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Removal of Methylene Blue Using Prepared Nano Titanium Dioxide (TiO_2) Photocatalyst

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Abstract

The technological and economic importance of photocatalysis has increased considerably over the past decade. Improvements and performance have been strongly correlated to advances in nanotechnology. The introduction of nano particulate photocatalysts has tremendously enhanced the catalytic efficiency of specific materials. Photocatalysis based on nano catalysts is a very promising method for the treatment of contaminated water. Nano sized anatase TiO_2 particle was prepared by time consuming cost effective sol-gel method, the synthesized particles was examined and their characteristics were investigated. The average grain size of the nano particle is nearly 20nm. The UV-Visible spectrum shows the absorbance of 356 nm which shows the band gap 3.7 eV. Photocatalytic activity of nano particle was evaluated by photo degradation of Methylene blue.

Key words : Methylene Blue ; Photocalyst ; Scanning electron microscope ; Transmission electron microscope.

1. INTRODUCTION

Synthetic dyes are suspected to be carcinogenic and toxic for human and aquatic life. There are several traditional methods available to treat the colored wastewater. Every method has its own advantages and limitations. Generally these methods transfer dye from water to solid. Hence, further treatment in many cases is necessary, advanced oxidation processes (AOPs) are alternative methods for the complete degradation of dye. Many processes have been proposed over the years and are currently used to remove organic toxins from wastewaters. Current treatment methods for these contaminants, such as adsorption by activated carbon and air stripping, merely concentrate the chemicals present, by transferring them to the adsorbent or air, but they do not convert them into non-toxic wastes. Thus, one of the major advantages of the photocatalytic process over existing technologies is that there is no further requirement for secondary disposal methods (Beydoun et al. 1999). Nanocrystalline photocatalysts are ultra-small semiconductor particles which are a few nanometers in size. During the past decade, the photochemistry of nano semiconductor particles has been one of the fastest growing research areas in physical chemistry. The interest in these small semiconductor particles originates from their unique photophysical and photocatalytic properties (Bahnemann et al 1993).

Nanomaterials reveal new functions which are derived both from the geometric size of

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nanostructures and from their material-specific properties. In the investigation of material properties, compounds that are employed as Photocatalysts include oxides such as TiO_2, ZnO, Nb_2O_5, WO_3, SnO_2 and ZrO_2, as well as sulfides such as CdS and ZnS (Ho chang et al. 2004; Abdolreza Nilchi et al. 2011; Ho Chang et al. 2004; Li Fa-Tang et al. 2007; Huei-Siou Chen et al. 2011.) Among the various photocatalytic materials that have been used, most attention has focused on titanium dioxide (TiO_2) as a photocatalyst in diverse areas ranging from water and air treatment to self-cleaning surfaces (Yi et al. 1990). TiO_2 is largely used as a photocatalyst due to its beneficial characteristics of high photocatalytic efficiency, physical and chemical stability, low cost and low toxicity (Ho chang et al. 2004; Abdolreza Nilchi et al. 2011).

Many methods have been developed to control the size of nanoparticles such as Langmuir– Blodgett films (Yi et al. 1990), vesicles (Youn et al. 1988), and reverse microemulsions (Fendler et al. 1987). The chemical and physical properties exhibited by these materials depend, among others, on both the composition and the degree of homogeneity. Therefore, different synthesis strategies have been developed (Toba et al. 1994; Gao et al. 1999) such as co-precipitation, flame hydrolysis, impregnation, chemical vapour deposition, etc. The sol-gel route has demonstrated a high potential for controlling the bulk and surface properties of the oxides (Ward et al. 1995; Liu et al. 1994; Schraml-Marth et al. 1992). Depending on the drying conditions the binary oxides could be obtained as aerogels, either by supercritical drying (Pajonk et al. 1991; Dusi et al. 1999) or by silanization of the material

