

Research Article

TiO₂ Nanocatalysts Supported on a Hybrid Carbon-Covered Alumina Support: Comparison between Visible Light and UV Light Degradation of Rhodamine B

Mphilisi M. Mahlambi,¹ Ajay K. Mishra,² Shivani B. Mishra,¹ Rui W. Krause,¹ Bhekile B. Mamba,² and Ashok M. Raichur^{1,3}

¹Department of Applied Chemistry, University of Johannesburg, P.O. Box 17011, Doornfontein 2028, South Africa

²Nanotechnology and Water Sustainable Unit, College of Science and Technology, University of South Africa, Florida Campus, Johannesburg 1710, South Africa

³Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

Correspondence should be addressed to Mphilisi M. Mahlambi; mmahlambi@yahoo.co.uk

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Titania nanoparticles were successfully supported on carbon-covered alumina (CCA) supports via the impregnation method to form carbon-covered alumina titania (CCA/TiO₂). The CCA supports were synthesised through an equilibrium adsorption of toluene 2,4-diisocyanate where the N=C=O irreversibly adsorbs on the alumina and pyrolysis at 700°C affords CCA supports. These CCA/TiO₂ nanocatalysts were tested for their photocatalytic activity both under UV and visible light using Rhodamine B as a model pollutant. The reaction rate constant of the CCA/TiO₂ was found to be higher than that of unsupported titania and the reaction kinetics were found to follow an apparent first-order rate law. The CCA/TiO₂ nanocatalysts had a much larger surface area than the unsupported titania and they exhibited overall higher photodegradation efficiency under both UV and visible light than unsupported TiO₂.

1. Introduction

The ability of photocatalysts to mineralise most organic pollutants to water and carbon dioxide as a low-cost advanced oxidation technology (AOT) has attracted interest for decades [1–4]. TiO₂ induced photocatalysis for the treatment of contaminated air and water is a well-established AOT technique [5–8] because of its high photoactivity, chemical and biological inertness, and commercial availability [1, 5, 9, 10]. The titania semiconductor absorbs a photon ($h\nu$) with energy equal to or higher than its band gap of 3.2 eV resulting in the excitation of electrons from the valence band into the conduction band, leaving excited holes behind in the conduction band and creating positive holes in the valence band [6, 11–16]. Generally the hole oxidises water or OH groups in the titania lattice to produce \cdot OH radicals which initiate the oxidation of the organics.

However, titania has a large band gap (3.2 eV) that can only absorb about 2% to 3% visible light; thus a number of ways have been attempted to shift its band gap to the visible-light region. The modifications towards visible-light degradation by TiO₂ include metal ion doping [5, 17–21], anion doping [22–24], binary oxides [25, 26], and dye sensitizers [27, 28]. Another phenomenon that has been studied to enhance visible-light photoreactivity includes size [29, 30] and shape tailoring [31–34].

Carbon in its various forms has been used to synthesise visible-light active TiO₂. These include carbon-covered titania [1], titania mounted on graphite [35], and nanotubes [36, 37] as well as activated carbon [8, 16, 38]. The advantage of carbon-titania composites is that the carbon does not only expand the absorption band to include visible light, it also suppresses phase transformations even at higher temperatures. Lin and coworkers [1] have reported on the successful

synthesis of carbon-covered titania through pyrolysis of sucrose over titania and its superior visible-light activity.

In this work we report on the photocatalytic activity of carbon-covered alumina supported titania in the degradation of Rhodamine B. Supports play an important role in determining the nature and extent of the catalytic activity of a catalyst. Carbon-covered alumina supported catalysts have been mostly used as supports for hydrotreating catalysts [39, 40] and ammonia synthesis [41, 42] but not for environmental remediation. The CCA/TiO₂ nanocatalysts show enhanced visible-light degradation (higher activity) than under UV light illumination of Rhodamine B. It is worth mentioning that the presence of carbon on the CCA support greatly increases the surface area of the CCA/TiO₂ catalysts and shifts the absorption edge of titania to the visible-light region resulting in visible-light degradation of Rhodamine B.

2. Experimental

2.1. Materials and Reagents. The materials used in this research study were purchased from suppliers and used without further purification. Only AR grade *n*-propanol which was obtained from SD's Fine Chemicals (Pty) Ltd was distilled before usage.

