Synthesis, Characterization, and Investigation of Visible Light Photocatalytic Activity of C Doped TiO$_2$/CdS Core-Shell Nanocomposite

Atul B. Lavand, Yuvraj S. Malghe, and Suraj H. Singh

1Department of Chemistry, The Institute of Science, 15 Madam Cama Road, Mumbai 400032, India
2Department of Energy Science & Engineering, Indian Institute of Technology, Mumbai 400076, India

Correspondence should be addressed to Yuvraj S. Malghe; ymalghe@yahoo.com

Received 15 May 2015; Accepted 7 September 2015

Academic Editor: Ana Cremades

Copyright © 2015 Atul B. Lavand et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Carbon (C) doped TiO$_2$/CdS core-shell nanocomposite (C/TiO$_2$/CdS) was synthesized using microemulsion method. Synthesized powder was characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), and UV-visible spectrophotometry. TEM images reveal that C/TiO$_2$/CdS core-shell heterostructure is successfully prepared with CdS as a core and C doped TiO$_2$ as a shell. UV-visible absorption spectra show that CdS nanoparticles act as a sensitizer and effectively enhance the photoabsorption capacity of C/TiO$_2$/CdS nanocomposite in visible region. Visible light photocatalytic activity of synthesized nanocomposite was evaluated for the degradation of methylene blue. C/TiO$_2$/CdS core-shell nanocomposite exhibits better photocatalytic activity as compared to bare TiO$_2$, CdS, CdS/TiO$_2$, and C doped TiO$_2$.

1. Introduction

Photocatalysis can be used as an abundant and clean energy source for different purposes like environmental remediation, clean energy production, and so forth [1–3]. Recent day’s lot of research is going on, to develop novel photocatalyst and improve its efficiency in visible/solar light [4–6]. In photocatalysis, light of energy greater than the semiconductor band gap which excites electron from valence band to conduction band is required. Among various photocatalysts reported TiO$_2$ has attracted special attention due to its unique physical and chemical properties such as strong oxidizing and reducing ability, good permeability, better optical properties, chemical stability, low cost, and corrosion resistance [7–9]. Among the various forms of TiO$_2$, anatase TiO$_2$ exhibits better photocatalytic activity [10]. It has the band gap 3.2 eV and requires UV light ($\lambda \leq 387$ nm) to activate. Solar spectrum consists of 5% UV and ~45 to 50% visible light. To utilize visible light portion it is necessary to modify TiO$_2$. One of the ways to modify TiO$_2$ is to couple it with semiconductor with narrow band gap. CdS with band gap 2.4 eV is considered as one of the ideal sensitizers due to unique position of its conduction and valence band edges [11–14]. Unfortunately CdS/TiO$_2$ composite suffers from major disadvantage that is quick recombination of photogenerated charge carriers which decreases the photocatalytic performance. To compensate this problem it is necessary to modify this composite by doping it with metals or nonmetals. Few reports are available in literature [13, 15, 16] regarding the preparation of hybrid materials in which Pt or C nanotubes are incorporated. These materials act as an excellent electron acceptor/transporter centre and effectively facilitate the migration of photoinduced electrons and suppress the charge combination in electron-transfer process due to electronic interaction between them and CdS/TiO$_2$ composite. This effectively increases the photocatalytic activity. Carbonaceous materials are very popular in photocatalysis due to their wide range visible light absorption capacity and better adsorption power of organic pollutants [17, 18]. In such hybrid materials strong synergetic effect can be achieved. Therefore, in a present work we have synthesized C doped TiO$_2$/CdS nanocomposite using microemulsion method and
its visible light photocatalytic activity was investigated for the degradation of methylene blue dye.

2. Materials and Methods

2.1. Materials. Methylene blue (MB) practical grade was obtained from Hi Media Laboratories, Mumbai, and used without any further purification. Titanium isopropoxide Ti(iOPr)\textsubscript{2} was purchased from Sigma Aldrich, Mumbai, and used as a source of titanium. All these chemicals, cyclohexane, n-butanol, N,N,N-cetyl trimethyl ammonium bromide (CTAB), acetone, cadmium nitrate (Cd(NO\textsubscript{3})\textsubscript{2}⋅4H\textsubscript{2}O), sodium sulphide flakes (Na\textsubscript{2}S), sodium hydroxide (NaOH), and ethanol (99.7%), used for synthesis are of AR grade and are procured from SD Fine Chemicals, Mumbai, India, and are used without further purification.

