Enhanced photocatalytic activity of TiO$_2$-CdS composite nanofibers under sunlight irradiation**

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Abstract: Pure TiO$_2$ and TiO$_2$-CdS composite nanofibers were synthesized through electrospinning technique. The effects of various levels of CdS loading in a TiO$_2$ nanofibers composite were investigated. Pure TiO$_2$ nanofibers were polycrystalline with an anatase phase, whereas anatase and wurtzite phases coexisted in the TiO$_2$-CdS composite nanofibers, according to X-ray diffraction (XRD) measurements. Using field emission scanning electron microscopy (FESEM) and UV-Visible spectroscopy, the impacts of composite CdS nanoparticles with TiO$_2$ nanofibers were investigated. Pure TiO$_2$ nanofibers have a smooth surface with several microns in length and 21–48 nm in diameter, but when CdS nanoparticles are added, the surface becomes granular. The energy band gap ($E_g$) evaluated from UV-Visible spectroscopy reduced from a value of 3.70 eV for pure TiO$_2$ nanofibers to 1.70 eV for TiO$_2$-0.5CdS nanofibers. Photocatalytic properties of pure TiO$_2$ and TiO$_2$-CdS composite nanofibers were calculated by a methylene blue (MB) aqueous solution degradation under sunlight irradiation. The results revealed that TiO$_2$-0.5CdS nanofibers have efficient photocatalytic activity of up to 98 % after only 60 min.

Keywords: TiO$_2$-CdS composite, nanofibers, photocatalytic activity

1 Introduction

Among the several treatment options, photocatalysis is thought to be the most cost-effective, successful, and environmentally friendly way for completely degrading organic contaminants in waste water [1, 2, 3]. The importance of choosing proper photocatalysts that can absorb sunlight and separate photoexcited electrons from holes has been verified. TiO$_2$ is the most effective photocatalyst among the documented semiconductor photocatalysts, due to its remarkable photoactivity, nontoxicity, cheap cost, high stability, and water unsolvable qualities under most situations [4]. The adjustment of TiO$_2$ photocatalysts for increased light absorption and photocatalytic activity under sunlight irradiation has become a key research area in recent years due to the energy band gap value (3.2 eV) in the UV region.

On the other hand, component optimizations such as coupling semiconductors with narrower band gap materials, which can absorb visible light, are performed. With a narrow band gap of 2.4 eV, CdS has been used to composite with TiO$_2$ due to its visible-light response [5, 6]. CdS excitation wavelength is ≤ 516 nm, and it has clear positive aspects in terms of solar spectrum absorption. As a result, the TiO$_2$-CdS nanocomposites are not only stimulated by visible light, but the photoelectron-hole pairs’ recombination possibilities are also limited [7, 8, 9].

One-dimensional nanostructures (1-D) of various oxide materials, such as nanowires, nanorods, nanotubes, and nanofibers, have gained a lot of interest in recent years. The massive quantity of thought is due to the critical scientific attention paid to these materials, in addition to their potential applications in a variety of practical instruments [10, 11, 12]. Electrospinning, in comparison to other technologies for generating nanofibers, has the benefits of the ability to control, simplicity, low-cost, and manageability in producing industrial amounts [13]. This method has an attractive potential for producing nanofibers from Polymers, Ceramics or Composites with diameters ranging from tens of nanometers to several microns. Furthermore, nanofibers diameter and length are controlled by the solution and processing parameters. The electrospinning technique has been widely employed to create oxide nanofibers [14, 15, 16].
In the current study, TiO$_2$-CdS composite nanofibers samples were manufactured in a simple manner and evaluated using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and UV–Visible spectroscopy. Under sunlight irradiation, the photocatalyst exhibited high photoactivity for the destruction of MB. The results showed that MB was entirely degraded after 60 min of exposure to sunlight.

2 Materials and methods

2.1 Materials

Titanium tetraisopropoxide Ti[OCH(CH$_3$)$_2$]$_4$ (TIP), (96 %Sigma Aldrich), acetic acid (99.5%), ethanol (98%), polyvinylpyrrolidone (PVP)(Sigma Aldrich Molecular weight Mw = 1,300,000), ethylene glycol (EG), and thiourea were all purchased from (Scharlau, Spain), and cadmium chloride was purchased from (CdCl$_2$, 98 % Sigma Aldrich).

