Visible light photocatalytic degradation of malachite green using modified titania

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ABSTRACT

Nanoparticles of titanium dioxide co-doped with carbon and iron (III) were prepared using the microemulsion method. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Photoluminescence spectroscopy (PL), and UV-visible diffuse reflectance spectroscopy were used to characterize pure and doped TiO2 nanoparticles. Doped C atoms exist as the O–Ti–C structure or interstitial C in TiO2 lattice, while the doped Fe3+ atoms substitute some of Ti4+ to form the Ti–O–Fe structure. In comparison with the pure and C-doped TiO2, all C, Fe co-doped TiO2 samples exhibit a narrower band gap and stronger visible light absorption. The assistance of the C and Fe3+ ion enhances the photocatalytic activity in the visible light region and also inhibits the electron–hole recombination. The photocatalyst co-doped with C and 2.01 wt% Fe shows the excellent photocatalytic activity and degradation efficiency improved by 78% under visible light irradiation as compared with the pure TiO2.

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1. Introduction

Titanium dioxide TiO2 (titania) is an important technological material having wide range of applications such as degradation of pollutants [1], water splitting [2], component material in dye sensitized solar cells [3], gas sensors [4], etc. TiO2 is commonly used as photocatalyst due to its nontoxic nature, chemical stability, low cost, specific optical and electronic properties [5]. Anatase form of TiO2 shows relatively better reactivity and chemical stability for water and air purifications than rutile and brookite phases [6]. However, there are several limitations, as titania has a large band gap (Eg = 3.2 eV) hence only small fraction (about 5%) of solar light can be utilized for its photoexcitation [7]. To enhance the effective exploitation and conversion of solar energy, i.e., for the improvement of catalytic performance in visible light and also to influence generation of charge carriers if irradiated with light, TiO2 has been to be modified by doping it with transition-metal cations [8,9] non-metal anions [10,11] and coating dye on TiO2 surface [12,13]. Simultaneou s doping of two kinds of atoms into TiO2 has shown higher photocatalytic activity as compared

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to single element doping. TiO$_2$ doped with transition metal cations was reported as a good tool to improve photocatalytic properties under visible light irradiation. Among them, Fe doping has been intensively studied [14,15]. Fe replaces some of Ti$^{4+}$ ions and reduces the band gap of TiO$_2$ by introducing new energy level within the band gap of TiO$_2$. Also, Fe dopants could act as hole and electron traps to inhibit recombination of the photogenerated charge carriers, leading to improved photocatalytic activity [16]. Photocatalytic activity is highly dependent on Fe concentration as the doping sites could also act as the electron–hole recombination centers at higher concentration. One of the advantages of Fe doping is that the trace amount of Fe that might be leached out from host lattice is non-toxic. Also, doping of TiO$_2$ with non-metals such as N, C, S, P, showed potential to induce visible-light activity. Among these, C doped TiO$_2$ showed excellent photocatalytic activity for degradation of various organic pollutants under visible light irradiation [17].

Particle size is one of the most significant factors, which affects the photocatalytic activity of titania. Many researchers reported that photocatalytic activity increases with decrease in particle size of titania (in nanometer scale region), due to high surface area and short interface migration distances for photo-induced holes and electrons [18,19]. There are numerous techniques used to synthesize nano-crystalline titania such as sol–gel method [20,21], hydrothermal method [22], chemical vapor deposition [23], chemical precipitation [24]. These methods need vigorous stirring, high temperature processing and long aging time which results in formation of big particles with wide size distribution. On the other hand, microemulsion method is very efficient for synthesis of nanosized TiO$_2$ [25]. Major advantages of this method are low reaction temperature, short processing time and prevents agglomeration of nanoparticles synthesized [26,27].

In this study iron is used as a transition metal modification on carbon doped titania using reverse microemulsion route. The enhanced photocatalytic activity of C, Fe modified TiO$_2$ was attributed to small particle size, increase in visible light absorption capacity and effective separation of electron–hole pair.

