

# Synthesis and photophysical studies of PVP capped Titania Nanostrips for photocatalytic applications

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PVP capped Titania (TiO<sub>2</sub>) nanostrips were prepared by co-precipitation method using titanium (IV) isopropoxide, with ethylene glycol as a solvent and H<sub>2</sub>O as a hydrolyzing agent. The synthesized samples were subjected to powder XRD analysis, which confirms anatase phase formation of TiO<sub>2</sub>. Strip-like morphology was observed using high resolution scanning electron microscopy (HRSEM). Crystallinity of the synthesized sample was analysed by high resolution transmission electron microscopy (HRTEM). Band gap estimated by UV-Reflectance spectroscopy with the value of 3.54 eV and the surface area of 91.87 m<sup>2</sup>/g of the sample were calculated by BET analysis and its functional groups were analyzed through FTIR spectroscopy. The photocatalytic activity of synthesised titania nanoparticles was studied on the photodegradation of rhodamine in water under ultraviolet light irradiation.

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## 1. Introduction

Nanocrystals of transition metal oxides have attracted a great deal of attention from researchers in various fields due to the numerous technological applications. Among them titania nanocrystals have been most intensively studied owing to their potential applications such as solar cells, photocatalysts and photochromic devices. TiO<sub>2</sub> photocatalyst has attracted much interest due to its capability of degrading a wide range of both gaseous and aqueous contaminants [1-3]. Photocatalysis aided by titanium dioxide nanoparticles is used in removing the organic chemicals which occur as pollutants in wastewater effluents from industrial and domestic sources. However, because of its wide band gap, only ultraviolet with the energy of more than 3.2 eV can stimulate its photocatalytic action.

TiO<sub>2</sub> is an indirect-bandgap semiconductor, which turns to high-energy state by receiving light energy and releases electrons from its illuminated surface. Titanium dioxide is a harmless substance widely applied in various fields such as cosmetics, toothpaste, extenders for medicines and coating. It was also an attractive multi-purpose material in gas sensors, catalytic oxidation of carbon monoxide and the photocatalytic decomposition of organic environmental contaminants [4]. Advanced oxidation technologies using heterogeneous photocatalysis by semiconductor oxide such as TiO<sub>2</sub> have made remarkable progress. To increase the photocatalytic activity and inhibit the photo induced electron-hole pair (exciton) recombination of TiO<sub>2</sub>, nanoparticles with large surface area are usually used. Generally, materials with

high surface area can adsorb a large amount of organic molecules. For this reason, synthesis of titania nanopowders with different structures with high surface area has been extensively studied. The direct oxidation of metals is usually exothermic and results in sintering. As a result, it is usually contradict for the preparation of oxides in nanoparticle form. While, many oxide materials can be prepared by hydrolysis in aqueous solution, it is difficult to incorporate a long-chain organic capping agent under these conditions. Many routes for preparation of oxide nanoparticles that have emerged recently are sensitive to these issues. Syntheses of transition metal oxide nanoparticles often involve water as solvent or reactant and thus result in particles with hydroxylated surfaces that influence properties of materials significantly [5-6]. Recently the phase-pure, monodisperse anatase titania nanocrystals has been synthesised with small grain size and high specific surface area [7]. The influence of TiO<sub>2</sub> particle size and morphology has also been addressed with the aim of increasing the photocatalytic efficiency of powdered materials [8-9]. One-dimensional (1D) TiO<sub>2</sub> structures on the nanoscale size regime are particularly attractive because of its unique chemical reactivity and photophysical behavior that arises when the morphology is in single direction [10].

In this present investigation, titanium dioxide TiO<sub>2</sub> nanostructures were synthesised using a well known capping agent, poly vinyl pyrrolidone (PVP) with ethylene glycol as a solvent. The structural and optical properties of the TiO<sub>2</sub> nanostructures were studied.

