Synthesis and Characterization of TiO_2 Nanopowders in Hydrothermal and Sol-Gel Method

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ABSTRCT

The main objective of the work is to present a systematic study on the growth, physical and chemical characterization of TiO_2 nanostructures prepared by sol-gel and hydrothermal method. The structural, morphological and photocatalytic activity of the prepared nanostructures were analyzed. The prepared samples were calcined at different temperatures and analyzed.

Keywords: Hydrothermal and sol-gel, Photo catalyst, XRD and SEM

1. Introduction

TiO_2, an exceptionally important material for application in photocatalysis, solar-photovoltaic, ceramic material, filler, coating, pigment and cosmetics, has been attracting attention in both fundamental research and practical development work. Reports of TiO_2 with different shape such as nanoparticles thin films, nanorods, nanowires and nanotubes have spurred a great interest in studies on TiO_2 nanostructure synthesis and their application [1]. Nanomaterials with different shape and structure usually have varied chemical, optical and electrical properties. Shape control has been significant concern in nanotechnology. Properties also vary as the shapes of the shrinking nano materials change. Many excellent reviews and reports on the preparation and properties of nano materials have been published recently.[6-10] The specific surface area and surface-to-volume ratio increase dramatically as the size of a material decreases.[13,21]. The performance of TiO_2 based devices is largely influenced by the sizes of the TiO_2 building units, apparently at the nanometer scale. As the most promising photocatalyst, [7, 11, 12, 33] TiO_2 materials are expected to play an important role in helping solve many serious environmental and pollution challenges. TiO_2 also bears tremendous hope in helping ease the energy crisis through effective utilization of solar energy based on photovoltaic and water-splitting devices. [9]

2. Materials and Methods:

2.1. Synthesis of TiO_2 by sol gel method:

The TiO_2 colloidal solution was prepared by hydrolysis of titanium tetra isopropoxide (TTIP) (Aldrich chemicals, USA). In a typical process, 1M of titanium tetra isopropoxide was mixed together with 4 M of acetic acid. The resultant solution is mixed with 10M of double distilled water and the solution was stirred vigorously for 1 h to obtain a clear solution. After an aging period of 24 h, the solution was kept in an oven at 70°C for 12 h to obtain $Ti(OH)_4$ colloidal solution. Then the obtained solution was dried at 100 °C to get TiO_2 crystals. It was then crushed into fine powders with mortar and pestle. Finally the fine powders were annealed at different temperatures viz. 300 and 600 °C for 1 h. For comparison as-prepared samples were also characterized.

2.2 Synthesis of TiO_2 nanoparticles by hydrothermal method:

For preparing nanoparticles by hydrothermal method, the above mentioned method was used initially. After aging for 24 h, the solution the solution was transferred to stainless steel autoclave and placed in to oven at 180 °C for 12 h. Then the autoclave was cooled down to room temperature. The solution was dried at 100 °C to get TiO_2 crystals. It was then crushed into fine powders with mortar and pestle. Finally the fine powders were annealed at 600 °C for 1 h before further characterization

3. Results and Discussion

3.1 Structural Analysis:

In all prepared TiO_2 (Fig.1.1) the peak positions and their relative intensities are consistent with the standard powder diffraction patterns of anatase-TiO_2 (JCPDS card # 21-1272). It has a main peak at 25.2° corresponding to the (101) plane. The peak position at 37.7, 47.8, 54.1, 62.5 and 69.4 are in accordance with the TiO_2 anatase phase. The lattice parameter of the pure TiO_2 [(Tetragonal) *a*=3.785 Å; *c*=9.513 Å] are also in accordance with the reported value (JCPDS card # 21-1272). For the TiO_2 particles prepared by sol gel method the peak intensity of anatase phase increases with the calcined temperature. For the hydrothermally prepared samples, we can observe very high peak intensity than any other samples. This indicates the fact that the sample treated with the hydrothermal method experienced higher crystallinity. Also the peak broadening indicates that the particle size of the hydrothermally synthesized particle is less than the samples prepared by sol-gel method. Importantly it is noted that the prepared samples by both sol-gel and hydrothermal methods shows pure form of anatase phase.