2.1.1. Synthesis of TiO₂. Anatase-rich titania nanocatalysts were synthesised through the hydrolysis of TTIP through an esterification reaction between formic acid and propanol [10]. This method is reported in our previous works [43–45].

2.1.2. Synthesis of Carbon Covered Alumina Supports. CCA supports were synthesised by modification of an equilibrium adsorption method [46]. The detailed procedure for the modified procedure is reported elsewhere [45].

2.1.3. Impregnation Experiments. The TiO₂ catalysts were then supported on the CCA catalysts using a simple impregnation method. This impregnation technique is described in detail in our previous research work [45]. To study the catalytic efficiency of the supported CCA catalysts, photocatalytic degradation studies were done under visible light.

2.1.4. Photocatalytic Degradation Experiments. To study the degradation and the kinetics of Rhodamine B by the titania photocatalysts, a Newport 9600 Full Spectrum Solar Simulator equipped with 150 W ozone-free xenon lamp was used, which produces a collimated beam of 33 mm diameter, an equivalent of 1.3 suns. For the purposes of this study, the distance between the solar simulator and the experimental setup was set such that the beam power was equivalent to 1 sun. UV light filter GG450 was used to ensure that the photocatalytic degradation experienced is only due to visible light irradiation. The photocatalytic activity of these nanophotocatalysts was studied using 100 mL (10 mg·L⁻¹) Rhodamine B. The visible light (solar) irradiation lamp was placed at about a 10 cm distance away from the reactant solution. The CCA-supported titania nanoparticles (100 mg nanoparticles per 100 mL of 10 mg·L⁻¹ dye) were used in suspension to determine the photoactivity of the nanoparticles. The solution was

stirred with a magnetic stirrer for 1 h prior to irradiation with the solar light to establish an adsorption-desorption equilibrium between the dye and the catalyst surface. Aliquots of 2 mL were extracted from the reaction chamber at 30 min intervals to study the extent of the degradation. The entire photo-reactor setup was set inside a 1 m × 70 cm wooden box and the experiment was carried in a dark room. The setup was the same for the free (unsupported) titania nanocatalysts and a UV light source was used for UV light degradation experiments.

Prior to the photodegradation experiments, Rhodamine B solution (without catalyst) was irradiated with the solar light (photolysis) for a maximum period of 5 h to establish whether there was any degradation due to the solar light alone. A Shimadzu UV-2450 UV-Vis spectrophotometer was used to determine the extent of photodegradation of Rhodamine B. After the irradiation process had been established, the kinetics of the photodegradation was studied. The apparent rate constant allows for the determination of photocatalytic activity independent of the previous adsorption period and the concentration of the Rhodamine B remaining in the solution [47]. The apparent first-order kinetic equation $-\ln(C_t/C_0) = K_{app}t$, where K_{app} is the apparent rate constant, C_t is the solution phase concentration, and C_0 is the concentration at $t = 0$, was used to fit the experimental data [48].

2.2. Characterization

2.2.1. UV-Vis Diffuse Reflectance Spectra. A Shimadzu UV-2450 UV-Vis spectrophotometer was used to record the UV-Vis diffuse reflectance spectra of the CCA-supported and free TiO₂ nanocatalysts using BaSO₄ as a reference sample. These were recorded in the range of $\lambda = 300$ nm to 800 nm, at room temperature and in air. This was done to ascertain the effect of the support on the band gap (E_g) of the titania nanoparticles. The equation $E_g = hc/\lambda$ was used where E_g is the band gap, h is Planck's constant, c is the speed of light (m·s⁻¹), and λ is the wavelength (nm). A tangent of the plot of $h\nu$ versus $(\alpha h\nu)^2$ gives an estimate of the band gap where α is the absorbance and ν is the wave number.

2.2.2. BET Surface Area Studies. The surface area (S_{BET}), pore volume, and pore-size distributions of the synthesised CCA-supported catalysts were studied using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The samples were degassed in nitrogen under vacuum for 24 h at 200°C prior to determination of the surface area. Surface area is an important parameter when studying the catalytic efficiency of the nanocatalysts embedded on CCA supports (CCA/TiO₂) since a high surface area means more active sites for extensive catalysis.