2.2. Synthesis of Photocatalyst

2.2.1. Synthesis of CdS Nanoparticles. 50 mL 1 M cadmium nitrate, 25 mL double distilled water, 25 mL ethanol, and 0.01 M CTAB were mixed in a beaker and stirred for 30 min continuously. 50 mL 1 M Na\textsubscript{2}S, 25 mL ethanol, and 25 mL double distilled water were added to the above solution and stirred for 30 min. To this mixture 20 mL 2 M NaOH was added dropwise with continuous stirring. It gives light yellow precipitate. Mixture thus formed was transferred to autoclave (with Teflon-inner-liner) and kept in an oven at 100°C for 2 h. Later it was cooled to the room temperature and the residue obtained was separated using centrifugation, washed several times with distilled water followed by ethanol and finally with acetone, and dried at 40°C to get pure CdS.

2.2.2. Synthesis of Pure and C Doped TiO\textsubscript{2} Nanoparticles. Pure and C doped TiO\textsubscript{2} nanoparticles were prepared using microemulsion method reported in our previous work [19]. 60 mL cyclohexane, 15 mL n-butanol, and 6 g CTAB were mixed together and mixture was stirred for 15 min. To this microemulsion solution containing 3 mL water and 9 mL 1 M titanium isopropoxide was added dropwise with constant stirring. This mixture was transferred to autoclave (with Teflon-inner-liner) and kept in an oven at 150°C for 2 h. Later it was cooled to the room temperature and the residue obtained was separated by centrifugation, washed several times with distilled water followed by ethanol and finally with acetone, and dried at 40°C. The product obtained was used as a precursor. This precursor was calcined in furnace at 300 and 500°C to get C doped and pure TiO\textsubscript{2}, respectively.

2.2.3. Synthesis of C Doped TiO\textsubscript{2}/CdS Core-Shell Nanocomposite (C/TiO\textsubscript{2}/CdS). 80 mL cyclohexane, 20 mL butanol, 4.0 g CTAB, and 6 mL 1 M cadmium nitrate were mixed in a beaker and stirred for 30 min. To this microemulsion 6 mL 1 M Na\textsubscript{2}S was added and mixture was stirred for 30 min. Afterwards, 6 mL 1 M titanium isopropoxide was added dropwise with constant stirring. This mixture was transferred to autoclave (with Teflon-inner-liner) and kept in an oven at 150°C for 2 h. Later it was cooled to the room temperature and the residue obtained was separated using centrifugation, washed several times with distilled water followed by ethanol and finally with acetone, and dried at 40°C for 2 h to get C doped and pure TiO\textsubscript{2}/CdS nanocomposite.

2.3. Characterizations. X-ray diffraction (XRD) patterns of all the calcined powders were recorded using Rigaku, (Model-Miniflex II) X-ray diffractometer with Cu Ka radiation (λ = 0.15418 nm) at a scan rate 2 min\textsuperscript{−1}. Average particle sizes were calculated using Debye-Scherrer equation \( t = nλ/B \cos θ \), where \( t \) is average particle size, \( n = 0.9 \), and \( B \) is full width of line at half of the maximum intensity (FWHM). FTIR spectra of samples were recorded with FTIR spectrophotometer (Bruker). Qualitative elemental analysis of the calcined powders was carried out using energy dispersive X-ray spectroscopy (EDX) using IEOLE-JSM instruments. Particle size of the compounds prepared in this work was studied using transmission electron microscope (TEM) (FEI, USA, Model-Technai-G\textsuperscript{2}). UV-visible spectrophotometer (Shimadzu, Model-1800) was used to study the band gap energy of synthesized nanopowders.