2. **Experimental**

2.1. **Materials**

Titanium isoproxide Ti(iOPr)$_4$ (Sigma Aldrich, Mumbai, India) is used as a source of titanium. Cyclohexane, n-butanol (AR grade, SD Fine, Mumbai, India) and distilled water were used as solvents. N,N,N-cetyl trimethyl ammonium bromide (CTAB) (AR Grade, SD Fine, Mumbai, India) was used as surfactant. Ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O) (SD Fine, Mumbai, India) was used as Iron source. Malachite green (MG) was procured from Hi Media Laboratories, Mumbai and used without any further purification.

2.2. **Catalyst preparation**

TiO$_2$ as well as C and Fe doped TiO$_2$ nanoparticles were prepared using microemulsion method. In a typical method, cyclohexane (120 mL), n-butanol (30 mL) and CTAB (12 g) were mixed and solution was stirred for 15 min. To this micro emulsion double distilled water (6 mL) and titanium isoproxide (18 mL, 1 mol/L) solution were added dropwise with constant stirring. This mixture was transferred to autoclave (with teflon-inner-liner) and autoclave was kept in an oven at 423 K for 2 h. Later, it was cooled to the room temperature. The precipitate formed was separated using centrifugation, washed several times with ethanol and distilled water and dried at 313 K. The product obtained was used as a precursor. This precursor was calcined in furnace at 773 K for 2 h to get nanosized TiO$_2$. Similarly, C doped TiO$_2$ was prepared. To get C doped TiO$_2$, precursor was calcined at 573 K for 2 h. To prepare C, Fe co-doped TiO$_2$ stoichiometric amount of Ferric nitrate was added in a microemulsion and precursor was calcined at 573 K for 2 h. Average particle size of pure and doped TiO$_2$ prepared in present work varies between 5 and 16 nm.

2.3. **Catalyst characterization**

Precursors (pure and doped) were heat treated at 573, 673 and 773 K for 2 h and the XRD patterns of the product obtained at different temperatures were recorded using X-ray diffractometer (Rigaku, Model-Miniflex II) using monochromatized CuK$_\alpha$ radiation (λ = 0.15405 nm) with scanning rate of 2° 2θ min$^{-1}$. Morphology of samples were examined using Scanning electron microscope (JEOL-JSM6360A) and transmission electron microscope (Phillips, CM200). Elemental composition study was carried out using energy dispersive X-ray (EDX) spectroscopy equipped with scanning electron microscope and X-ray photoelectron spectrum (XPS) with PHI VersaProbe-II photoelectron spectroscopy (Physical Electronics, USA) with Al K$_\alpha$ radiation. Photoluminescence spectra of samples were recorded at room temperature using Fluorescence spectrophotometer (Perkin Elmer-LS-55) with excitation wavelength 325 nm. UV-visible diffuse reflectance spectra of the samples were recorded using UV-Vis spectrophotometer (Shimadzu, UV-1800) equipped with integrating sphere and BaSO$_4$ was used as a reference. The scanning range was from 200 to 800 nm. The band gap energy value was calculated using Kubelka–Munk plot.

2.4. **Measurement of photocatalytic activity**

Photocatalytic activities of pure and doped TiO$_2$ photocatalysts were investigated for degradation of MG solution. Reaction suspension was prepared by adding 0.05 g photocatalyst in 50 mL (10 ppm) MG solution. pH of this solution was found to be 6.71. This aqueous suspension was stirred in the dark for 30 min to attain adsorption-desorption equilibrium. Amount of malachite green dye adsorbed on different photocatalysts in the dark varies between 0 and 10% (Fig. 9). Later the solution was irradiated with visible light. The visible light irradiation was carried out in a photo reactor using a compact fluorescent lamp (65 W, λ > 420 nm, Philips, Mumbai). The distance between the fluorescent lamp and the reaction vessel was fixed at 10 cm. Intensity of the light reaching to the test solution is 42 W m$^{-2}$. Temperature of test solution was maintained constant throughout the experiment by circulating water around the solution. The reactant solution
was irradiated under visible light for different time intervals. The catalyst was separated by centrifugation and the concentration of MG in the supernatant solution was estimated using UV-visible spectrum recorded in the wavelength range 200–800 nm.