## 2. Experimental

High crystalline anatase TiO<sub>2</sub> nanostructures were synthesised at a temperature as low as 150°C, with water as a hydrolyzing agent following the procedure explained Wang et al [11]. Here PVP has been used as a surfactant to cap titania nanostructures. In a typical synthesis, 0.6 g of Titanium (IV) isopropoxide was added into 10 mL of ethylene glycol under vigorously stirring at ambient temperature. After 30 min, 3.0 mL DI water (resistivity 10<sup>-18</sup> mΩ) was injected into the solution. For fastening the reactions, the additional 3.0 mL of DI water was injected into the mixed solution as a hydrolyzing agent. Before heating the solution, 20 mL aqueous solution of (0.1g in 50 ml of DI water) poly (*N*-vinyl-2-pyrrolidone) PVP was added with constant stirring.

After stirring for one hour, the solution was heated to 120°C for 90 min. The stirring was done throughout the heating process. After the solution was cooled to room temperature, 20 mL of absolute ethanol and 25 mL of anhydrous ether were added simultaneously into the stock solution with duration of 10 minutes, to precipitate the nanoparticles. Initially, pH of the stock solution was measured as ~6.5 and it was increased up to ~11.5, by the addition of aqueous NaOH solution. The addition of DI water and maintaining the pH plays an important role for the formation of nanostructures by this method. Then, the precipitate was centrifuged at 4000 rpm for 10 min to separate the nanoparticles and solvent. The resultant powder was washed for several times with ethanol and water to washout the organic residue present in the sample and dried at 80°C in a hot air oven for 24 h before characterization.

X-ray diffraction pattern was recorded for the synthesised sample, with CuKα radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the range of 20°-80° (2θ) at a scanning rate of 0.05°/min. FTIR spectroscopic analysis was done to study the various stretching and bending modes present in the sample using PERKIN ELMER FTIR spectrometer. Morphology of the synthesised sample was analyzed with S-3400 Scanning electron microscopy (SEM) with accelerating volts of 15kV. For this, a small quantity of the synthesised PVP capped titania was well dispersed in ~50 ml of DI water with ultrasonication for 60 min and dried using a glass substrate. High resolution transmission electron microscopy JEOL JEM 3010 with LaB6 filament at 200 KeV was used to study the crystallinity of the synthesised TiO<sub>2</sub> nanostructure. Band gap of the TiO<sub>2</sub> was measured with CARY 5E UV-VIS diffuse reflectance mode spectrophotometer and the specific surface area of the sample was performed by using N<sub>2</sub> adsorption/desorption isotherms following Brunauer-Emmett-Teller (BET) method in a Micromeritics ASAP 2020 surface area analyser apparatus. Photodecomposition of rhodamine was used to test the photocatalytic efficiency of the synthesised titania. Irradiation was provided by a high energy mercury lamp ( $\lambda < 330 \text{ nm}$ ) of 300 W and the photocatalytic tests were performed at room temperature.

## 3. Results and discussion

### 3.1 X-ray diffraction analysis

Fig. 1 shows the powder X-ray diffraction pattern of the PVP capped anatase phase TiO<sub>2</sub> nanostructure, which indicates the obtained product is free of rutile or brookite phases. The diffraction pattern was compared with standard JCPDS data (21-1272) for the confirmation of anatase phase formation. It clearly illustrates that the phase of the as-synthesized TiO<sub>2</sub> nanostructures apparently depends on the preparation method. Beside the morphology, the crystallographic quality of nanocrystallites also impacts the properties. The Scherrer formula was used to calculate the average crystallite size from FWHM of most intense peak (101) and it was found to be 10.34 nm. It was reported that [12], titanium dioxide nanoparticles with preferred orientation and high active site density on the (001) and (101) surfaces could significantly enhance the photocatalytic efficiency. In this study high intense diffraction pattern observed by powder XRD confirms the growth of TiO<sub>2</sub> nanostrips along (101) direction.

