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The role of pH on the Structural properties and Photocatalytic applications of TiO_2 nanocrystals prepared by simple sol-gel method

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Abstract: Titanium dioxide (TiO_2) nanocrystals were synthesized by simple sol-gel method at room temperature. Titanium iso prophoxide and absolute ethanol were used as precursors to prepare the sol. The pH of the solution was adjusted by adding nitric acid and sodium hydroxide solution. The prepared TiO_2 nanocrystals are annealed at 525°C. The effect of pH on the surface morphology, structural property and photo catalytic activity of TiO_2 nanocrystals was analyzed and it was compared with commercial TiO_2 nanocrystals.
Key words: TiO_2 nanocrystals, sol-gel method, pH value, surface morphology, photo catalytic activity.

1. Introduction

Nowadays the degradation of dissolved organic compounds in water using photocatalysis has attracted much attention because it is easy to handle, inexpensive, stable and effective method [1-3]. Among the various metal oxide semiconductors available, Titanium dioxide (TiO_2) has received prime importance due to its chemical stability and adoptable electronic structure, low cost, environmental friendliness and optical band gap [2,4,5]. On excitation, electrons are promoted to reduce and oxidize many species adsorbed on the semiconductor particles and induces the oxidative destruction of organics up to their mineralization [3-5]. However, this process has limited surface area with the declined efficiency of photocatalytic reaction compared to using TiO_2 powder in aqueous suspension. Therefore, synthesis of the TiO_2 nanocrystals as thin film with larger surface area and a better structure is a key step for its practical. The photocatalytic performance of TiO_2 mainly depends on the preparation method. Among the available methods, doctor blade method is one of the attractive method [6]. This process offers many advantages like, excellent control of the stoichiometry of precursor solutions, ease of compositional modifications, customizable microstructure, requires relatively low annealing temperatures and ease of introducing various functional groups. In recent years most of the research is focused to improve the photocatalytic property by varying the surface morphology of the material. Senthil et al [7] have prepared and reported anatase TiO_2 nanocrystalline films using sol–gel spin coating method for different concentrations of ethanol and acetic acid. But up to this there is no reports related to the role of pH on the surface morphology, structural property and photo catalytic applications. In the present work the role of pH on the surface morphology and photocatalytic activity of TiO_2 nanocrystals has been studied in detail. The Methylene Blue (MB) degradation by commercial TiO_2 nanocrystals and synthesized TiO_2 nanocrystals in UV radiation is taken in to account.

2. Experimental

Titanium iso propoxide (Alfa Aaser 99.9%) is used as titanium precursor; the matrix sol was prepared by mixing titanium iso propoxide (2 ml) with 10 ml absolute ethanol (Hayman 99.9%) and dilute nitric acid at room temperature. The molar ratio of the titanium iso propoxide and ethanol is 1:5 respectively. Nitric acid and sodium hydroxide are used to change the pH of the solution. The TiO_2 nanocrystals were synthesized using different pH conditions (2.6, 7 and 10.6) as reported by one of our earlier work [8]. The TiO_2 thin films for photo catalytic applications was prepared as described in one of our earlier works [9]. The structural properties of the prepared TiO_2 nanocrystals have been studied by using X-ray diffractometer (PANalytical) with a copper Kα (λ =1.5406Å) radiation. The surface morphology and features of the nanocrystal are examined by scanning electron microscopy (Hitachi S-500). Optical characterization of the prepared nanocrystals has been carried out by using UV–VIS–NIR spectrophotometer (Jasco V-570).

3. Results and Discussion

X-ray diffraction (XRD) pattern has been applied to investigate the phase of the prepared TiO_2 nanocrystals. The X-ray diffraction patterns of TiO_2 nanocrystals prepared using different pH values and annealed at 525°C is shown in Fig. 1. Typical peaks in XRD pattern are observed at 2θ values of 25.28°, 37.90°, 47.97°, 53.89°, 55.29°, and 62.61° which are assigned to (101), (004), (200), (105), (211) and (204) planes of anatase TiO_2, and are good agreement with JCPDS data (84-1285,1286). It should be noted that for all the three pH values, the intensity of the diffraction peaks has been observed to increase with increase of pH values. This is due to the improvement in the crystalline nature of the prepared TiO_2 nanocrystals with increase of pH values. The particle size is calculated using Scherer's formula [9] and the calculated values are 18, 20 and 22 nm for pH=2.6, 7 and 10.6 respectively. It clearly shows that the particle size increases with increase of pH values.