3. Results and discussion

3.1. Structural analysis

XRD patterns of precursor heated at various temperatures were recorded and are presented in Fig. S1. The peaks at 2θ values 25.26, 38.16, 48.17, 54.03, 64.69, 68.16, 71.10 and 76.4° are fitted and their hkl planes were identified as (101), (004), (200), (105), (211), (204), (110), (220) and (215), respectively, which are consistent with JCPD card number 84-1285 (anatase TiO₂). The diffraction pattern reveals that, as synthesized TiO₂ nanoparticles consists of pure anatase phase having tetragonal structure. As the calcinations temperature increases from 573 K to 773 K intensity of diffraction peaks increases which indicates the increase in crystal size. XRD patterns of C, Fe co-doped precursor calcined at 573 K are presented in Fig. 1, which consists of purely anatase phase. No additional peaks are observed for C and Fe doping, which might be due to lower Fe concentration in TiO₂ samples. Here Ti⁴⁺ ions are substituted by Fe³⁺ ions, as Ti⁴⁺ and Fe³⁺ have comparable radii, 0.745 Å and 0.69 Å, respectively [28–30]. As the Fe concentration increases diffraction peaks are shifted toward lower angles which indicate successful doping of Fe into TiO₂ lattice. The shifting of diffraction peak positions generally depends on synthesis procedures and precursor used. The average crystallite sizes of pure and doped TiO₂ were calculated using Debye–Scherrer equation and results indicate that doping of Fe³⁺ decreases the crystal size of TiO₂ (Table 1).

3.2. Elemental composition analysis

EDX spectra of (a) undoped TiO₂ precursor calcined at 773 K, (b) 573 K and Fe doped precursor with (c) 1.16 (d) 2.01 (e) 3.08 (f) 4.87 and (g) 6.68% Fe calcined at 573 K were shown in Fig.S2.

![XRD patterns of TiO₂](image)

Fig. 1 – XRD patterns of (a) Pure TiO₂ and TiO₂ doped with (b) 1.16, (c) 2.01, (d) 3.08, (e) 4.87, (f) 6.68% Fe precursor calcined at 573 K.

Elemental composition of C and Fe in TiO₂ are presented in Table 1.

3.3. Morphology and size analysis

The surface morphology and size of pure and doped TiO₂ samples were investigated using SEM and TEM techniques. Fig. 2 represents SEM images of pure and doped TiO₂ samples. It shows that TiO₂ particles are having a spherical shape and are uniformly distributed. The particle size of as synthesized samples was measured using TEM technique (Fig. 3). These images show that TiO₂ particles are spherical in shape. Surface morphologies are not affected by C and Fe doping, indicating that C and Fe are successfully incorporated into the TiO₂ lattice crystal. Selected area electron diffraction (SAED) pattern confirms the crystalline nature of TiO₂ nanostructures. The d-spacing of the rings corresponding to the hkl planes (101), (103), (200) and (105) are identified. The hkl planes of pure anatase TiO₂ phase indicating tetragonal structure and is in good agreement with the XRD data. It can be seen from the TEM images that the particle sizes of TiO₂ particles are in the range 6–15 nm, which is in good agreement with the crystallite size obtained from XRD results.

These images indicate that particle size goes on decreasing with introduction of C and Fe co-doping into TiO₂ lattice. The decrease in crystallite size may be caused by a number of defects in the anatase crystals produced by the substitution of part of the Ti⁴⁺ site by Fe³⁺ ions. It also indicates that in case of pure TiO₂ particle size varies between 8 and 15 nm (Fig. 3a). Whereas C doped TiO₂ prepared at 573 K (Fig. 3c) having particle sizes between 8 and 11 nm. C, Fe co-doped TiO₂ with 2.01 wt% of Fe have a particle size varies between 6 and 9 nm.