2.2 Synthesis of TiO$_2$ nanofibers

1 g of titanium tetraisopropoxide was mixed with 2 ml acetic acid and 2 ml ethanol to make a solution in a typical procedure. After resting for 10 minutes, the solution was mixed with 7 mL of PVP solution in ethanol. This PVP solution was held in a concentration of 10 wt%, and the combination that resulted was regularly stirred for 15 min. This final solution was directly injected into a syringe with a 21 gauge needle (used as the nozzle). The emitting electrode from a Gamma High Voltage Research ES30P power supply capable of generating direct current voltages of up to 25 kV was attached to the needle. The grounding electrode from the same power supply was attached to a plate of aluminum with clean glass substrates fixed on it, which was used as the collector plate and was placed 22 cm in front of the tip of the needle. From the nozzle, a fluid jet was ejected when a voltage of 20 kV was subjected across the needle tip and the collective plate. The fluid was fed at a rate of 1 ml/h, which was controlled by a syringe pump. The solvent evaporates as the jet advanced toward the collecting plate, leaving only extremely fine fibers on the collector plate, as seen in Figure 1. To permit whole hydrolysis of TIP, the produced fibers were exposed in a moisture bath for about 8 h and then calcined at 500°C for 3 hours at a rate of 10°C/min to eliminate any leftover PVP material.

2.3 Synthesis of TiO$_2$-CdS composite nanofibers

Around (0.5, 1, 2) g of cadmium chloride CdCl$_2$ was dissolved into 12.5 ml ethylene glycol under continuous stirring at 70-80 °C. Around (0.67, 1.35, 2.7) g of thiourea was dissolved separately in 12.5 ml ethylene glycol and added to the above solution containing Cd ions drop wise. Now the obtained pure TiO$_2$ nanofibers samples were immersed in this final solution and the temperature was then increased to 100 °C and kept at this value for 2.5 h. The samples are then washed in water and ethanol. Finally, the three TiO$_2$-CdS samples with varying CdS concentrations were heated for 2 hours at 300 °C. TiO$_2$-XCdS composite nanofibers. The samples were generated with varying amounts of CdS, and the results were labelled as TiO$_2$-XCdS, where X is the molar concentration of CdS (X = 0.25, 0.5, and 1).

2.4 Characterization

2.4.1 XRD, UV-VIS, FESEM measurements

X-ray diffraction (XRD) technique was used to describe a crystalline phase of the produced TiO$_2$ and TiO$_2$-XCdS nanofibers, using X-ray diffractometer with CuKα1 (U.S. Monoger). A UV-Vis spectrophotometer (Shimadzu UV-1601) was used to record the absorption spectrum of pure TiO$_2$ and TiO$_2$-XCdS composite nanofibers. Also, field emission scanning electron microscope (FESEM; TESCAN MRI3) was used to observe the samples after being gold coated.

2.4.2 Photocatalysis studies

The degradation of an MB aqueous solution in a photochemical container was used to test the photocatalysis of pure TiO$_2$ and TiO$_2$-CdS composite nanofibers. The photo-
catalytic activity of TiO$_2$-CdS was measured using a 25 mg/L MB aqueous solution made with distilled water as a model pollutant. In a glass cup inclosing 50 mL of MB solution, 20 mg TiO$_2$-CdS composite nanofibers were introduced. To validate the establishment of desorption and adsorption equilibrium of MB on the TiO$_2$-CdS surface, the solution was placed in a photocatalytic container and stirred in the dark for 1 hour. Later, the suspension was exposed to sunlight. To maintain the suspension’s stability, it was moderately stirred throughout the experiment. 4 mL of the suspension was removed at 10 min intervals and UV–Vis analysis was utilized to produce a time-dependent variation in the absorbance of the supernatant between 550 and 750 nm. The color change of MB was assessed by using a UV–Vis spectrophotometer standardized according to Beer Lambert’s law to measure the absorbance value at $\lambda = 664$ nm.