2.2.3. SEM and TEM Studies. A JEOL J2100 F transmission electron microscope (TEM) was used to study the microstructure of the nanocatalysts. The sample powders were dispersed in ethanol and sonicated for 10 min before analysis. A drop of the suspension was then placed on a carbon coated copper grid and dried in air prior to visualisation. To analyse and visualise the surface morphology of the nanocatalysts,

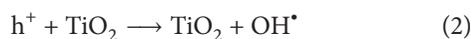
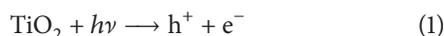
TABLE 1: Comparison of photodegradation efficiencies of Rhodamine B by free and CCA/TiO₂ under UV and visible-light illumination.

Light source	Catalyst	Degradation efficiency (%)	Time taken (min)
Visible light	Photolysis (no catalyst)	4	270
Visible light	Unsupported TiO ₂	20	270
Visible light	CCA-supported TiO ₂	100	180
UV-visible light	Unsupported TiO ₂	100	270
UV-visible light	CCA-supported TiO ₂	100	240

a quanta FEI-SIRION scanning electron microscope (SEM) was used. For SEM analysis, the powder samples were placed on a carbon tape and analysed without gold coating.

3. Results and Discussions

3.1. Degradation Process. The photodegradation process of Rhodamine B can be summarised in (1) to (3) when disregarding the role of the electrons (e^-) which is in the oxidation of metal ions. The titania nanocatalysts absorb a photon ($h\nu$) resulting in the excitation of an electron (e^-) from the valence band (VB) to the conduction band (CB) leaving an electron vacancy or a hole (h^+) in the valence band (1). The holes then migrate to the surface of the titania where they react with surface hydroxyl groups in the TiO₂ lattice or water to produce hydroxyl radicals (2):



The hydroxyl radicals then react with the Rhodamine B producing intermediates, carbon dioxide, water, and inorganic ions (3).

3.2. Degradation Studies. Figure 1 shows the UV spectra of Rhodamine B with its peak maximum at 554 nm. It also shows the disappearance of the peak after illumination with either UV or visible light in the presence of different titania catalysts. For the photodegradation studies, the dye was illuminated with visible light in the absence of the catalyst to determine the extent of degradation under visible light since Rhodamine B has been reported to absorb light which is in the range of 400 nm to 600 nm [26, 28]. The results obtained showed that photolysis, on average, degraded about 4% of the Rhodamine B. The mixture was stirred in the dark for an hour to reach equilibrium between the catalyst and the dye before illumination with either the UV or visible light and the concentration was monitored. It was found that there was only about 2% adsorption of the dye on the catalysts when equilibrium was reached.

3.2.1. UV Light Degradation of Rhodamine B. Photodegradation of Rhodamine B was tested using the different catalysts under UV light irradiation. As shown in Table 1, both the CCA/TiO₂ and the free titania nanocatalysts achieved complete degradation after 270 min. The linear transform curve of the photodegradation of Rhodamine B (Figure 2) shows that

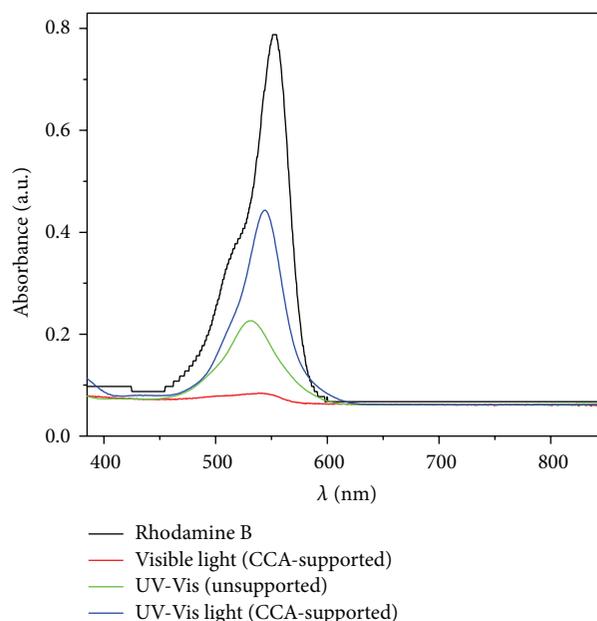


FIGURE 1: Graph showing absorbance of Rhodamine B before and after illumination with visible light.

the CCA/TiO₂ nanocatalysts had an apparent rate constant (K_{app}) of 0.0215 min⁻¹ and the free TiO₂ nanocatalysts had a K_{app} value of 0.0167 min⁻¹. From these results the CCA/TiO₂ nanocatalysts show a higher reaction rate than the free anatase titania.