2.4. Photocatalytic Activity Study. Visible light photocatalytic activities of synthesized catalysts were evaluated for the degradation of methylene blue (MB) using 65 W compact fluorescent lamp (λ > 420 nm, Philips, Mumbai). Photodegradation was carried out using a homemade photo reactor with water jacket to maintain temperature through experiment. Distance between the light and the reaction vessel is fixed at 10 cm. 0.05 g photocatalyst powder was dispersed in 50 mL 10 ppm MB solution. Prior to photocatalytic measurements, the aqueous suspension was stirred in the dark for 30 min to attain adsorption-desorption equilibrium. After reaction suspension was irradiated with visible light. At specific time intervals, 5 mL aliquot was taken out, catalyst was separated using centrifugation, and concentration of MB in the supernatant solution was estimated from UV-visible spectra recorded in the wavelength range 200–800 nm.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD) Study. XRD patterns of C doped TiO\textsubscript{2}, CdS, and C doped TiO\textsubscript{2}/CdS core-shell nanoparticles were recorded and are presented in Figure 1. XRD pattern of CdS shows peaks which correspond to crystal planes (111), (200), (220), (311), (400), and (420) and are in good agreement with pure cubic CdS phase (ICPDS card number: 65-2887). Broadness of the peaks suggests that CdS particles are very small. XRD pattern of TiO\textsubscript{2} precursor calcined at 300°C (C doped TiO\textsubscript{2}) suggests that at this temperature TiO\textsubscript{2} formed is having anatase phase. Peaks at 2θ equal to 25.26, 38.16, 43.17, 54.83, 64.69, 68.16, 71.30, and 76.4° are assigned for (101), (004), (200), (105), (211), (204), (110), (220), and (215) hkl planes and are in good agreement with JCPD data file number 841285 (lattice planes of anatase TiO\textsubscript{2} phase). XRD pattern of C/TiO\textsubscript{2}/CdS core-shell nanocomposite suggests that this composite formed is a mixture of cubic CdS
and anatase TiO\textsubscript{2} phase. Average crystallite sizes of all the compounds were calculated using Debye-Scherer equation and data is presented in Table 1.

3.2. FTIR Study. FTIR spectra of CdS, C/TiO\textsubscript{2}/CdS precursor, C doped TiO\textsubscript{2}, and C/TiO\textsubscript{2}/CdS nanocomposite are shown in Figure 2. Precursor samples show bands at 3000–3500 cm\textsuperscript{-1} attributed to stretching vibration modes of OH group (TiO\textsubscript{2}-OH) (Figure 2(a)). It was believed that such TiO\textsubscript{2}-OH groups arise due to the hydrolysis reaction in the microemulsion process [20]. Peak at 1628 cm\textsuperscript{-1} is attributed to bending modes of –OH groups of water molecules adsorbed on the surface of catalyst [21]. Peak at 1389 cm\textsuperscript{-1} can be assigned to C–O stretching in carbonyl. Peak at 2920 cm\textsuperscript{-1} is assigned as characteristic peak of ammonium. Peak at 2851 cm\textsuperscript{-1} is due to symmetrical stretching vibration of methyl group. This information indicates that –OH and –C=O functional groups are present in precursor. Figure 2(b) shows that C doped TiO\textsubscript{2} and C/TiO\textsubscript{2}/CdS samples show a band corresponding to Ti-O-Ti vibration at about 419 cm\textsuperscript{-1}. Pure CdS shows a band at 605 cm\textsuperscript{-1} ascribed to Cd-S stretching [22, 23]. C/TiO\textsubscript{2}/CdS sample does not show peak which corresponds to Cd-S stretching at 605 cm\textsuperscript{-1} which might be due to formation of core-shell structure with CdS as core and C doped TiO\textsubscript{2} as shell. FTIR spectra of product obtained after heating the precursor at 300°C for 2 h show no absorption peak in higher frequency region but give the sharp peak below 500 cm\textsuperscript{-1} which may be due to stretching frequency of Ti-O-Ti bond in titanium dioxide.