3 Results and discussion

Figure 2 illustrates the XRD patterns of pure TiO$_2$ and TiO$_2$-X CdS nanofibers. The peaks in Figure 2a agree to the (101), (004), (200), (105), (211), and (204) planes of the TiO$_2$ anatase (tetragonal) phase. No peak for the rutile and brookite phases was distinguished, showing that the product samples are of high purity. Additional peaks appear in Figure 2b, c, and d, which belong to CdS hexagonal wurtzite phase, and correspond to the (100), (101), and (110) crystal planes. The intensity of hexagonal CdS peaks increased with the increasing of the molar concentration of CdS from 0.25 to 1. As a result, the XRD patterns obviously indicate the coexistence of pure TiO$_2$ anatase and CdS wurtzite phases.

Figure 2: XRD spectra of (a) pure TiO$_2$ nanofibers, (b) TiO$_2$-0.25CdS, (c) TiO$_2$-0.5CdS, (d) TiO$_2$-1CdS composite nanofibers.

Figure 3: FESEM images of (a) pure TiO$_2$ nanofibers, (b) TiO$_2$-0.25CdS, (c) TiO$_2$-0.5CdS, and (d) TiO$_2$-1CdS composite nanofibers.

FESEM images of pure TiO$_2$ and TiO$_2$-X CdS nanofibers produced at various CdS molar concentrations are shown in Figure 3. Pure TiO$_2$ shows uniform fibers with a length of several microns and a diameter of 21–48 nm in Figure 3a. The as-synthesized products retain the nanofiber framework after composite with CdS, and there are abundant CdS nanoparticles (approximately 17–35 nm) attached outside
these TiO$_2$ nanofibers. The nanocomposites stoichiometry of CdS to TiO$_2$ and homogenous surface morphology are investigated using FESEM images. These micrographs reveal that the smooth surface of pure TiO$_2$ nanofibers changes to granular surface when adding CdS nanoparticles. This situation indicates that CdS nanoparticles stick on the surface of the fibers as clearly shown in Figures 3b, c, and d, and definitely increased the total surface area and this result is critical for the use of photocatalytic activity.

The UV–Vis absorbance spectra of pure TiO$_2$ and CdS–TiO$_2$ composites are shown in Figure 4a. As demonstrated in this Figure, adding CdS to TiO$_2$ increases its absorbance under sunlight, and the absorption intensity of the CdS–TiO$_2$ samples improves as the amount of CdS increases, owing to CdS’s higher photocatalytic activity and narrower energy band gap than TiO$_2$. Semiconductor materials absorb light less than a threshold wavelength (fundamental absorption edge $\lambda_g$) \cite{17}, and it is clear that pure TiO$_2$ has the absorbing edge below 330 nm, whereas the shift to visible region reaches 350 nm for TiO$_2$-0.25CdS and TiO$_2$-1CdS, and continues to increase to 375 nm for TiO$_2$-0.5CdS and TiO$_2$-1CdS. As shown in Figure 4b, the band gap reduces from 3.70 eV for TiO$_2$ nanofibers to 3.05 eV for TiO$_2$-0.25CdS nanofibers and then to 1.70 eV for TiO$_2$-1CdS nanofibers. All results indicate that adding CdS nanoparticles to TiO$_2$ considerably improve its visible light absorption capabilities \cite{18}. Photocatalytic degradation results display a considerable improvement in the photocatalytic effectiveness of TiO$_2$-CdS nanocomposites, owing to the combined effect of enhanced charge carrier life time and the major function of sulphate species found at the surface \cite{7}.

Figures 5 and 6 show the yield of MB during photocatalytic testing as a function of irradiation time. The results obviously specify that the photocatalytic performance of TiO$_2$ can be seriously enhanced by introducing inorganic CdS semiconductor into TiO$_2$ structure. When CdS nanoparticles contact with TiO$_2$ nanofibers, the electrons at the TiO$_2$-CdS interface would rearrange and migrate from CdS to TiO$_2$, leaving holes on the CdS. Then a depletion layer can be formed on CdS on the CdS, while an accumulation layer can be formed on TiO$_2$ surface, leading to the formation of the internal electric field at the interface. The internal electric field, directing from the CdS surface to the TiO$_2$ surface, restrained the further migration of electrons. Finally, the two Fermi levels reach the same level and the mobility of electron from CdS to TiO$_2$ reaches equilibrium \cite{19}. Figure 6 shows the time-dependent photodegradation of MB in pure TiO$_2$ and TiO$_2$-0.25CdS nanofibers when exposed to sunlight.

