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Synthesis and Characterization of Visible Light Active Titanium Dioxide Nanomaterials for Photocatalytic Applications

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Abstract: Carbon doped TiO_2 (C-TiO_2) nanomaterials were successfully synthesized by microwave irradiation method and subsequently the surface characterization of C-TiO_2 was carried out using X-ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-Visible spectroscopy. The XRD pattern shows the formation of anatase structure of synthesized C-TiO_2 and SEM image shows the nanoporous morphology of synthesized C-TiO_2 nanomaterials. The synthesized C-TiO_2 nanomaterials were successfully decomposed the methylene blue dye under UV light irradiation. The higher colour removal efficiency of 91.32 % was achieved for the sample calcinated at 400^{o}C.
Keywords: Carbon doped Titanium Dioxide; Nanoporous; Microwave; Photocatalytic activity.

1. Introduction

Nowadays, photocatalytic degradation process to decompose the organic pollutants have been attracted a remarkable interest among the researchers. Photocatalytic degradation using metal oxides have been paying attention as a useful tool to eliminate the organic pollutants in waste water. Several semiconductor nanoparticles (ZnO, SnO_2, WO_3 and TiO_2) have been utilized for the photocatalytic applications [1-13]. Among the metal oxides, TiO_2 is one of the most attractive photocatalyst for degradation of organic pollutants. TiO_2 has many advantages such as high stability, biocompatibility, corrosion resistance, low cost, availability and non-toxicity [14, 15]. Regrettably, TiO_2 has large band gap energy of 3.2 eV and it can be sensitive only under UV light irradiation [16]. Recently, researchers are trying to rectify this problem by lowering the band-gap energy with the doping of metal and/or non-metals into TiO_2 to improve the photocatalytic activity. Non-metal dopants, such as nitrogen, fluorine, sulfur and carbon have been attracted to increase the photocatalytic activity of TiO_2 [17-21]. Carbon absorbs a wide range of visible light and carbon doped TiO_2 can reduces the band gap energy or creates localized electronic states in the band gap that could improve the absorption of visible light [22-31]. Studies on the effect of carbon-doping with TiO_2 in improving the visible light activity have been seldom reported. The C-doped TiO_2 was synthesized by various methods such as chemical vapour phase deposition, pyrolysis and sol-gel method. Here, we attempted to develop C doped TiO_2 material for photocatalytic degradation process using simple and low cost Microwave irradiation method [32-34]. Microwave irradiation is one of the attractive eco-friendly methods for the preparation of C doped TiO_2 materials. In this work, we successfully synthesized C doped TiO_2 nanomaterials through microwave treatment and calcinated at 300^{o}C and 400^{o}C subsequently structural characterization was also carried out using X-ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-visible spectroscopy. The photocatalytic activity of the synthesized C doped TiO_2 nanomaterials was also investigated.

2. Experimental

2.1. Materials preparation

The C-TiO_2 nanomaterial was prepared by microwave irradiation method. 7.296g of starch was dissolved in 45 ml of hot water and stirred for 30 min. The 5 ml of ammonium hydroxide (NH_4OH) and 6 ml of 2-proponal was added into the starch solution. Then the solution was stirred continuously for 1 hr. Then, the solution of titanium tetra-isopropoxide and 2-proponal was added to the above solution and subsequently white colour precipitate was immediately obtained. The obtained precipitate was treated under microwave irradiation using the power of 560 W for 10 min. Finally, the microwave irradiated powder was calcinated at 300^{o}C and 400^{o}C for 2 hr. The as-prepared sample and samples calcined at 300^{o}C and 400^{o}C were denoted as T1, T2 and T3, respectively.

2.2. Photocatalytic degradation

The photocatalytic activity of C doped TiO_2 nanomaterials was studied by decomposing the methylene blue dye. Photocatalytic degradation experiments were carried out in a photocatalytic chamber containing 6W lamps (254 nm) as source of UV light. The methylene blue dye solution of 200 ml with initial concentration of 10 mg/l and photocatalyst dose of 0.1 g was used. The solution was ultrasonicated for 5 min to remove aggregates and it was kept in the dark for 1 h to ensure an adsorption-desorption equilibrium [35, 36]. Then, the solution was poured into photocatalytic reactor and the solution was continuously stirred using magnetic stirrer. Decolourization of methylene blue dye was tested at different time intervals (15 min) and the removal efficiency was recorded. The colour removal efficiency of dye solution was calculated using the following equation:

$$\eta\% = (abs_0 - abs_t)*100 / abs_0$$

Where, abs_0 is absorbance of the dye solution at the initial and abs_t is the absorbance of the dye solution at the time t, respectively.