3.2.2. Visible Light Degradation of Rhodamine B. The degradation of Rhodamine B was also tested under visible light illumination. The results obtained (Table 1) show that CCA/TiO₂ nanocatalysts were photocatalytically active under visible light. While the unsupported titania could only degrade about 20% of Rhodamine B in 270 min with an apparent rate constant of 0.000832 min⁻¹, the CCA/TiO₂ nanocatalysts completely degraded the dye within 180 min and a high apparent rate of 0.0294 min⁻¹.

From the results obtained, the CCA/TiO₂ nanocatalysts exhibited superior photocatalytic activity compared to the unsupported titania both under UV and visible-light illumination. This could be a result of the modification of the surface area of the titania catalysts by the carbon-covered alumina supports. Also, this showed that CCAs are good supports for titania nanocatalysts as they result in an enhanced photocatalytic activity. The presence of carbon could be

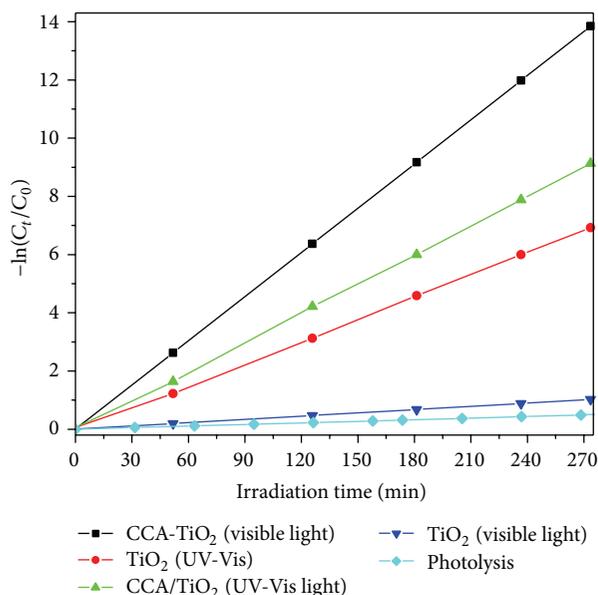


FIGURE 2: Linear transform graph of degradation of Rhodamine B by free titania CCA/TiO₂ under UV and visible-light illumination.

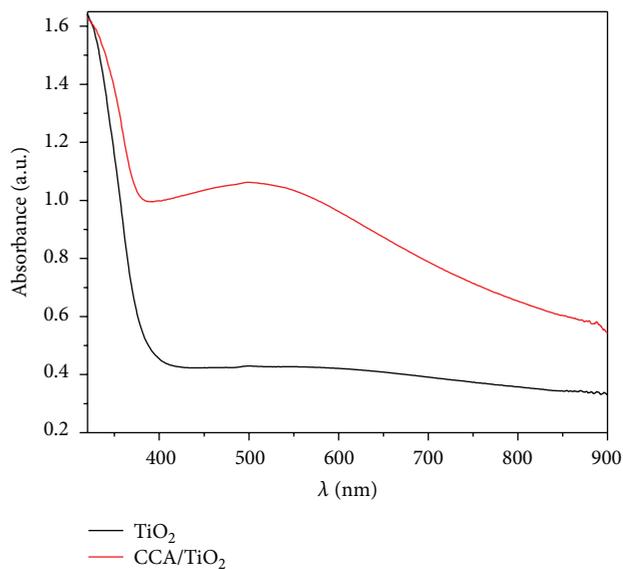


FIGURE 3: UV-Vis diffuse spectra of TiO₂ and CCA/TiO₂ nanocatalysts.

responsible for perturbing the transmission of both UV and visible light to the surface of titania resulting in an increased photocatalytic activity of titania. Furthermore, the presence of aluminium on the support system could prove efficient in that it could act as an electron trapper and hence prohibit or reduce the possibility of electron-hole recombination thus resulting in an enhanced photocatalytic activity.