Figure 2 shows the SEM image of TiO_2 nanocrystals prepared using different pH values and annealed at 525°C. The SEM images clearly show that the nanocrystals are more in dispersed phase and very less in the aggregation at lower pH. The size of the TiO_2 nanocrystal increases with increase of pH values and is in good agreement with the XRD results. The crystallization growth usually increases with increase of annealing temperature. It is clearly seen from the figure that the nanocrystals prepared at pH=10.6 and annealed at 525°C significantly affects the surface morphology.

Figure 3 shows the absorption spectra of TiO_2 nanocrystals prepared using different pH values and annealed at 525°C. For a particular annealing temperature (525°C), the absorption edge of the UV–Vis absorption spectra is found to red shifted (towards longer wavelength) with increase of pH values. This is due to the fact that increase of pH values varies the grain size and the amount of light absorbed on the surface. By the extrapolation of the absorption edge onto the x-axis the band gap of the samples have been calculated and the calculated values are 3.609, 3.536 and 3.035 eV for pH=2.6, 7 and 10.6 respectively. The estimated values are in agreement with the reported values [10]. It is clearly observed that the band gap value decreases with the increase of pH values. Methylene blue is one of the hazardous organic dyes which exist in the waste water and causes serious environmental problems [11]. We use this dye as model sample to evaluate the photo catalytic activity of the synthesized TiO_2 nanocrystals. The photo catalytic experiments were carried on the catalysts sample with definite dye concentration (10 ppm). Figure 4 depicts the absorbance spectra of the typical time dependent UV–Vis spectra of methylene blue dye during photo irradiation with nanocrystalline TiO_2 thin films prepared at pH=10.6. The rate of decolourization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak is observed at λ_{max} of 615.50 nm which decreased gradually with increase of irradiation time from 1 hour to 3 hour and the percentage of degradation (% D) was calculated. Figure 5 shows the effect of irradiation time of the catalyst on the decolourization of methylene blue. It can be observed that the initial slopes of the curves representing rate of decolourization increases greatly with increasing irradiation time. The degradation of methylene blue by the thin film prepared using commercially available TiO_2 nanocrystal after three hours is 30%. This poor degradation of methylene blue by the film is due to positive surface charge on the TiO_2 surface. The positive charge on the TiO_2 surface does not pay attention to attract the methylene blue molecule since it is a cationic dye [12]. The degradation of methylene blue by the TiO_2 nanocrystals synthesized at pH=10.6 is 50%. This may be due to the negative surface charge on the TiO_2 surface these charge readily attract the methylene blue molecule and degrade it. This result reveals that the TiO_2 nanocrystals synthesized at higher pH encourage more decolourization.

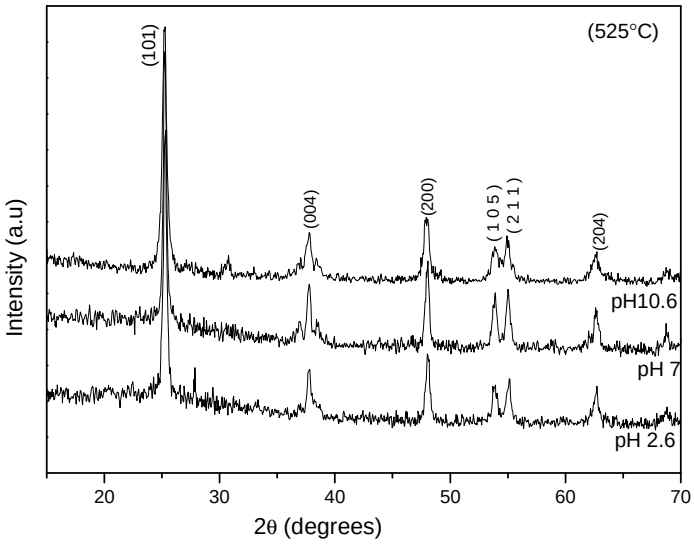

Figure.1 X-ray diffraction patterns of TiO_2 nanocrystals prepared at different pH values