The following relationship was used to compute the photodegradation efficiency for each test, as shown in Figure 7:

$$\text{Efficiency} (\%) = \frac{C_0 - C}{C_0} \times 100\%$$

where efficiency (%) is the photodegradation efficiency, $C_0$ is the concentration of MB before illumination, and C is the concentration of MB in the suspension after time t (mg/L).

The pseudo first-order rate constant $k$ (min$^{-1}$) can be calculated using the slope of the line from Figure 8. The value of k is 0.0120 min$^{-1}$ for pure TiO$_2$ and 0.0362, 0.0525, 0.0159 min$^{-1}$ for TiO$_2$-0.25CdS, TiO$_2$-0.5CdS, TiO$_2$-1CdS nanofibers respectively. TiO$_2$ nanofibers’ efficiency (after 60 minutes) is 50%, while of TiO$_2$-0.25CdS is 94% and 98% for TiO$_2$-0.5CdS nanofibers, but this value is higher than that of TiO$_2$-1CdS which is 63%. The highest efficiency value was obtained by using (TiO$_2$-0.5CdS) nanofibers and the reason can be attributed to the value of the energy gap in this case (2.45 eV) which corresponds to the absorption edge (506 nm) and this value is approximately in the middle of the visible region and most appropriate and preferred for absorbing visible light, while the other values of the energy gap which are due to (TiO$_2$-0.25CdS) and (TiO$_2$-1 CdS) nanofibers are on the edge of the visible region (400 nm and 775 nm) re-
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Figure 5: UV-Vis photocatalytic absorption spectrum of MB recorded by TiO$_2$ photocatalyst prepared with various intervals. (a) pure TiO$_2$ nanofibers (b) TiO$_2$-0.25CdS (c) TiO$_2$-0.5CdS (c) TiO$_2$-1CdS composite nanofibers.

Table 1: Fundamental results for pure TiO$_2$ and TiO$_2$-CdS nanofibers.

| Sample       | absorption edge $\lambda_g$ (nm) | Energy gap $E_g$ (eV) | $k \times 10^{-4}$ (min$^{-1}$) | Efficiency (%) (after 60 min) |
|--------------|----------------------------------|-----------------------|----------------------------------|------------------------------|
| Pure TiO$_2$ | 340                              | 3.65                  | 120                             | 50                           |
| TiO$_2$-0.25CdS | 400                             | 3.10                  | 362                             | 94                           |
| TiO$_2$-0.5CdS | 506                              | 2.45                  | 525                             | 98                           |
| TiO$_2$-1CdS  | 775                              | 1.60                  | 159                             | 63                           |

spectively. The efficiency obtained in this research is very high when compared to other researches. Gomathi Thanga Keerthana et al. [20] obtained an efficiency amounted to 77% after 180 min, while the efficiency amounted to 85.9% after 120 min in the research carried out by Makama et al. [21]. Table 1 summarizes the fundamental results for pure TiO$_2$ and TiO$_2$-CdS nanofibers.

4 Conclusions

Electrospinning was used to successfully produce TiO$_2$-CdS nanocomposites with various CdS loadings in order to examine the photocatalytic activity of these materials as a function of CdS relative quantity. UV-Vis tests show that CdS–TiO$_2$ composite nanofibers extend the absorption band edge in the visible range. The addition of CdS nanoparticles to TiO$_2$ nanofibers dramatically improves the photocatalytic activity. TiO$_2$-0.5CdS composite nanofibers displays the best photocatalytic activity under sunlight and the efficiency reaches 98% after only 60 min. The as-synthesized TiO$_2$-CdS composite nanofibers exhibit better photoactivity under sunlight irradiation than that of pure TiO$_2$.

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Figure 6: Time-dependent photodegradation of MB in the presence of pure TiO$_2$ and a composite with varying CdS loadings under sunlight irradiation.

Figure 7: Efficiency of MB degradation using pure and composite TiO$_2$ with various CdS loadings.

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