2.3. Materials Characterization

The prepared nanopowder was analyzed using X-ray diffractometer (XPERT-PRO) with monochromatic CuK□□radiation (λ=1.5406Å). The particle shape and morphology was observed by SEM. The SEM images were recorded on a JEOL-JSM-66101V using an accelerating voltage of 15.00 kV. UV–Vis absorption spectrum of the samples was obtained with a UV–Vis spectrophotometer (Shimadzu UV-1800, Japan).

3. Results and Discussion

3.1. XRD analysis

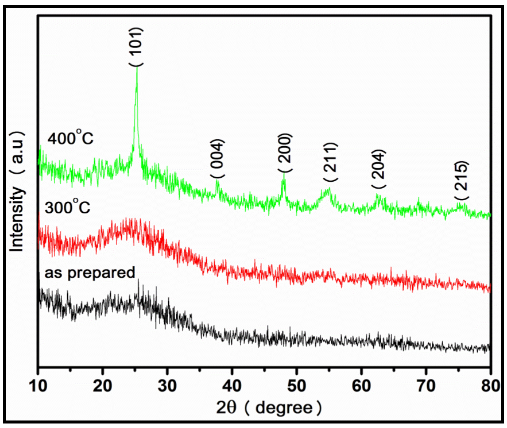

Fig. 1. XRD patterns of C-TiO_2 samples as prepared and calcined at 300^{o}C and 400^{o}C

The XRD pattern of the C doped TiO_2 samples such as as-prepared and calcined at 300^{o}C and 400^{o}C are shown in Fig. 1. Fig. 1 describes the characteristic peaks of the as-prepared and calcined samples, respectively. The as-prepared and calcined at 300^{o}C samples show broad X-ray peaks and it may be due to the presence of nanosized particles. The sample calcined at 400^{o}C show peaks corresponds to anatase phase with a preferred orientation of (101) plane at 2θ-25.29^o in accordance with with the JGPDS card No: 84-1285. The crystallite size was calculated using Scherrer's equation. The calculated average crystallite size of C doped TiO_2 sample (heat-treated at 400^{o}C) is 17.19 nm.

3.2. SEM analysis

Fig. 2 shows the scanning electron microscopic image of the synthesized nanomaterials. Fig. 2a shows the SEM image of as prepared C doped TiO_2 sample prepared by the microwave irradiation of 10 min (T1 sample) and shows the nanoporous morphology with aggregated particles. Fig. 2b shows the SEM image of the sample calcined at 300^{o}C (T2) and it has also show the nanoporous morphology with aggregated particles. Fig 2c shows the SEM image of the sample calcined at 400^{o}C (T3) and it has shows open porous morphology. Careful observation of SEM pictures shows the nanoporous morphology with formation of nanoparticles.

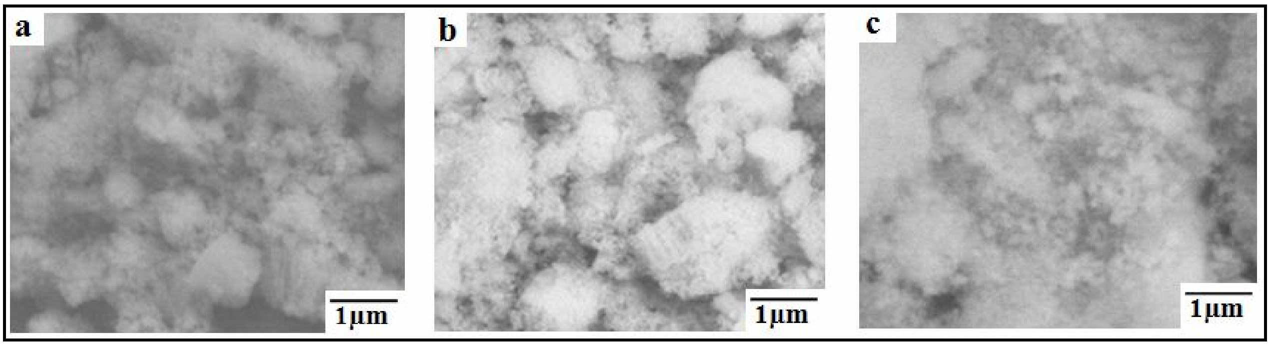

Fig. 2. SEM images of C-TiO_2 samples as-prepared (a) and calcined at 300^{o}C (b) and 400^{o}C (c)

3.3. Photocatalytic activity test

The photocatalytic activity of C doped TiO_2 samples were studied by photocatalytic degradation of methylene blue dye under UV light irradiation. The concentration of the dye was fixed as 10 mg/l for photocatalytic measurement. The amount of photocatalyst used for the dye degradation study is 0.1g (T1, T2 and T3 samples). The higher colour removal efficiency was observed with T3 photocatalyst and it is shown in Fig. 3. The maximum colour removal efficiency of 91.32 % was achieved within 180 min by addition of 0.1g T3 photocatalyst. Fig. 4 displays the UV-Vis spectra of methylene blue dye in the presence of T3 sample under UV light. The characteristic peak of the methylene blue dye showed absorption at 665 nm and the intensity of the methylene blue absorption decreases with the increase of the reaction time.