3.4. Chemical composition analysis

Fig. 4 shows the XPS survey spectra for Pure, C doped and C, Fe (2.01 wt%) co-doped TiO₂ nanoparticles. The Ti 2p₁/₂ and Ti 2p₃/₂ spin-orbital splitting photoelectrons for TiO₂ are located at binding energies of 457 and 463 eV, respectively, which is consistent with the values of Ti⁴⁺ in the TiO₂ lattices [31]. The comparison between the Ti 2p₃/₂ spectra of undoped TiO₂ and those of C and C, Fe doped TiO₂ indicates that the doped TiO₂ samples exhibit small binding energy shifts. It infers that the doped C and Fe ions may diffuse into TiO₂ lattices to form the O–Ti–C and Fe–O–Ti bond. The O 1s main peak at 528 eV is assigned to the metallic oxides, which is consistent with the binding energy of O₂ in the TiO₂ lattices [32].

A shoulder to the main O 1s peak observed at high binding energy, which can be attributed to the hydroxyl groups or chemisorbed water molecules adsorbed on TiO₂ surface [33]. It is noted that the O 1s spectra of C and C, Fe co-doped TiO₂ have a small binding energy shift compared with undoped TiO₂. The results can be ascribed to an increase in the ionic state of the oxygen bond causing the binding energies of all electronic states of oxygen to shift and successful incorporation of C and Fe atoms [34,35]. The oxygen content increases from 31.6%, and 36.8 (C, Fe co-doped TiO₂ and C doped TiO₂ prepared at 573 K) to 46.3% in pure TiO₂ prepared at 773 K as a result of the decomposition of the carbonaceous groups at
Table 1 – Some characteristic properties of photocatalyst.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>C content (wt%)</th>
<th>Fe content (wt%)</th>
<th>Band gap ($E_g$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure TiO$_2$</td>
<td>16.2</td>
<td>–</td>
<td>–</td>
<td>3.14</td>
</tr>
<tr>
<td>2</td>
<td>C doped TiO$_2$</td>
<td>13.4</td>
<td>–</td>
<td>–</td>
<td>2.86</td>
</tr>
<tr>
<td>3</td>
<td>C, Fe codoped TiO$_2$</td>
<td>12.3</td>
<td>3.10</td>
<td>1.16</td>
<td>2.84</td>
</tr>
<tr>
<td>4</td>
<td>C, Fe codoped TiO$_2$</td>
<td>10.1</td>
<td>2.76</td>
<td>2.01</td>
<td>2.81</td>
</tr>
<tr>
<td>5</td>
<td>C, Fe codoped TiO$_2$</td>
<td>12.1</td>
<td>2.93</td>
<td>3.08</td>
<td>2.77</td>
</tr>
<tr>
<td>6</td>
<td>C, Fe codoped TiO$_2$</td>
<td>12.1</td>
<td>3.10</td>
<td>4.87</td>
<td>2.29</td>
</tr>
<tr>
<td>7</td>
<td>C, Fe codoped TiO$_2$</td>
<td>13.8</td>
<td>2.81</td>
<td>6.68</td>
<td>2.15</td>
</tr>
</tbody>
</table>

a Particle sizes are calculated from XRD results using Debye–Scherrer equation.
b C and Fe content obtained from EDX measurement.
c λ values are obtained from onset of light absorption edges and $E_g$ values were calculated using Kubelka–Munk plot.

Fig. 2 – SEM images of undoped TiO$_2$ precursor calcined at (a) 773 K, (b) 573 K and TiO$_2$ precursor doped with (c) 1.16, (d) 2.01, (e) 3.08, (f) 4.87, (g) 6.68% Fe calcined at 573 K.