3.3. UV-Diffuse Spectra and Band-Gap Studies. To further study the origin of this enhanced photocatalytic activity, the UV-diffuse reflectance spectra (Figure 3) of the CCA/TiO₂

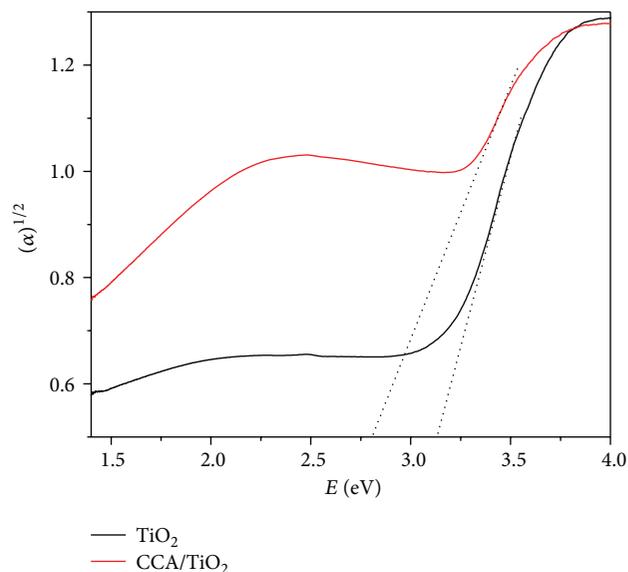


FIGURE 4: Band-gap studies of TiO₂ and CCA/TiO₂ nanocatalysts.

and free titania were studied. The CCA/TiO₂ spectrum showed a significant red shift of the band edge from 380 nm to 416 nm, that is, in the visible range. This shift in the absorption edge is responsible for the visible-light photocatalytic activity of the CCA-supported titania.

The data obtained from the UV-Vis diffuse spectra of the CCA/TiO₂ and free titania were used to indirectly measure the band gap (Figure 4). The band gap of the free titania was found to be 3.19 eV which is close to the known literature value of free anatase titania nanocatalysts. The CCA-supported catalysts showed a significant decrease in the band gap from 3.19 eV to 2.82 eV. The decrease by 0.37 eV is much higher than the decrease of 0.14 eV reported for carbon-doped titania [1]. The presence of alumina might have contributed to the decrease in the band gap and subsequently enhanced the photocatalytic activity.

3.4. BET Surface Area and Pore-Size Distribution Measurements. The nitrogen adsorption-desorption isotherms were measured in order to understand the influence of supporting titania nanocatalysts on the CCA (Figures 5 and 6). Figure 5 shows the adsorption-desorption isotherm of pure titania and the insert graph shows the pore-size distribution graph of the titania. Figure 6 shows the adsorption-desorption isotherm of the CCA/TiO₂ with the insert showing the pore-size distribution graph. Evidence of the occurrence of open pores in the CCA/TiO₂ is shown by the presence of the hysteresis loop. The narrow hysteresis loop observed on the titania graph is an indication of a uniform pore-size distribution of the nanoparticles. The CCA/TiO₂ graph on the other hand shows a wider hysteresis loop, an indication of a wider range of pore distribution, that is, the presence of titania, carbon, and alumina pores which play an important role in the observed enhancement of the photodegradation of Rhodamine B.

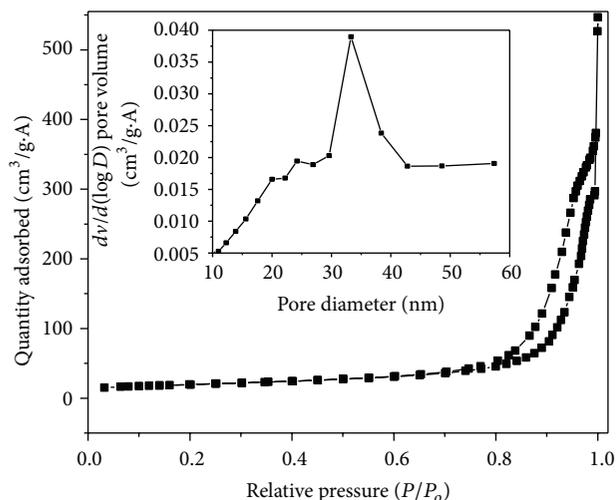


FIGURE 5: Nitrogen adsorption-desorption isotherm of titania nanocatalysts.