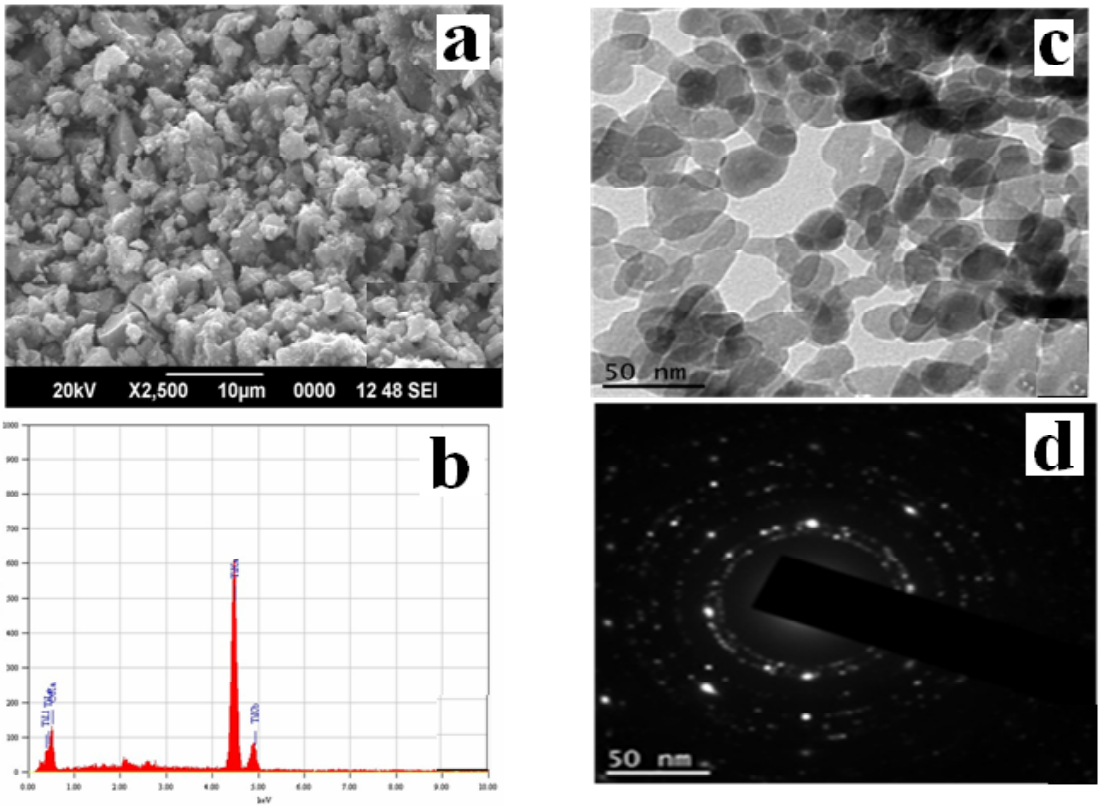

Fig. 1 : a) SEM image of TiO_2, b) EDAX analysis of TiO_2, c) TEM image of TiO_2, d) SAED

previously to a conventional drying (Sotelo et al. 1999). Additionally, non-hydrolytic sol-gel routes have been also reported in the literature (Hay et al 1998).

In this work, we report photocatalytic decomposition of methylene blue by Sol-gel derived TiO_2 nanoparticles. The composite was analyzed for grain size by XRD and TEM, surface morphology by SEM-EDAX, metal oxide bonds by FTIR and band gap, photocatalytic decomposition studies by UV.

2. EXPERIMENTAL

2.1. Materials

All reagents used were of analytical grade purity and were procured from Merck Chemical Reagent Co. Ltd. India.

2.2. Preparation of TiO_2 nanoparticles

In the synthesis of TiO-$_2$ particles, Titanium tetra isopropoxide was used as a precursor and was mixed with acid, ethanol and deionised water mixture, stirred for half an hour, in pH range of 1-2. 10 ml of deionised water was added to the above mixture and stirred for 2 hours at room temperature. Finally the solution was dried at room temperature and the powder was heated at 120°C for 1 hour.

2.3. Characterization

The prepared nanoparticles were characterized for the crystalline structure using D8 Advance X-ray diffraction meter (Bruker AXS, Germany) at room temperature, operating at 30 kV and 30 mA, using Cu*Ká* radiation (*ë* = 0.15406 nm).

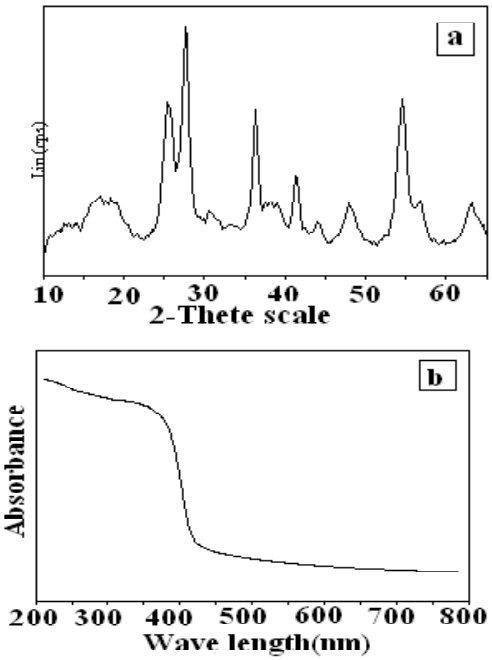

Fig. 2. : a) XRD patterns of TiO_2, b) FTIR spectra of TiO_2 nanoparticles

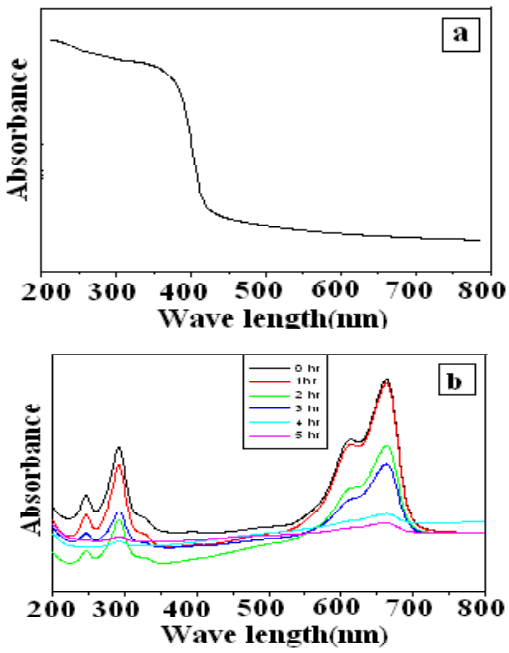

Fig. 3 : .a) UV-visible spectra of TiO_2, b) photocatalytic decomposition of MB by TiO_2 nanoparticles

