRO, PANalytical) pattern of the as-prepared TiO_2 showed the presence of very broad peaks. The broad peaks indicate either the TiO_2 nanopowder containing particles of very small crystallite size or particles which are semi-crystalline in nature (Yeha *et al* 2004). All the diffraction lines have been found to correspond to anatase crystalline phase of titanium dioxide. It should be noted that only anatase TiO_2 can be detected and no rutile phases have been found for these TiO_2 powder samples. This can be attributed to the contribution of the low concentration of oxygen vacancies hindering the transformation of anatase to rutile phase (Rulison *et al* 1996). As it has been mentioned the efficiency of the TiO_2 as a catalyst is higher when it consists of a single phase (anatase phase) (Francisco and Mastelaro 2002; Diebold 2003). The TiO_2

which has been synthesized in the present investigation consists of only anatase phase, hence, it can act more effectively as a catalyst.

Figure 3(a and b) shows the SEM (Philips, XL-20) micrograph of the TiO₂ powder samples. It is clear that very fine particles of TiO₂ are joined with each other forming the cluster of particles. It appears from the SEM micrograph that the average crystallite size of pure TiO₂ are in the range of ~40–50 nm. The TEM (Tecnai G20, 200 kV) images and corresponding selected area electron diffraction patterns of the TiO₂ powder has been shown in figure 4(a and b). This micrograph reveals that the nanopowder consists of very fine particles corresponding to only anatase phase of TiO₂.

Figure 1. Schematic diagram of the fabricated photocatalytic reactor.

Figure 2. XRD pattern of TiO₂ photocatalyst prepared through sol-gel method.

3.2 Optical characterization

UV-visible absorption spectrum was carried out in order to characterize the optical absorbance of the TiO₂ nanopowder. The absorption spectrum of pure TiO₂ is shown in figure 5 with a value of the absorption edge at ~410 nm. Due to the improved grain size for modified TiO₂ photocatalyst, the absorption edge undergoes a red-shift to some extent. The optical bandgap energy can be estimated by using the following equation for a semiconductor

$$\alpha = \left[\frac{(K(h\nu - E_g)^{n/2}}{h\nu} \right],$$

where α is the absorption coefficient, K a constant, E_g the bandgap, and n is equal to 1 for a direct transition. The bandgap can be estimated from a plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$). The intercept of the tangent to the plot will give a good approximation of the bandgap energy for this direct bandgap material (shown in the inset of figure 5) (Wang and Herron 1991). The bandgap of the TiO₂ powder was calculated to be ~3.02 eV.

Figure 3. (a&b). SEM images of nanostructured TiO₂ photocatalysts.

Fluorescence spectra were recorded at room temperature on the TiO_2 photocatalysts with the excitation wavelength, 350 nm and has been shown in figure 6. This spectrum possesses peaks at ~ 418 for pure TiO_2 samples. In this case, the band peaking at 427 nm can be ascribed to electron transition mediated by defects levels in the bandgap such as oxygen vacancies formed during sample preparation (Vanheusden *et al* 1996). Oxygen vacancies have been considered as the most common defects and usually act as radiative centres in luminescence processes (Gu *et al* 2004). In the present case, due to TiO_2 nanostructures with high surface-to-volume ratio, favour the existence of large quantities of oxygen vacancies. The peak positions in the corresponding fluorescence spectrum represent the bandgap energy of TiO_2 powder photocatalyst. It may be noted that these peaks correspond to the bandgap energy of ~ 2.97 eV. These results are quite consistent

with the bandgap energy calculated by UV measurements techniques (i.e. ~ 3.02 eV).

3.3 Results on photocatalytic degradation of phenol in water

The photocatalytic analysis using UV-vis light irradiation of phenol in the aqueous solution was examined in the photocatalytic reactor as shown in figure 1. UV-light was made to fall on the reactor through the tube walls. To determine the concentration of phenol in the solution, samples were collected after every 10 min interval upon UV-induced degradation of phenol. The concentration of

Figure 4. (a&b). TEM image and corresponding electron diffraction pattern of nanostructured TiO_2 photocatalyst.

Figure 5. Absorption spectrum of nanostructured TiO_2 photocatalyst powder. Inset shows the corresponding plot of $(\alpha h\nu)^2$ vs photon energy of the sample.

Figure 6. Fluorescence spectra of nanostructured TiO_2 powder. The excitation wavelength is 350 nm.

Figure 7. Variation of concentration of phenol with irradiation time using as synthesized nanostructured TiO₂ and commercial TiO₂ (P-25, Degussa) photocatalyst. (The excitation wavelength is ~ 269 nm).

phenol was determined by UV-visible absorption spectroscopic technique, where the absorbance was measured at a fixed wavelength (e.g. ~ 269 nm) for all the samples. Possible mechanism for photocatalytic degradation of phenol using nanostructured TiO₂ films as photocatalyst has been described by us (Srivastava *et al* 2005).

Variation of phenol concentration using TiO₂ photocatalysts after irradiation as a function of time have been shown in figure 7. It can be seen that the concentration of the phenol decreases from 100% (initial concentration of phenol, ~ 100 ppm) to $\sim 68\%$ (final concentration of phenol, ~ 68 ppm) after ~ 1 h illumination. The total decrease in the phenol concentration using nanostructured TiO₂ synthesized in the present investigation is $\sim 32\%$, which is nearly the safe limit of the phenol concentration in the solution. On the other hand, the decrease in phenol concentration employing commercial TiO₂ nanopowder (P-25, Degussa), is only $\sim 25\%$. Thus the TiO₂ nanopowder prepared in the present investigation is more effective than the degradation of phenol through the commercial TiO₂ nanopowder. Also analysis of water after photocatalytic degradation showed that no other compounds including any toxic components get formed. Thus the only effect of photocatalytic reaction is the dissociation of phenol.

4. Conclusions

Based on the above results, it can be concluded that ultrafine nanostructured TiO₂ photocatalysts have been synthesized through a cost effective (i.e. sol-gel) technique. XRD results show that the as synthesized TiO₂ photocatalysts consist of a single phase TiO₂ nanopowder (i.e. anatase phase). SEM and TEM investigations revealed that

the average sizes of the TiO₂ particles are fine and are in the nanometric range. Optical characterizations revealed that the bandgap of the as synthesized TiO₂ photocatalysts are ~ 3.02 eV. The emission peak in the fluorescence spectrum at ~ 418 nm corresponds to the bandgap energy, ~ 2.97 eV. Concentration of phenol (initial concentration, ~ 100 ppm) with illumination time was monitored for the as synthesized TiO₂ and commercial TiO₂ (P-25, Degussa) photocatalysts and it was found that the decrease in the phenol concentration was significant for the as synthesized TiO₂ photocatalysts ($\sim 32\%$), whereas for the commercial TiO₂ (P-25, Degussa) photocatalysts, the decrease in phenol concentration was only $\sim 25\%$.

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