The surface properties of CCA/TiO₂ and free titania, that is, specific surface area, pore volume, pore size, and pore-size distribution, were analysed according to the BJH method (insert graphs in Figures 5 and 6). The free titania nanoparticles had a surface area of 69.34 m²·g⁻¹ while the CCA/TiO₂ nanocatalysts had a surface area of 149 m²·g⁻¹. This is an increase of about twice the initial surface area and this is a result of the creation of new pore structures after the modification of the CCA support surface. A decrease in the mean diameter of the pores was also observed, from 35 nm to 5.41 nm for the titania and the CCA/TiO₂, respectively. This is an indication that the titania occupied the inner pores of the carbon-covered alumina supports, hence the decrease. The increase in the surface area and decrease in particle size therefore played an important role in the enhanced photocatalytic degradation of Rhodamine B shown by the CCA-supported catalysts.

3.5. SEM and TEM Studies. The high surface area of the CCA/TiO₂ nanoparticles observed in the BET surface area analysis was further confirmed by the SEM images (Figure 7). From the SEM micrographs the titania nanoparticles appear evenly distributed on the surface of the carbon-covered alumina supports. The even distribution of the titania nanocatalysts on the surface of the CCA support is a result of the titania nanocatalysts occupying the inner pores of the CCA supports. This distribution of the TiO₂ nanoparticles therefore results in the increased surface area exhibited by the CCA/TiO₂ nanocatalysts over the unsupported TiO₂ nanocatalysts.

The TEM images (Figure 8) of the CCA/TiO₂ nanocatalysts showed that the nanocatalysts were not only successfully embedded on the pores of the CCA supports but were also evenly distributed on the CCA surface. From these TEM images it can be seen that the TiO₂ nanocatalysts (Figure 8(a)) did not lose their crystallinity upon embedding on the CCA supports (Figure 8(b)). This was further confirmed by the electron diffraction (ED) patterns. The ED patterns of

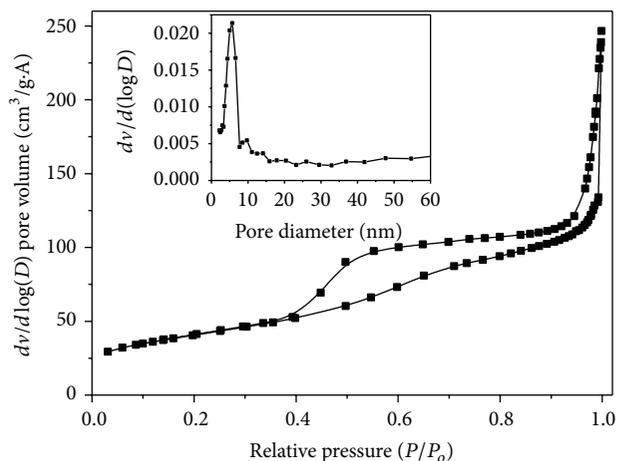


FIGURE 6: Nitrogen adsorption-desorption isotherm of the CCA/TiO₂ nanocatalysts.

the CCA/TiO₂ nanocatalysts show that embedding the TiO₂ nanocatalysts on the CCA supports did not destroy their crystal lattice (Figure 8(a)). These ED patterns are characteristic of the 101 plane of the TiO₂ nanoparticles (Figure 8).

Both the SEM and the TEM studies revealed that the physical morphology of the CCA-supported titania nanocatalysts played a major role in the photocatalytic degradation properties of these nanocatalysts. The SEM studies revealed that the CCA/TiO₂ nanoparticles had a high surface area while the TEM studies showed that the nanoparticles were evenly distributed on the surface of the CCA supports and that they still exhibited high crystallinity (ED patterns). Therefore the increased surface area and the preserved crystallinity are responsible for the high photocatalytic activity exhibited by the CCA/TiO₂ nanocatalysts.

The elemental composition of the synthesized catalyst and supports was identified using the EDS spectroscopy and this is shown in Figure 9. The EDS spectrum of the CCA-TiO₂ nanocatalysts showed the presence of Al, O, C, and Ti elements. From the EDS we were able to confirm not only the successful incorporation of carbon on the surface of alumina but also the successful impregnation of the CCA with the TiO₂ nanocatalysts.

4. Conclusions

The CCA-supported titania nanocatalysts demonstrated superior photocatalytic activity compared to the free titania catalysts both under UV and visible-light illumination. The presence of the CCA supports resulted in an increased surface area and decreased the rate of electron-hole recombination (electron scavengers) hence resulting in an increased photocatalytic activity. Also, embedding the titania catalysts on the CCA supports resulted in a sharp decrease in the band gap of titania thus shifting the absorption edge of titania towards the visible-light region resulting in an enhanced visible-light photoactivity of the CCA-supported catalysts.