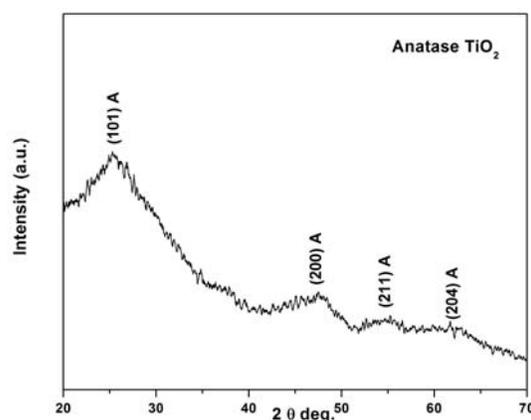


Fig. 1. Powder XRD pattern of anatase phase PVP capped TiO<sub>2</sub> nanostructures.

### 3.2 FTIR analysis

The FTIR spectrum of nanostructured TiO<sub>2</sub> is shown in Fig. 2. The band at 1454 cm<sup>-1</sup> is attributed to the Ti-O-Ti vibration which was compared for pure TiO<sub>2</sub> at 1400 cm<sup>-1</sup> [13]. A prominent band centered at 750 cm<sup>-1</sup> is attributed to Ti-O and Ti-O-Ti stretching vibration modes [14]. The peak around 1620-1640 cm<sup>-1</sup> is due to the bending vibration of the O-H bond of chemisorbed water and it was believed that broad peak around 3000-3500 cm<sup>-1</sup> and at around 1500-1650 cm<sup>-1</sup> corresponds to the surface adsorbed water and hydroxyl groups. Porous TiO<sub>2</sub> of larger surface area can offer more active sites to adsorb water and hydroxyl groups.

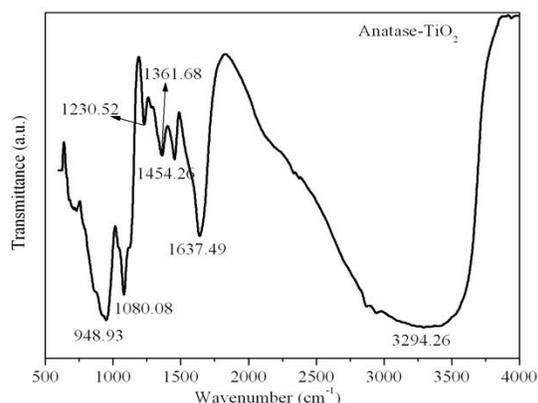


Fig. 2. FTIR spectrum of  $\text{TiO}_2$  nanostructures.

### 3.3 UV-reflectance spectra

The intercept of the tangent to the plot will give a good approximation of the band gap energy for the  $\text{TiO}_2$  by reflectance-UV spectrum at 350 nm (3.54 eV) in Fig. 3, which is higher than that of bulk titania (3.2 eV). The blue shift compared to the bulk titania may be attributed to quantum size effect due to the decrease in the crystallite size. It has been reported earlier that the ethylene glycol could greatly reduce the hydrolysis rates of titanium alkoxides. The simplicity and reproducibility of this method makes this route to be possible for large scale production.

### 3.4 Elemental and surface area analysis

It was observed that the precursor hydrolyses immediately, when the DI water (3 mL) was used, in which only  $\text{TiO}_2$  nanoparticles were obtained with no crystal faceting [11]. The composition of the synthesised titania sample was analyzed using EDAX spectrum as shown in Fig. 4. The synthesised powder shows that Ti and O are the major elements and it was confirmed that there is no other impurities present in the synthesised titania nanostructures. The measured BET surface area for the synthesised titania was  $91.87 \text{ m}^2/\text{g}$ . The observed surface area is higher compared to that of recent reports on C-doped  $\text{TiO}_2$  and Ag/C-doped  $\text{TiO}_2$  [15]. Hence, it is clear that the synthesised particles are well crystallised in the nanoscale. The effective way of controlling the particle size is to synthesis the material at low temperature and to cap particles at the desired size to prevent further growth and to provide stability through the coordinative saturation of dangling bonds on the particle surface. The poly vinyl pyrrolidone (PVP) plays a role in capping the particles well in the nanoscale regime.

### 3.5 Morphological studies

From the HRSEM image in Fig. 5 the mean length and thickness of the titania strips are estimated to be 200

nm and 20 nm respectively. It was clearly shown the formation of well defined nanostrips with uniform size distribution.

