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Photocatalytic Activity of Titanium Dioxide Nanoparticles Prepared by Eco-Friendly Chemical Method

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Abstract

In this work, the effect of structure on the photocatalytic activity of titanium dioxide nanoparticles for the degradation of methylene blue dye in aqueous solution was introduced. The titanium dioxide nanoparticles were prepared by two different methods (solvothermal and dc reactive sputtering) with three different structures (anatase only, anatase:rutile with 2:1 and 1:1). According to the obtained results, the TiO_2 nanoparticles prepared by solvothermal method showed better photocatalytic activity than the other samples prepared by dc reactive sputtering. The solvothermal method can be described as a green method to prepare nanoparticles as photocatalyst for environmental and biomedical applications.

Keywords: Photocatalytic activity; Titanium dioxide; Nanoparticles; Structural phase
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1. Introduction

Photocatalysts are classified into two categories: homogeneous and heterogeneous photocatalyst, Homogeneous photocatalysts are dispersed in the same phase as the reactants in the presence of light. The heterogeneous photocatalysts are in a different phase than the reactants, separated from them by a phase boundary under light [1]. Most common heterogeneous photocatalysts are transition metal oxides and semiconductors, which have unique characteristics. Unlike the metals which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of electrons and holes produced by photoactivation in the solid [2].

Crystallinity is an important factor to be considered in the optimization of the photodegradation efficiency. It has been shown that amorphous TiO_2 has negligible photodegradation efficiency compared with TiO_2 of high crystallinity. The low efficiency of amorphous TiO_2 is caused by the high recombination rate of electrons and holes due to the large amount of defects [3,4].

The primary criteria for an efficient semiconductor photocatalyst is that the redox potential of the charge couple, *i.e*., e^-/h^+, lies within the band gap domain of the photocatalyst. The energy level at the bottom of conduction band determines the reducing ability of photoelectrons, while the energy level at the top of valence band determines the oxidizing ability of photogenerated holes [5]. The internal energy scale is given on the left for comparison to normal hydrogen electrode (NHE). The positions are derived from the flat band potentials in a contact solution of aqueous electrolyte at pH equal to 1. The pH of the electrolyte solution influences the band edge positions of the various semiconductors compared to the redox potentials for the adsorbate [6].

TiO_2 is close to be an ideal photocatalyst and the benchmark for photocatalysis performance. TiO_2 is cheap, photostable in solution and nontoxic. Its holes are strongly oxidizing and redox selective. For these reasons, several novel heterogeneous photocatalytic reactions have been reported at the interface of illuminated TiO_2 photocatalyst, and TiO_2-based photocatalysis has been researched exhaustively for environmental cleanup applications. The single drawback is that it does not absorb visible light [7]. To overcome this problem, several methods including dye sensitization, doping, coupling and capping of TiO_2 are proposed.

In this work, the photocatalytic activity of three samples of TiO_2 nanoparticles different in their structures was introduced and compared. These nanoparticles were prepared by two different methods;

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solvothermal and dc reactive sputtering. The photocatalytic activity was studied as a function of photodegradation methylene blue dye in aqueous solution.

2. Experimental Part

Two methods were used in this work to prepare titanium dioxide (TiO_2) nanoparticles. In the first method, solvothermal method, the TiO_2 nanoparticles were synthesized from the titanium isopropoxide and banana peels. The synthesized nanopowder was polycrystalline and containing both anatase and rutile phases (1:1) of TiO_2, with minimum nanoparticle size of 25.41, and good structural purity. For more details on this work, see reference [8]. In the second method, dc reactive magnetron sputtering, a highly-pure titanium sheet was sputtered in presence of $Ar:O_2$ gas mixture inside a vacuum chamber at gas pressure of 0.5mbar and discharge current of 40mA to deposit TiO_2 thin films on glass substrates. The deposited films were containing both rutile and anatase phases of TiO_2. In order to deposit TiO_2 films with only anatase phase, a heat sink was placed under the substrate to avoid the thermal transition of anatase into rutile phase. For more details on this technique, see references [9-14]. The nanopowder was extracted from the tin film samples by the conjunctional freezing-assisted ultrasonic extraction method [15].

The photocatalytic activity of the prepared TiO_2 nanoparticles was determined by monitoring the degradation of the methylene blue (MB) dye in aqueous suspensions containing TiO_2 nanopowders under UV-radiation exposure. A 50 mL of aqueous suspension was prepared by completely dissolving 0.0159 gm of the MB dye in the deionized water. The MB dye placed in a quartz tube with TiO_2 nanopowder and stirred in the dark (without UV-radiation exposure) for one hour to stabilize the adsorption of the MB dye over the surface of TiO_2 nanoparticles.