3.3. Energy Dispersive X-Ray Spectroscopy (EDX) Study. Figure 3 represents EDX spectra of (a) C doped TiO\textsubscript{2}, (b) CdS, and (c) C/TiO\textsubscript{2}/CdS core-shell nanocomposite. EDX analysis shows that CdS nanoparticles contain only Cd and Se elements with 60.83 and 39.17 at%, respectively. TiO\textsubscript{2} precursor calcined at 300°C contains C, Ti, and O with
Table 1: Characteristic properties of photocatalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size/nm</th>
<th>C/at% b</th>
<th>Band gap (E_g)/eV c</th>
<th>Reaction parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rate constant (k)/min(^{-1})</td>
</tr>
<tr>
<td>Pure TiO(_2)</td>
<td>16.2</td>
<td>—</td>
<td>3.14</td>
<td>0.0045</td>
</tr>
<tr>
<td>C doped TiO(_2)</td>
<td>11.3</td>
<td>13.41</td>
<td>2.86</td>
<td>0.0108</td>
</tr>
<tr>
<td>CdS</td>
<td>6.2</td>
<td>—</td>
<td>1.82</td>
<td>0.0053</td>
</tr>
<tr>
<td>C/TiO(_2)/CdS core-shell</td>
<td>10.5</td>
<td>14.62</td>
<td>2.28</td>
<td>0.0326</td>
</tr>
</tbody>
</table>

a: particle sizes were obtained from TEM images.
b: C content was obtained from EDX spectra.
c: \(\lambda\) values were obtained from onset of light absorption edges and \(E_g\) values were calculated using Tauc plots.

Figure 3: EDX spectra of (a) Cdoped TiO\(_2\), (b) CdS, and (c) C/TiO\(_2\)/CdS.

13.42, 18.72, and 67.86 at%, respectively. EDX analysis clearly showed the presence of Cd, S, C, Ti, and O elements in the composite sample with 4.42, 3.79, 14.64, 36.83, and 40.32 at%, respectively.

3.4. Transmission Electron Microscopy (TEM) Study. TEM image of C doped TiO\(_2\) is presented in Figure 4(a). This image shows that C doped TiO\(_2\) particles are spherical in shape and average particle size was found to be 10 to 12 nm. TEM image of CdS nanoparticle is shown in Figure 4(b). This image shows that CdS nanoparticles are spherical in shape and well dispersed. Average particle size is varying between 6 and 7 nm. Figure 4(c) represents the TEM image of C/TiO\(_2\)/CdS core-shell nanocomposite. From this figure we can see that CdS particles act as a core and C doped TiO\(_2\) as a shell. A selected area electron diffraction (SAED) pattern of all the samples (inset) shows distinct rings indicating their crystalline nature.

C/TiO\(_2\)/CdS core-shell nanospheres were prepared by the microemulsion method. First Cd\(^{2+}\) ions from the aqueous Cd(NO\(_3\))\(_2\) solution form Cd(OH)\(_2\) microemulsion. Addition of sulfur in this solution gives CdS nanospheres by substituting OH\(^-\) ions with S\(^{2-}\) ions. After the addition of TTIP, Ti(OH)\(_4\) layer gets formed on CdS. This precursor was heated at 300°C for 2 h yielding C/TiO\(_2\)/CdS core-shell nanocomposite. The possible mechanism of the formation of C/TiO\(_2\)/CdS core-shell nanocomposite is described schematically in Figure 5.
3.5. UV-Visible Spectrophotometry Study. Photo response of pure CdS, C doped TiO$_2$, and C/TiO$_2$/CdS was studied from their UV-visible absorption spectra and presented in Figure 6. Pure TiO$_2$ sample obtained at 500$^\circ$C is white color and exhibits fundamental absorption edge at 387 nm. C doped TiO$_2$ prepared at 300$^\circ$C is blackish in color and shows absorption peak in visible region with band edge located at 433 nm. It indicates that C doping enhances absorption power and shifts absorption edge from UV to visible region. CdS nanopowder is yellow color and shows absorption edge around 680 nm. C/TiO$_2$/CdS core-shell nanopowder obtained at 300$^\circ$C is light grayish yellow color and shows absorption edge near 600 nm, indicating the effective enhancement in photoabsorption capacity in visible
region. Optical band gap ($E_g$) was determined using Tauc equation, $\alpha h \nu = A(\nu - E_g)^n/2$, where $\alpha$ is absorption coefficient, $\nu$ is light frequency, $A$ is proportionality constant, and $E_g$ is band gap. Band gaps of CdS, C doped TiO$_2$, and C/TiO$_2$/CdS nanocomposite estimated from Tauc plots (Figure 6) are 1.82, 2.86, and 2.28 eV, respectively. This suggests that nanosized CdS works as a sensitizer and effectively increases the visible light absorption capacity of C doped TiO$_2$.