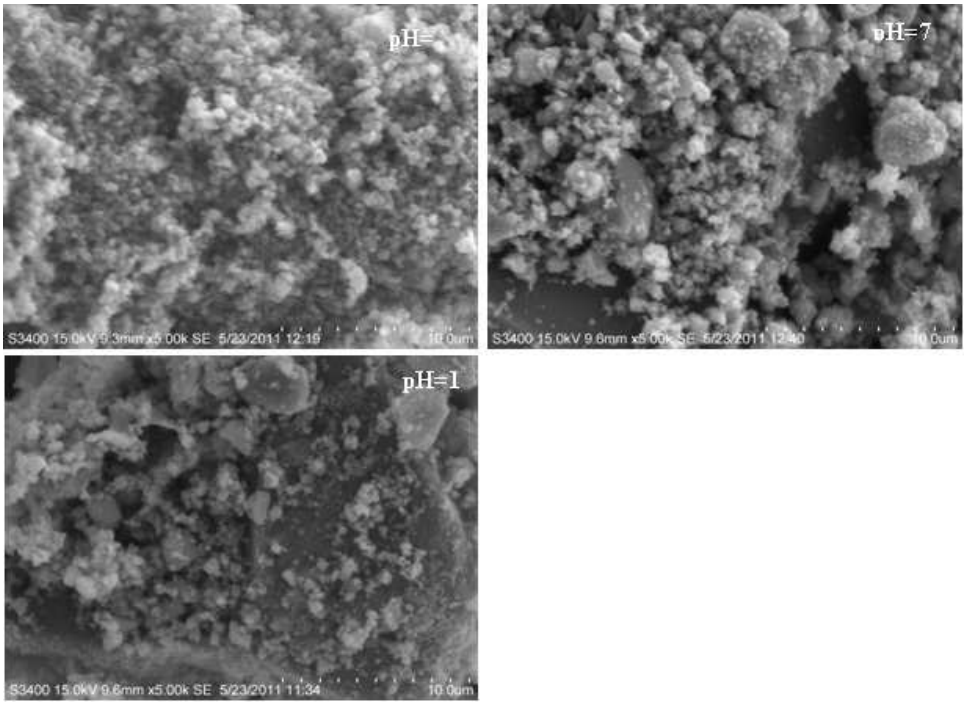

Figure. 2 SEM images of TiO_2 nanocrystals prepared at different pH values

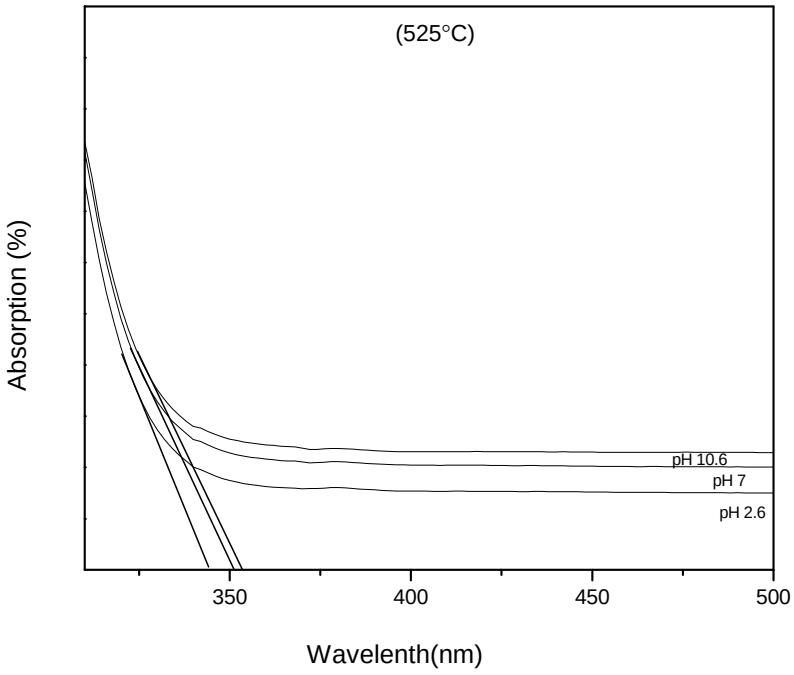

Figure 3. Absorption spectra of TiO_2 nanocrystals prepared at different pH values