The aqueous suspension was then exposed to the UV radiation; whose wavelength is in the range 300-410 nm. The UV radiation source was placed at a distance of 10 cm from the quartz tube. Following UV radiation exposure, 3 mL of aqueous suspension was taken out of the test chamber after each 30 min of UV-radiation exposure to record the absorption spectrum.

The intensity of the main absorption peak (A) of the MB dye solution was taken as a measure of the residual MB dye concentration (C). The UV-visible absorption spectrum of the MB dye solution, without the addition of TiO_2 nanopowder and the UV-radiation exposure, was also recorded as a reference spectrum corresponding to the initial MB dye concentration (C_0). The normalized residual MB dye concentration was calculated using the following relationship [16]:

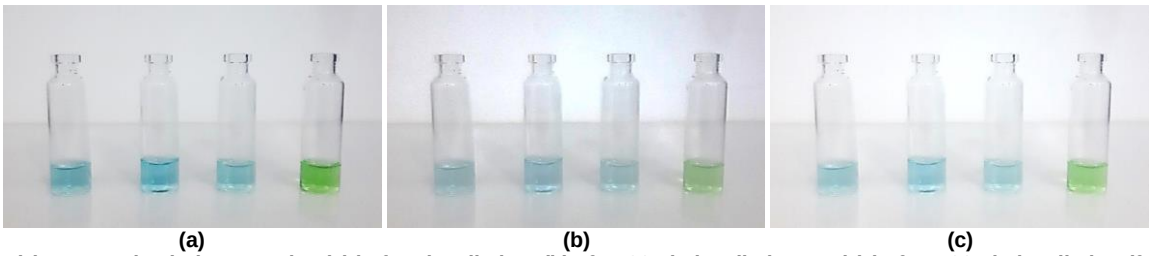
$$\left(\frac{C}{C_O}\right)_{MB} = \left(\frac{A_{time=t}}{A_{time=0}}\right)_{656\,nm} \quad (1)$$

where $A_{time=0}$ is the initial intensity of main absorption peak located at 656 nm, $A_{time=t}$ is the intensity after exposure time of t, C_0 is the initial concentration of MB dye before adding the TiO_2 nanoparticles to the solution, and C is the residual concentration of MB dye after exposure time (t)

It is observed that the kinetics of the photocatalytic activity is measured in terms of the degradation of the MB dye.

3. Results and Discussion

Figure (1) shows the solution samples prepared in this work after 30 min of irradiation with UV source. The effect of catalytic activity of TiO_2 nanoparticles on the degradation of the MB dye solution is generally clear. However, slight differences can be observed due to the structure of these nanoparticles. Also, the degradation of the MB dye solution is increased with irradiation time.



(a) (b) (c)

Fig. (1) Prepared solution samples (a) before irradiation, (b) after 30min irradiation, and (c) after 120min irradiation (from left to right: MB with (2:1) TiO_2 NPs, MB with (1:1) TiO_2 NPs, MB with anatase TiO_2 NPs, and MB only)

Figure (2) shows the absorbance decay of methylene blue (MB) dye with UV irradiation time in presence of anatase TiO_2 nanoparticles in the MB solutions. It shows that after two hours, the absorbance was decreased to about 72% of its initial value soon after irradiation of the dye solution with UV radiation. This decrease is obviously attributed to the effect of anatase TiO_2 nanoparticles in the MB

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solution. The dye solution containing anatase:rutile (2:1) TiO_2 nanoparticles showed a decrease by 65% while the green-synthesized TiO_2 nanoparticles (1:1) showed 71% decrease in absorbance.

The packing factor (PF) concept was developed to evaluate inherently existing internal fields that can be used to rank the charge separation abilities among oxide materials. Due to the lower value of PF for anatase TiO_2 (0.6455) when compared to that of rutile TiO_2 (0.7045), the loosely packed structure of anatase TiO_2 is favorable for photocatalytic activity. However, the mixed-phase (1:1) TiO_2 nanoparticles can be better for the MB degradation. This may be attributed to the synergetic effect originated from the existence of both structural phases in the final sample.

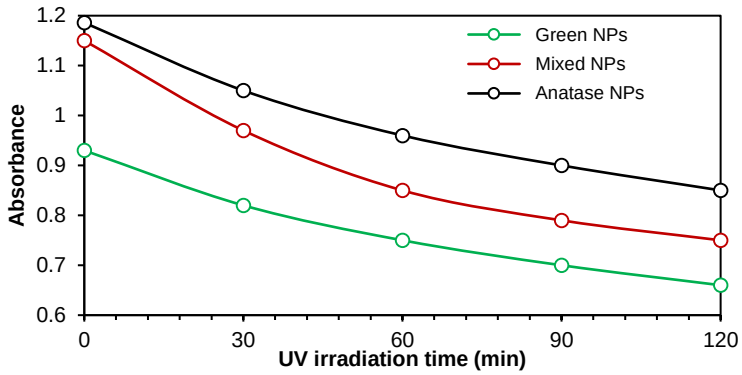

Fig. (2) Absorbance decay of methylene blue (MB) dye with UV irradiation time in presence of TiO_2 nanoparticles in the MB solutions