High temperature. Fe 2p spectrum was used to evaluate the electronic nature of iron in C, Fe doped TiO$_2$. Fe2p core level spectrum indicates that binding energy centers of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ peaks are located at 710 and 724 eV, respectively. Binding energy at 718 eV suggests that Fe is incorporated into the TiO$_2$ lattice in Fe$^{3+}$ ionic state and have Fe–O–Ti environment within the TiO$_2$ lattice. The C 1s peaks located at 284 and 287 eV, which may be due to the remaining organic precursor not yet completely removed at 573 K. The doping of C species in TiO$_2$ might exist as O–Ti–C and Ti–O–C. From the XPS elemental analysis of samples, it was confirmed that carbon-containing species exist in the samples. This may be due to the reaction between titanium isopropoxide, cyclohexane, n-butanol and CTAB the carbon-containing species get trapped in the growing TiO$_2$. At appropriate post calcinations temperature around 573 K, C may get incorporated into TiO$_2$ lattice. At higher calcination temperature (773 K) C may get decomposed and replaced by oxygen atoms.
Fig. 3 – TEM images of (a) pure TiO$_2$, (c) C doped TiO$_2$, (e) C,Fe (2.01 wt%) co-doped TiO$_2$ and SAED patterns of (b) pure TiO$_2$, (d) C doped TiO$_2$, (f) C,Fe (2.01 wt%) co-doped TiO$_2$.

Fig. 4 – (a) XPS survey spectra for pure TiO$_2$, C doped TiO$_2$ and C, Fe (2.01 wt%) co-doped TiO$_2$ photocatalysts and (b) high resolution XPS spectra of Ti 2p, O 1s, C 1s and Fe 2p.
3.5. Band gap energy

The color of C doped TiO₂ sample prepared at 573 K is gray; however, the sample prepared at 773 K is almost white. C, Fe co-doped TiO₂ sample is grayish brown in color and as the concentration of Fe increases it changes to dark brown. Their optical properties were studied using UV-Visible diffuse reflectance spectra and the results are presented in Fig. 5 and Fig. S3.

The band gap energies of pure and doped TiO₂ samples were calculated from the diffuse-reflectance spectra by performing a Kubelka-Munk analysis using the equation: \( F(R) = (1 - R)^2/2R \). Where, \( R \) is the diffuse reflectance. The band gap energies can be calculated by plotting the \( F(R)/hv \) as a function of the energy in electron volts. The pure anatase TiO₂ is having the band gap energy 3.14 eV. The band gap for C modified TiO₂ sample is 2.86 eV, which is lower than that of pure anatase TiO₂. It is due to the fact that C 2p level from the interstitial carbon could hybridize with O 2p level to form an upshift valence band and then narrows the band gap [39]. The absorption edge shifts to lower energies/higher wavelength with increasing Fe concentration. The band gap was 2.84 eV for 1.16 Fe/C-TiO₂, 2.81 eV for 2.01Fe/C-TiO₂, 2.77 eV for 3.08 Fe/C-TiO₂, 2.29 eV for 4.87 Fe/C-TiO₂, and 2.15 eV for 6.68 Fe/C-TiO₂. This result is consistent with the changes in the color of the samples. Besides the effect of C, the origin of this visible light absorption was also due to the formation of a dopant energy level within the band gap of TiO₂ with iron doping [9]. Shift in visible region (Red shift) upon increasing the doping concentration corresponds to a sp-d exchange interaction between the band electrons and the localized d electrons of the substituted dopant ions.