Polymer surfactant (PVP) is effective to cap the grown titania and to avoid the agglomeration of the strips together. Appropriate concentration of PVP is critical for the construction of superstructure of the synthesised nanoparticles. The capping mechanism of PVP in the growth process with the sufficient PVP may form a continuous layer to wrap the entire surface of  $\text{TiO}_2$  crystals and accelerates the growth of the nanoparticles in the particular plane to form the strip like patterns. In the absence of salt or acid, extensively agglomerated and poor crystalline  $\text{TiO}_2$  nanoparticles were formed. The presence of salt or acid is essential to synthesize the  $\text{TiO}_2$  nanocrystals with unique shapes and crystal structures [16].

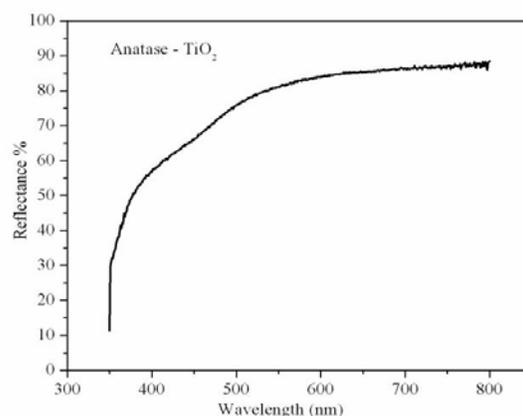


Fig. 3. UV-reflectance spectrum of anatase phase PVP- $\text{TiO}_2$  nanostructures.

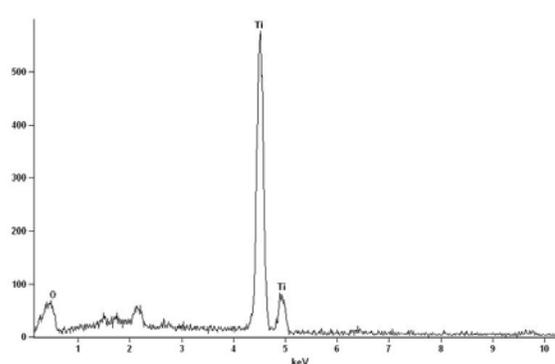


Fig. 4. EDAX spectrum of the  $\text{TiO}_2$  nanostrips.

### 3.6 HRTEM analysis

High resolution TEM was used for further investigation of structure and crystalline quality of the synthesised nano titania. The nanoparticles inside the  $\text{TiO}_2$  strips can be seen very clearly from the higher-

magnification TEM images (Fig. 6). The bar scale represents 5 nm in size. Fig. 6 (a) and (b) indicate the strips of  $\text{TiO}_2$  contain fairly monodispersed nanoparticles with high crystallinity. The image also shows the solid composition of isolated nanoparticles of  $\text{TiO}_2$  with considerable size distribution.

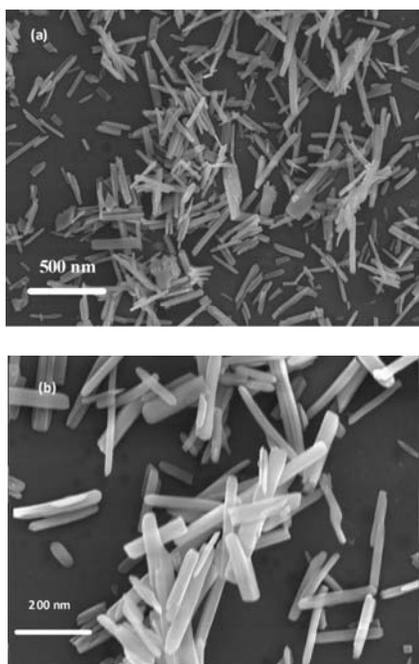


Fig. 5. (a) and (b) HRSEM image of anatase phase titania nanostrips.