Typical variation in the normalized residual MB dye concentration as a function of UV radiation exposure time for the TiO_2 nanoparticles is presented in Fig. (3a). It is observed that the kinetics of the photocatalytic activity, measured in terms of the degradation of the MB dye, is enhanced by about 33% for the anatase TiO_2 nanoparticles, 34% for the green synthesized nanoparticles, and 43% for the mixed-phase nanoparticles. The values of the apparent first-order reaction rate constant (k_{app}) were obtained using the data presented in Fig. (2). The k_{app} values for the (1:1), (2:1) and anatase TiO_2 nanoparticles are obtained from the slopes of these fitted straight lines to be $2.8x10^{-3}$, $3.5x10^{-3}$ and $2.7x10^{-3}$ min^{-1}, respectively, which reflects the rate of degradation of the photocatalyst against the pollutant.

The photocatalytic activity of the TiO_2 nanoparticles was introduced by monitoring the degradation of methylene blue (MB) dye in an aqueous solution containing these nanoparticles under UV-radiation exposure. The normalized residual MB dye concentration [$(C/C_0)_{MB}$] was given by Eq. (1).

The kinetics of the photocatalytic activity measured in terms of the degradation of the MB dye are observed. So, after this process, the mixed-phase (2:1) TiO_2 nanoparticles showed much more degradation than the green-synthesized (1:1) and anatase TiO_2 nanoparticles, as shown in Fig. (3b).

This can be ascribed to a strong electronic interaction between the rutile and anatase TiO_2 structures, which may result in an improvement in the kinetics of the photocatalytic activity of mixed-phase (2:1) TiO_2 nanostructures. A photocatalysis experiment was also carried out in the absence of TiO_2 nanoparticles as photocatalysts to confirm the stability of MB dye in an aqueous solution under continuous exposure by UV radiation. Under this condition, the initial concentration (C_0) of MB dye remained constant even after irradiation time of 210 min.

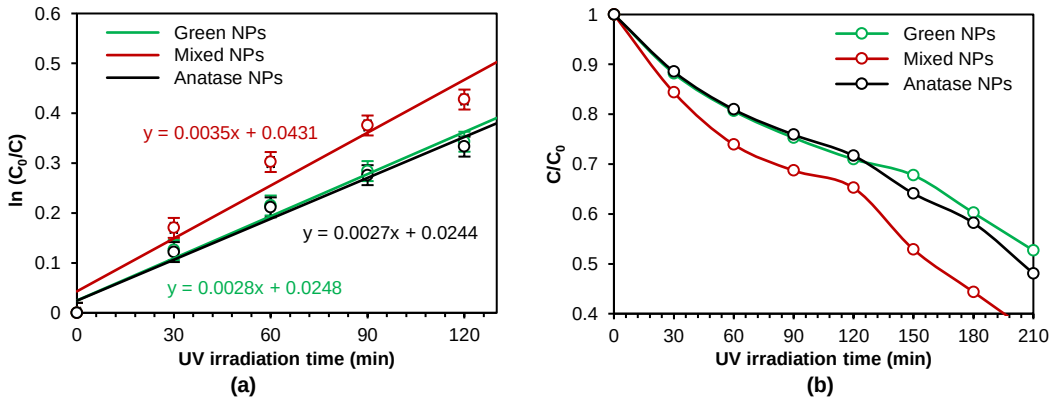

Fig. (3) (a) Typical variation in the normalized residual MB dye concentration as a function of UV radiation exposure time for the TiO_2 nanoparticles, (b) The photocatalytic activity of the TiO_2 nanoparticles in MB dye aqueous solution under UV-radiation exposure

4. Conclusion

In this work, the effect of structure on the photocatalytic activity of titanium dioxide nanoparticles for the degradation of methylene blue dye in aqueous solution was introduced. The titanium dioxide nanoparticles were prepared by two different methods (solvothermal and dc reactive sputtering) with three different structures (anatase only, anatase:rutile with 2:1 and 1:1). According to the obtained results, the TiO_2 nanoparticles prepared by solvothermal method showed lower photocatalytic activity than the mixed-phase (2:1) TiO_2 nanoparticles prepared by dc reactive sputtering but better than the anatase TiO_2 nanoparticles prepared by dc reactive sputtering. The solvothermal method can be described as a green method to prepare nanoparticles as photocatalysts for environmental and biomedical applications.

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