3.6. Photoluminescence study

The photoluminescence emission (PL) is a useful technique to reveal the efficiency of electron–hole pair trapping, immigration and transfer in semiconductor particles. The PL emission spectra of all samples are presented in Fig. 6. Pure TiO₂ exhibits emission bands at 403 and 460 nm. Emission centered at 403 nm is attributed to excitonic recombination corresponding to the near band edge emission of TiO₂. The emission in the blue-green region at 460 nm is attributed to the electron transition between a shallow donor and a deep acceptor. It is observed that the peak positions were similar, but PL intensities varies among these samples. It is known that photoluminescence effect, is a result of direct radiative recombination of electron–holes and lower recombination of generated carriers causes the decrease of PL intensity [40]. Lower the excitonic PL intensity, stronger the capacity of dopants to capture photo-induced electrons, higher the separation rate of photoinduced electrons and holes, and higher the photocatalytic activity [41]. The PL intensity of pure TiO₂ is highest among all samples, indicates the increase of recombination of electron and hole. C and Fe co-doped TiO₂ shows decrease in PL intensity which confirms that the recombination of electron–hole pairs is effectively suppressed because Fe(III) cations could act as shallow traps in the lattice of TiO₂. Here, Fe(III) cations are acting as photogenerated hole trappers. The trapped holes by Fe(III) cations migrate to the surface adsorbed hydroxyl ion to produce hydroxyl radicals. 2.01 Fe-CT sample shows lowest PL intensity, implying that the charge carriers are separated more effectively, which reasonably led to a higher photocatalytic activity.

3.7. Visible-light photocatalytic activity study

Visible light photocatalytic degradation of malachite green (MG) was studied in presence of nanosized pure and doped
TiO$_2$ photocatalysts. UV visible spectra of aqueous solution of MG irradiated with visible light at different time intervals in presence of C, Fe (2.01 wt%) co-doped TiO$_2$ (obtained at 573 K) photocatalyst were recorded at different time intervals and are presented in Fig. 7. These spectra show characteristic peak maxima located at 616 nm. As irradiation time increases the height of peak at 616 nm decreases. This is due to photocatalytic degradation of malachite green. Appearance of a peak around 370 nm in the UV-Visible spectra after 75 and 90 min may be due to the formation of less hazardous byproducts.

3.7.1. Effect of calcination temperature of catalyst

UV-visible spectra of MG solution (20 ppm) irradiated with visible light for different time intervals in presence of TiO$_2$ photocatalyst obtained by calcining precursor at various temperatures were recorded. Effect of calcination temperature on the degradation of MG in the presence of visible light (90 min of irradiation time) is presented in Fig. 8. It reveals that photocatalytic activity depends on calcination temperature of catalyst.

In absence of catalyst there is slight decrease in MG concentration it indicates that MG is quite stable in visible light. Photocatalyst prepared at 573 K exhibits better photocatalytic activity and as calcination temperature increases the photocatalytic activity decreases. This is due to the fact that with increasing the calcination temperature particle size of catalyst increases and photocatalytic activity decreases. Also, TiO$_2$ prepared at 573 K contains 7.59% C and as the calcination temperature increases the amount of C on TiO$_2$ decreases. It is known that C doped TiO$_2$ exhibit better photocatalytic activity than bare TiO$_2$. Precursor calcined at 573 K exhibit better visible light activity as compared to the precursors calcined at high temperatures. Therefore, the C, Fe co-doped precursors were calcined at 573 K and used for further study.

3.7.2. Effect of co-doping

Compared to bare TiO$_2$, C doped TiO$_2$ exhibit better visible light catalytic activity for degradation of MG. To enhance the visible light activity further, TiO$_2$ was co-doped with Fe and the photocatalytic activity of C, Fe co-doped TiO$_2$ was studied and results are presented in Fig. 9. It shows that compared to bare and C doped TiO$_2$, C, Fe co-doped TiO$_2$ has better degradation efficiency. As the amount of Fe increases degradation of MG increases up to 2.01% Fe doping. Further increase in the amount of Fe results in decrease in MG degradation. The photocatalytic activity of Fe and C modified TiO$_2$ is higher due to Fe doping, because it effectively captures photo induced electrons and inhibits the electron–hole recombination and improves photocatalytic activity. Synergistic effects of C and Fe co-doping increases the utilization of visible light by narrowing the band gap and also enhances the separation of photo generated holes and electrons which leads to increase in photo degradation rate of malachite green [42]. Higher doping of Fe, i.e., above 2.01 wt% may be responsible for recombination of electron and holes and hence photocatalytic activity decreases.
3.7.3. Recycling of catalyst
Stability of photocatalyst during photodegradation process is an important factor for practical application. Stability tests were performed by repeating the reaction three times using recovered photocatalyst. The data obtained is presented in Fig. 10. This figure shows that up to the third cycle there is no noticeable decrease in photocatalytic efficiency. It indicates that C, Fe co-doped TiO$_2$ prepared in the present work is stable and reusable photocatalyst.