3.6. Visible-Light Photocatalytic Activity Study. UV-visible spectra of MB solution irradiated with visible light in presence of C/TiO$_2$/CdS core-shell nanopowder at different time intervals were recorded and are presented in Figure 7. These spectra show that peak intensity at 688 nm decreases as the irradiation time increases. This is may be due to degradation of MB. Decrease in the concentration of MB was monitored by examining the variation in UV-visible spectra at 688 nm. Degradation of MB as a function of irradiation time in presence of different catalysts is presented in Figure 8(a). It shows that in absence of catalyst (i.e., photolysis process) MB dye is quite stable. In presence of C/TiO$_2$/CdS core-shell nanocomposite ∼97% of MB was degraded within
90 min. Kinetics of MB degradation in visible light was also studied. Graph of ln\((\frac{C_0}{C_t})\) against reaction time shows linear relationship, which indicates that photodegradation of MB follows first-order kinetics (Figure 8(b)). Rate constants \((K)\) and \(R^2\) values for corresponding reactions were calculated and are presented in Table 1. The order of rate constants in presence of different catalyst is C/TiO\(_2\)/CdS > C doped TiO\(_2\) > CdS > pure TiO\(_2\). It is in good agreement with the results obtained from photocatalytic degradation curves. C/TiO\(_2\)/CdS core-shell nanocomposite shows higher photocatalytic activity as compared to pure CdS, pure TiO\(_2\), and C doped TiO\(_2\). It may be attributed to small size of catalyst and increase in its photoabsorption strength by lowering the band gap energy. Reusability of C/TiO\(_2\)/CdS core-shell nanocomposite was tested by reusing the recovered photocatalyst for multiple cycles and results obtained are presented in Figure 9. This figure shows that photocatalytic activity of catalyst does not change significantly up to third cycle indicating that the catalyst is quite stable and can be reused.

3.7 Degradation Mechanism. Photocatalytic degradation of MB dye can be attributed to the chemical reactions of active species like OH\(^-\) and O\(_2\)\(^{2-}\) with dye molecules on the surface of photocatalyst [24]. The enhancement of photocatalytic activity of C/TiO\(_2\)/CdS core-shell nanocomposite heterostructure is due to effective coupling of CdS and C doped TiO\(_2\) as shown in Figure 10. Interstitial C doping can create intraband gap state close to the valence band edge of TiO\(_2\). Thus C doping leads to the narrowing of the band gap in TiO\(_2\) which increases its photoabsorption capacity in visible region. When C/TiO\(_2\)/CdS nanocomposite is exposed to visible light, photogenerated electrons are injected from conduction band of CdS to the conduction band of TiO\(_2\), producing high concentration of electrons in the conduction band of TiO\(_2\). On the other hand, holes generated on CdS remain on the valence band of CdS which gives effective charge separation of electron and holes [25]. Meanwhile, the C species could trap the part of photogenerated holes, which potentially reacts with the water adsorbed on the surface of photocatalyst and forms reactive hydroxyl radicals (OH\(^-\)). Conduction band electrons accumulated on the surface of TiO\(_2\) react with dissolved oxygen in water and produce highly oxidative species such as superoxide radical (O\(_2\)\(^{2-}\)). These highly reactive radicals (OH\(^-\) and O\(_2\)\(^{2-}\)) subsequently decompose organic substrate (MB) into CO\(_2\) and H\(_2\)O.

4. Conclusions

C/TiO\(_2\)/CdS core-shell nanocomposites have been successfully synthesized using microemulsion method. C/TiO\(_2\)/CdS nanocomposite shows red shift in the absorption spectra
attributed to enhancement in the photoabsorption capacity. C/TiO₂/CdS nanocomposite prepared in the present work exhibits better visible light photocatalytic activity compared to other photocatalysts for MB degradation. Photocatalyst prepared is stable and reusable.

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

Acknowledgments
The authors are thankful to Professor Sagar Mitra, Department of Energy Science and Engineering, Indian Institute of Technology, for kindly permitting use of EDX facility. The authors are also thankful to SAIF, IIT, Mumbai, for recording the TEM images of sample. One of the authors Atul B. Lavand is grateful to UGC, New Delhi, for providing BSR fellowship.

References