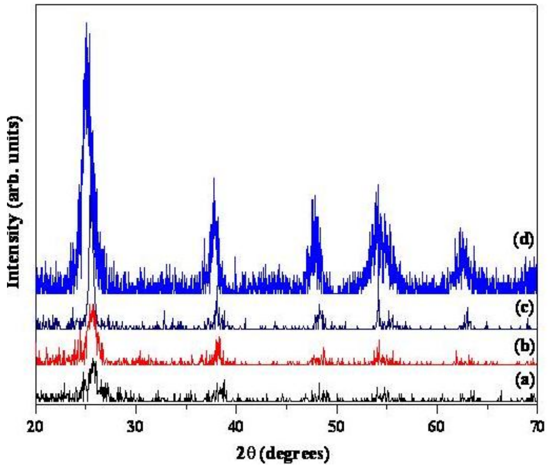

Figure 1: XRD pattern of TiO_2 nanoparticles prepared by sol gel method (a) as prepared (b) calcined at 300 °C (c) 600 °C (d) hydrothermally prepared and annealed at 600 °C.

3.2 Morphological Analysis:

The microstructure of the TiO_2 nanoparticles synthesized by sol gel and hydrothermal method in the present study was observed by FESEM which is shown in figure.2 .As it can be seen in the morphologies of TiO_2 nanoparticles (Fig.2a), the as- prepared (sol-gel) sample shows particle with great aggregation. The size of the particle is around 50 nm. The shape of the particle is not uniform and it looks like spherical in shape. The microstructure of the sol-gel sample calcined at 300 °C shows reduction in the agglomeration (Fig.2b). The formed nanoparticles are visible clearly. Here also the shape of the particle was observed almost sphere like morphology with different size. Further increasing the calcinations temperature to 600 °C also not showed much difference in the morphology of the product. But the visibility of the separate nanoparticles is increased. Also the size distribution is almost uniform compared to other particles. But for the samples treated with hydrothermally shows much difference compared to sol-gel method. The distribution of the particle is very uniform and the size of the particle is almost same. It is observed that the particle posses clear spherical shape.

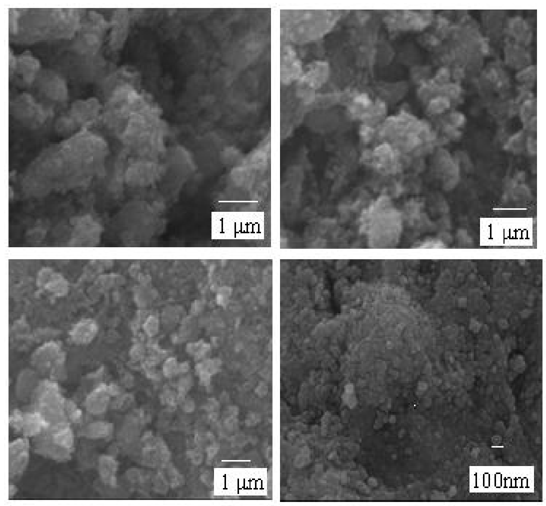

Figure 2: SEM image of TiO_2 nanoparticles prepared by sol gel method (a) as prepared (b) calcined at 300 °C (c) 600 °C (d) hydrothermally prepared and annealed at 600 °C.

3.3. Photocatalytic activity:

The photo catalytic activity was assessed by degrading 0.1 mM of methyl orange (MO) in aqueous solution (MO concentration 0.1mM; TiO_2: 2 gm). The changes of MO concentration with ultraviolet irradiation were observed by measuring the absorption spectra using a JASCO V-670 UVvis spectrometer. The photocatalytic activity of different TiO_2 nanopowders was assessed by degrading 0.1 mM of Methyl Orange (MO) in aqueous solution under exposure to UV light. MO solution was added with the samples and kept in a reaction chamber. The samples were taken out for every 10 min to record absorption spectra. The intensity of the absorbance spectra of MO decreases after UV irradiation with the presence of TiO_2 nanopowders. In all samples, the absorption at 463 nm was taken into account to determine the rate of degradation. Fig. 3 (a), (b) and (c) shows the absorbance spectra UV treated MO solution for the different TiO_2 powders. For as prepared TiO_2 addition the degradation of MO is slow. The increase in TiO_2 calcination temperature increases the photocatalytic activity. For 300 °C sample shows better photocatalytic activity (Fig.3 a) Fig.3 (b) shows the absorption spectra of MO solution treated with UV light, which shows better activity then before. The TiO_2 which is prepared by hydrothermal method shows very good photo catalytic activity (Fig.3c). The decomposition of MO solution is faster than any other powders. The may be due to the change in the crystallinity of the sample. The sample treated with hydrothermal method shows higher crystallinity hence the activity also increases.