3.7.4. Origin of visible light absorption and photoexcitation mechanism over C, Fe co-doped TiO$_2$
Carbon and iron co-doping have synergistic effects on improving the photocatalytic activity of TiO$_2$ under visible light irradiation. We proposed a possible mechanism for the synergistic effects of C and Fe, which is illustrated in Fig. 11. Pure TiO$_2$ due to its large band gap can be activated in UV light only. For C-doped TiO$_2$, C can create new energy level just above the valence band of TiO$_2$ and reduces the band gap. Hence, C-doped TiO$_2$ can be activated in visible light. On the one hand, C, Fe co-doped TiO$_2$ shows further decrease in band gap due to simultaneous doping of two atoms. Here, interstitial carbon dopant could create intra-band-gap states close to the valence band edges and Fe$^{3+}$ present in the substitutional positions into the TiO$_2$ lattice would introduce a dopant energy level below the conduction band of TiO$_2$. Due to this reason C and Fe modified TiO$_2$ shows highest absorption in visible light region. Consequently, more photons from visible region are utilized to generate photogenerated electrons and holes. C and Fe doping in TiO$_2$ systems may improve the separation efficiency of photogenerated electrons and holes. Under visible light irradiation, Fe ions act as shallow electron-trapping centers. Subsequently, Fe$^{3+}$ could be oxidized to Fe$^{2+}$ by transferring electrons to absorbed O$_2$ on the surface of TiO$_2$ and a neighboring surface Ti$^{4+}$, which then lead to interfacial electron transfer [15].

\[
\begin{align*}
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+} \\
\text{Fe}^{2+} + \text{O}_2(\text{ads}) & \rightarrow \text{Fe}^{3+} + \text{O}_2 \\
\text{Fe}^{2+} + \text{Ti}^{4+} & \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+} \\
\text{Ti}^{3+} + \text{O}_2(\text{ads}) & \rightarrow \text{Ti}^{4+} + \text{O}_2.
\end{align*}
\]

In the intervening time, the C species could trap the part of photogenerated holes [17]. Thus, the recombination rate of photogenerated electrons and holes is concealed. As a consequence, the photocatalytic degradation efficiency of C and Fe modified TiO$_2$ is improved. The synergistic effects of C and Fe not only enhance the utilization efficiency of solar energy due to narrowing the band gap because of C and Fe co-doping, but also sufficiently endorse the separation of photogenerated electrons and holes and then lead to high photodegradation of MG under the visible light irradiation.

4. Conclusions
In the present work, the synthesis and characterization of TiO$_2$ and C, Fe modified TiO$_2$ prepared by a microemulsion method was described. The photocatalysts calcined at 573 K are spherical particles with a crystallite size about 7-20 nm and the crystal phase is purely anatase. Diffuse reflectance spectra indicate that C and Fe co-doping improves visible light absorption capacity of TiO$_2$ samples. The results of the XPS study suggest that Fe ions are predominantly in Fe$^{3+}$ states and have Fe–O–Ti environment within the TiO$_2$ lattices. The C and Fe(III) doped TiO$_2$ samples shows better photocatalytic activity as compared to bare and C doped TiO$_2$ and the optimum doping amount of Fe is 2.01 wt%. The high rate of photodegradation of MG with visible light irradiation is due to synergistic effect of C and Fe, which efficiently promotes separation of photogenerated electrons and holes. Also, synthesized photocatalyst is highly stable and reusable photocatalyst.
Conflicts of interest
The authors declare no conflicts of interest.

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Appendix A. Supplementary data
Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmrt.2017.05.019.

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