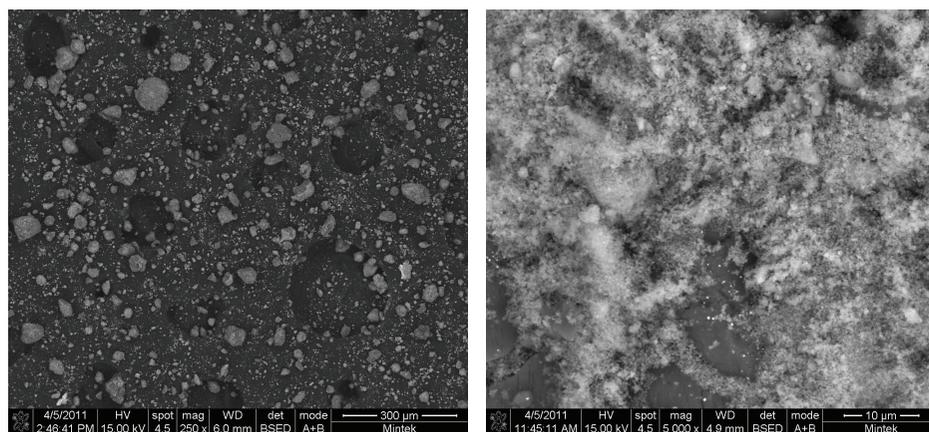


FIGURE 7: SEM images of the CCA/TiO₂ nanocatalysts.

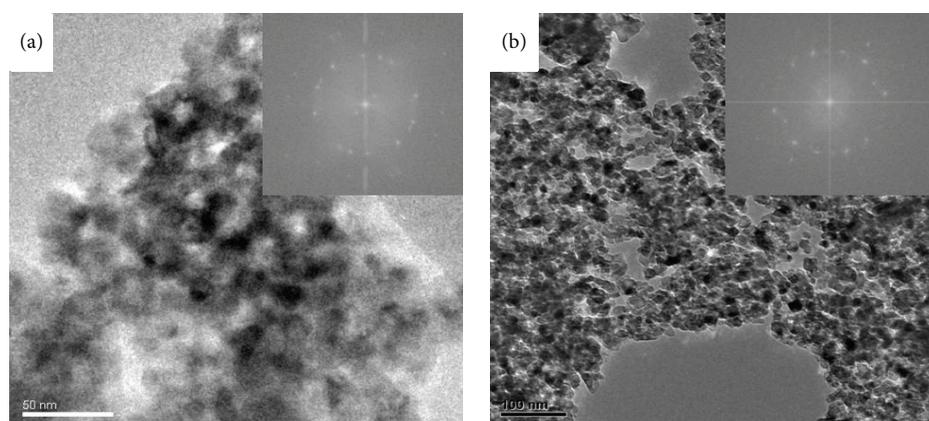


FIGURE 8: TEM images of the (a) TiO₂ and (b) CCA/TiO₂ nanocatalysts.

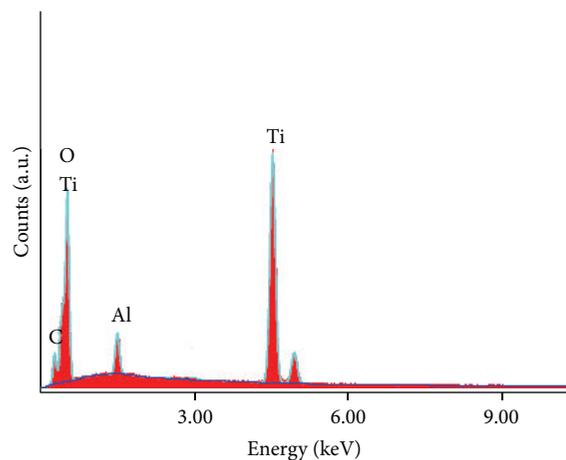


FIGURE 9: EDS spectrum of the CCA/TiO₂ nanocatalysts.

Furthermore, the CCA-TiO₂ nanocatalysts had a high surface area, were evenly distributed on CCA support surface, and were highly crystalline thus making the CCA supports a superior support for titania nanocatalysts for environmental pollution remediation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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