### 3.7 Photodegradation studies

Due to the high reactivity of titanium precursors such as  $\text{TiCl}_4$  and titanium alkoxides, the control of the reaction rate is a key factor for obtaining  $\text{TiO}_2$  nanocrystals with the desired crystalline structure and/or shapes. Normally, the surface area and hence the dye adsorption increases as a function of length because of which, an increase in solar cell performance with nanostructure length is expected [17].

The photodegradation studies of PVP capped  $\text{TiO}_2$  nanostructures were carried out using UV light with source power of 300 W. Absorption spectra of an aqueous solution of rhodamine B (tetraethyl-rhodamine, RhB) in the presence of  $\text{TiO}_2$  nanoparticles under exposure to UV light for various time intervals is shown in Fig. 7. At given time intervals, the mixture was sampled to assay by recording variations of the maximum absorption at 554 nm. The absorption peak corresponding to the rhodamine molecule decreases gradually as the exposure time increases. It was clearly observed that the degradation ratio corresponding to rhodamine increases gradually with the exposure time. It shows that all products possess obvious photocatalytic activity.

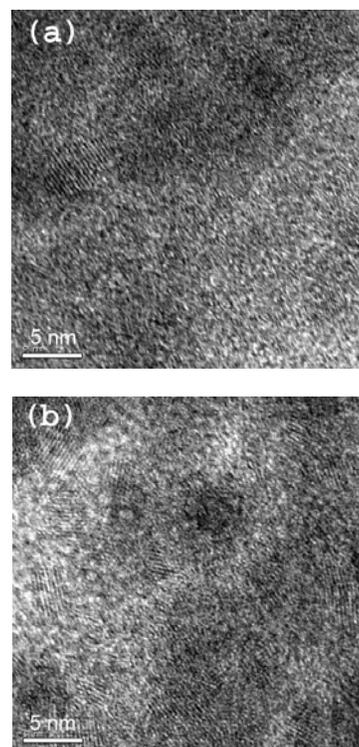


Fig. 6. (a), (b) HRTEM images shows the high crystalline PVP capped Titania nanoparticles.

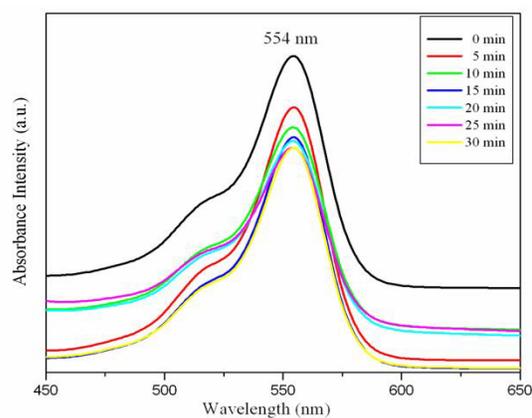


Fig. 7. Photodegradation of RhB under UV light irradiation with the addition of anatase phase  $\text{TiO}_2$  nanoparticles.

## 4. Conclusions

A well developed PVP capped titania ( $\text{TiO}_2$ ) nanostrips were prepared by co-precipitation method using titanium (IV) isopropoxide, with ethylene glycol as a solvent and  $\text{H}_2\text{O}$  as a hydrolyzing agent. This method produced well crystallized  $\text{TiO}_2$  nanoparticles of relatively high surface area with an anatase phase formation, which was confirmed by powder X-ray diffraction analysis. High

resolution SEM image shows the formation of nanostrips with length of ~200 nm.

HRTEM analysis revealed the crystalline nature of the synthesised titania. From this observation, it was observed that the synthesised titania nanostrips were along (101) direction with the crystallite size of ~10 nm. Use of polymer stabilizing agent (PVP) and increase in the pH value plays an effective role in the formation of nanostructure of titania. PVP capped TiO<sub>2</sub> nanostrips have a blue shift in the absorption band edge with a higher band gap energy of 3.54 eV. With a suitable amount of titania nanoparticles, a maximum degradation of rhodamine under UV irradiation can be attained. The increase in the surface area, band gap energy and the anatase phase formation of titania are essential for the enhancement of photocatalytic activity.

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