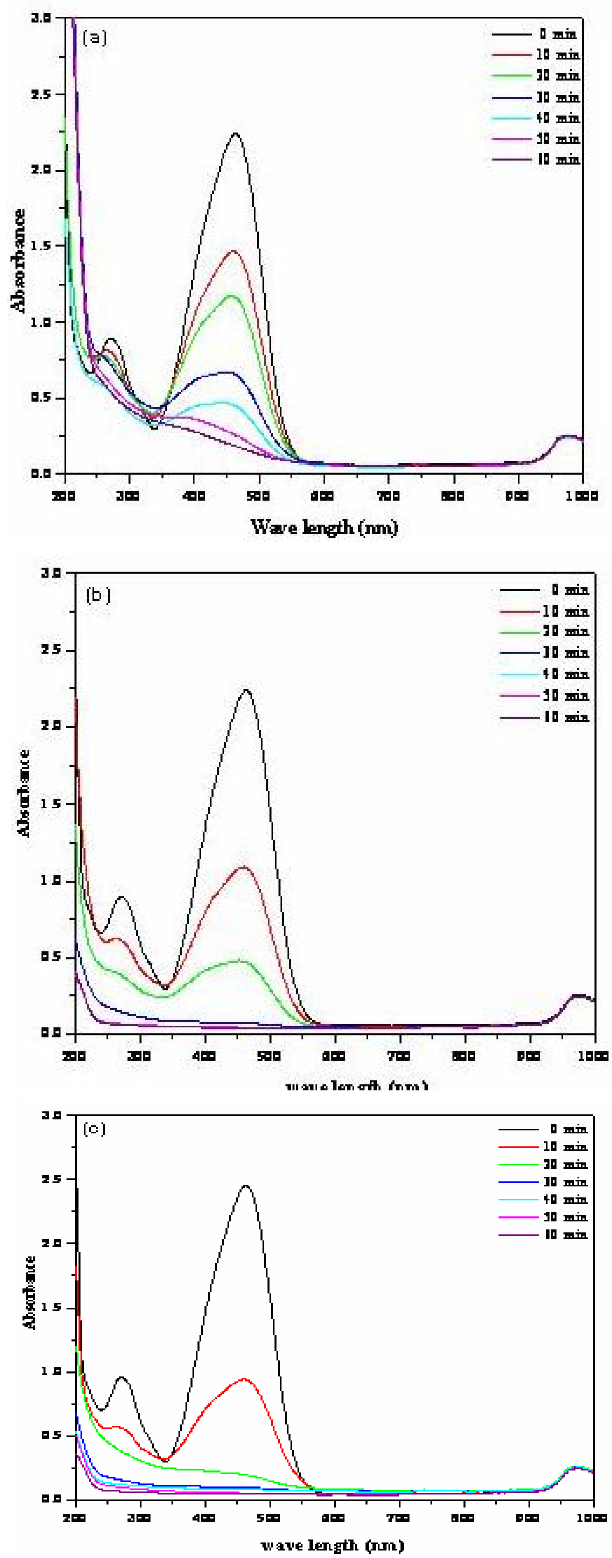

Figure: 3
UV absorption spectra of MO solution treated with TiO_2 prepared by (a)sol-gel method and calcined at 300 °C (b) at 600 °C (c) hydrothermally method and annealed at 600 °C.

4. CONCLUSION

The TiO_2 nanoparticles were prepared by sol gel method and annealed at 300 and 600 °C for 1 h. The structure of the prepared nanopowders have been analyzed by X-ray diffraction technique which suggesting a high chemical and thermal stability of TiO_2 anatase phases at both 300 and 600 °C. For the sample prepared by hydrothermal method shows very good crystallinity than other powders. From SEM, the size distribution was not uniform everywhere for the samples prepared by sol-gel method. For the samples prepared by hydrothermal method shows clear sphere like structure. The particle size was around 50-70 nm. The photo catalytic activity shows little difference with the preparation method and for the temperature treatment. As the calcinations temperature increases the photocatalytic activity also increases. For hydrothermally prepared TiO_2 particles shows very fast degradation of MO solution. Hence, we can conclude that, the nanoparticles prepared by hydrothermal method shows better structural, morphological and photocatalytic property.

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