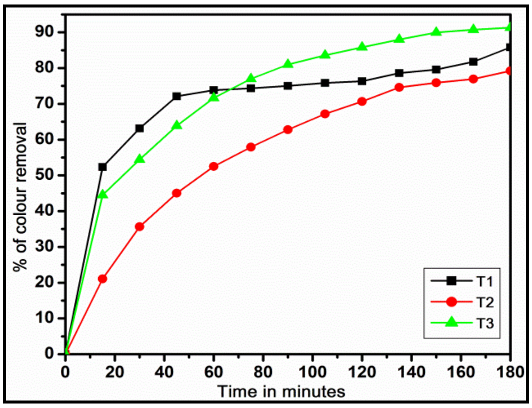

Fig. 3 Comparison of dye degradation efficiency in presence of C-TiO_2 samples as prepared (T1) and calcined at 300^{o}C (T2) and 400^{o}C (T3) under UV light irradiation

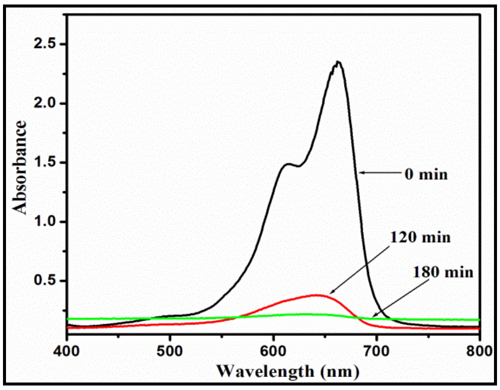

Fig.4. UV-visible spectra of methylene blue in presence of calcined sample C-TiO_2 T3 under UV light irradiation

3.4. Kinetics

Kinetic study was performed to study the photocatalytic activity of C-TiO_2 nanomaterials. The photodegradation of methylene blue was found to follow the first-order kinetics. The kinetics equation can be expressed as follows:

$$\ln C_0/C_t = kt$$

where, Ct is the concentration of the reactant at t time, C_0 is the initial concentration of the reactant and k is the first-order rate constant.

The kinetic study of the methylene blue dye degradation with C-TiO_2 samples (T1, T2 and T3) are shown in Fig. 5 [37-39]. As prepared (T1) and 400^{o}C calcinated sample (T3) exhibit similar rate constant value with higher photocatalytic activity compared with T2. The rate constants of the methylene blue degradation calculated for T1, T2 and T3 samples were 0.03639 min^{-1}, 0.01139 min^{-1} and 0.03572 min^{-1}, respectively.

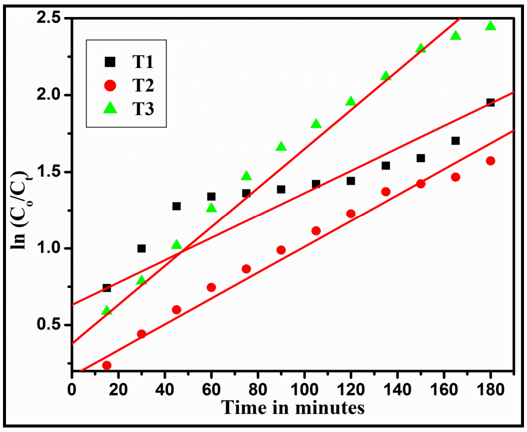

Fig. 5. Kinetics of the photocatalytic activity of C-TiO_2 samples (as prepared (T1) and calcined at 300^{o}C (T2) and 400^{o}C (T3) under UV light irradiation

4. Conclusions

C doped TiO_2 nanomaterial was synthesized by simple and cost effective microwave irradiation method. The synthesized material was characterized using XRD, SEM and UV-visible spectroscopy. The prepared C doped TiO_2 could successfully decompose the methylene blue dye under UV light irradiation. The maximum colour removal efficiency of 91.32 % was achieved within 180 minutes by addition of 0.1 g of T3 photocatalyst.

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