The crystal size was calculated by Scherrer's formula. Surface morphology was studied by using SEM-EDS (Model JSM 6390LV, JOEL, USA), UV–Vis diffuse reflectance spectra were recorded with a Carry 5000 UV-Vis-NIR spectrophotometer (Varian, USA) and FTIR spectra were measured on an AVATAR 370-IR spectrometer (Thermo Nicolet, USA) with a wave number range of 4000 to 400 cm^{-1}.

Photocatalytic activity of the as-prepared particles for the environmental application was evaluated by measuring the photo degradation of methylene blue (MB) in water under sunlight irradiation. The initial concentration of MB was 50mgl and the concentration of nanoparticles was 1.0g l^{-1}.

3. RESULTS AND DISCUSSION

The topographical analysis of TiO_2 nanoparticles were examined through electron microscopic methods. The SEM, TEM and EDAX images of the as prepared TiO_2 nanoparticles are shown in the Fig.1. The scanning electron microscopic images show the uniform sized particles with spherical morphology. Transmission electron microscopic analysis strongly supported the nanophase formation of TiO_2 nanoparticles. The average particle size measured from TEM was found to be in the range of 15-20nm. From the TEM scale it was clearly observed that the particles exhibited in spherical in shape and in nanometer size. The average particle size measured from TEM was slightly varied from the particle size evaluated from diffraction method since in X-ray analysis it was assumed that the crystallites are formed without any local strain. The monodispersed state of the system was clearly identified from the study. The selected area electron diffraction pattern showed spotted as well as oriented ring pattern that further established the high crystalline and nano dimensional state of TiO_2 particles.

Figure .2 a. shows the XRD patterns of sol-gel derived TiO_2 nanoparticles. The crystallite type of the TiO_2 nanoparticles was the pure anatase. The most intense reflection at $2\theta = 25.3^o$ is assigned to anatase (d_{101}). The powders showed the crystalline pattern and the observed d-lines match the reported values for the anatase phase. The average crystallite size was determined by carrying slow scan of the powders in the range 24–27° with the step of $0.01^o min^{-1}$ from the Scherrer's equation using the (101) reflections of the anatase phase assuming spherical particles. An estimate of the grain size (G) from the broadening of the main (101) anatase peak can be done by using the Scherrer's formula below:

$$G = 0.9\lambda \setminus \Delta(2\theta) \cos \theta$$

Where λ is the Cu Kα radiation wavelength and $\Delta(2\theta)$ is peak width at half-height. The nanocrystallite sizes were found to be 20 - 25nm

Figure. 2b represents the FT-IR spectra of sol-gel derived TiO_2, nano particles. The peaks at 3400 and 1650cm^{-1} in the spectra are due to the stretching and bending vibration of the -OH group. In the spectrum of pure TiO_2, the peaks at 550cm^{-1} show stretching vibration of Ti-O and peaks at 1450cm^{-1} show stretching vibrations of Ti-O-Ti.

Figure. 3a represents the UV–V absorption spectra of composite after drying showing a good transparency between 400 and 800nm. Actually, the band edge of bulk anatase is and is also shown on the same graph. After heat treatment, a small modification was observed, due to the presence of anatase nano crystallites. Indeed, the gel was highly transparent, and any absorbance which appeared at energies below the bandgap energy was a result of interference fringes and of the high refraction index of Titania.

3.1. Photocatalytic decomposition of MB

Figure. 3b. shows the photocatalytic decomposition of MB by TiO_2 nanoparticles. The UV-Visible spectrum of initial solution and product under sunlight for 5 hr reaction over TiO_2 was

recorded to determine how deeply MB was decomposed. The primary absorption peaks of the dye solution show 666nm in the range of 200-800nm. As the reaction time increases the peaks disappear gradually and the full spectrum pattern changes obviously after 5 hr, at the end of the 5th reaction time there is no evident absorption peak observed. It indicates that the main chromophores in the original dye solution are destroyed with photocatalytic reaction and proves that the methylene blue was decomposed in the UV/TiO_2 system.

4. CONCLUSION

Anatase phase TiO_2 nanoparticles were synthesized by sol-gel method. XRD and TEM shows the particles were in nano size. An EDAX and FTIR spectrum shows presence of metal oxide bonds. In 5 hour reaction time the concentration level of MB solution lowered down significantly, which indicates TiO_2 nanoparticles effectively decompose the dye molecules.

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