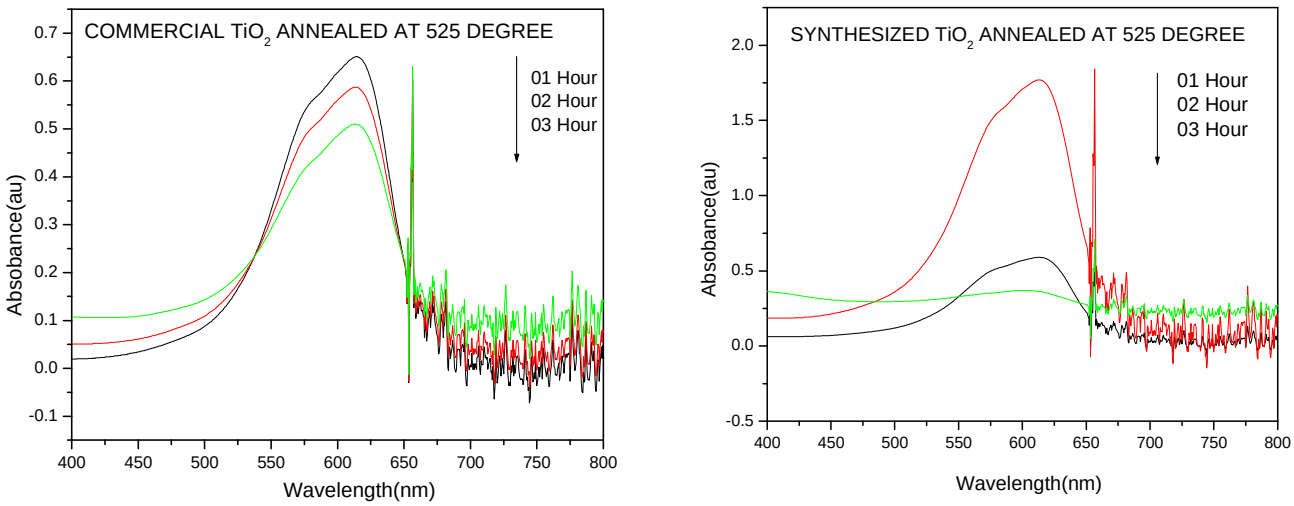

Figure 4. The time dependent UV-Vis absorption spectra of methylene blue subjected to TiO_2 nanocrystals prepared at pH = 10.6

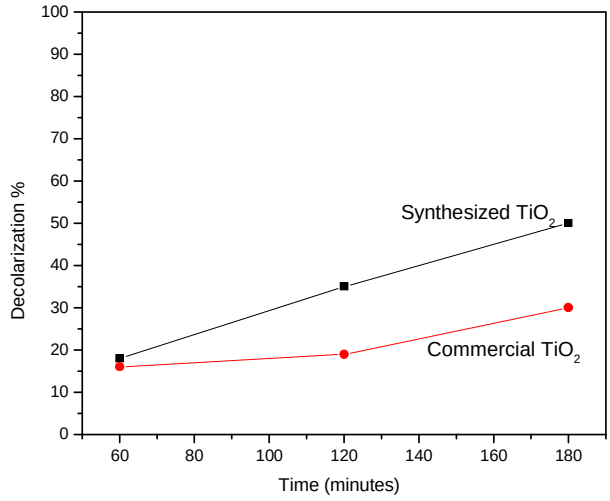

Figure 5. Photocatalytic decolorization of methylene blue as a function of irradiation time

4. Conclusion

TiO_2 nanocrystals were synthesized from sol-gel method at three different pH values (pH values=2.6,7 & 10.6). The prepared TiO_2 nanocrystals were annealed at 525°C. The X-ray diffraction results show that the pH of the precursor solution affect the particle size of the TiO_2 nanocrystals. TiO_2 nanocrystals prepared at pH= 10.6 shows the minimum band gap value of 3.51 eV. The degradation of methylene blue by the synthesized TiO_2 nanocrystal is greater than that of the commercially available TiO_2 nanocrystals.

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