Ceria doped TiO₂ as photocatalyst for water treatment under visible light

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Abstract. The photocatalytic activity of bare titania and ceria supported mesoporous titania (CeO₂/TiO₂) catalysts were assessed for the degradation of caffeine by visible light irradiation in absence of the oxidants. Different wt % metal loaded (bare, 0.1, 0.5 and 1.0) materials were synthesised by a sol-gel method using anionic surfactants. Various instrumentation techniques were used to characterise the prepared photo-catalysts such as P-XRD, BET, TEM, SEM-EDX, FT-IR, Raman, UV-DRS and photoluminescence spectroscopy. 0.5% CeO₂ doped titania exhibited excellent efficiency in photo degradation of caffeine in aqueous solution relative to all the other prepared heterogeneous catalysts. All the materials showed good efficiency and were recyclable without loss of catalytic activity up to three times. Analysis of degradation products was carried by Liquid chromatograph-mass spectrometry. Two reaction products 6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetradropimidin-5-ly)-methylcarbamic acid (ATCA) and N-methyl-N-(methylcarbomoyl)-2-oxoacetamide (MMO) were positively identified.

1. Introduction

The persistence of organic pollutants in water systems is one of the major concerns for the environmental protection and the entire world. Pharmaceutical compounds are a group of organic pollutants that have become an environmental topic of discussion. Wastewater treatment plants (WWTP) and sewage treatment plants (STP) have been noticed as main causes of environment discharge. Due to they were not designed to deal with this type of contaminants. As a result, pharmaceutical compounds have been perceived in surface waters and ground waters in sediments [1-4]. Pharmaceuticals may reach the aquatic environment through different pathways, i.e. from domestic wastewater from urban areas, effluent from pharmaceutical manufacturing industries, hospital disposal, and the disposal of unused medicine [5,6]. The metabolites originating from the human consumption of medicines entering the water bodies and reservoirs is an issue of concern for environmental health and sustainability. Appropriate eco-friendly technologies for effective removal or degradation of such organic chemicals is vital.

In recent years, heterogeneous photo-catalysts have been widely investigated for water purification and degradation of emerging contaminants in wastewater [7,8]. Particularly, titania (TiO₂) is one of the most promising and developing technology semiconductors that has been applied in the degradation of organic contaminates in aqueous system. Some of the attractive qualities of TiO₂ are its high activity, strong oxidizing power, chemical stability, robustness against photo-corrosion, low toxicity, eco-friendliness and cost-effectiveness [9,10]. The water molecules and the hydroxides effectively act as photo-excited hole traps on the catalyst surface and generate OH⁻ radicals, which are powerful
oxidants in degrading organic compounds [11,12]. UV and visible light are used as the energy source of photons to excite the semiconductor across the band gap. Then it leads to the excitation of an electron from the valence band to the conduction band, thereby generating an electron-hole pair. Further, the combination of the photo-generated electrons and holes lead to the release of heat or photon. Sometimes, there is a possibility of the relocation of the photo-generation holes to move into the surface of the semiconductor [13,14]. There are some limitations with using TiO$_2$ as a photocatalyst, such as the large band gap energy (3.2eV) for anatase. This limits the use of TiO$_2$ in the ultraviolet region (< 380 nm), which is only about 5 % of the solar spectrum [15].

Various techniques including surfactants in preparation and loading the metal ions are employed to decrease the bandgap of the semiconductors to be sensitive to visible light. Rare earth metals having empty 5d and incomplete 4d orbitals are ideal metals to serve as dopants and they promote photocatalysis [16,17]. Ceria has a good redox pair Ce$^{3+}$/Ce$^{4+}$, which plays a vital role as a catalyst, which led to its application as photo-catalyst in degradation of dye [18]. Ryu et al has showed that doping TiO$_2$ with Ce increased its photocatalytic activity in degradation of 2-mercaptobenzothiazole (MBT) [19].

In this present work, we report ceria doped on TiO$_2$ photo catalysts in degradation of caffeine using visible light. Ceria used as a metal dopant to reduce the band gap energy of anatase into visible region. Caffeine used as a model compound, which among the pharmaceuticals are the mostly found in wastewater treatment plant effluents.

2. Experimental section

2.1. Catalyst synthesis

This sol-gel procedure was adopted for the preparation of the ceria doped on titania (CeO$_2$/TiO$_2$) (wt% 0.1, 0.5, and 1.0) and bare TiO$_2$. For a model synthesis, 2 g of Pluronic F-127 was dissolved in absolute ethanol (60 mL) into a closed 400 mL Pyrex beaker. Then it was stirred for 4 h. Six mL of titanium (IV) isopropoxide was added dropwise to the solution and stirring was continued for 2 h, followed by dropwise addition of deionised water (36 mL). The mixture was continuously for 24 h till it turned from clear to white gel followed by aging it 12 h in the dark at room temperature. Next, the gel was dried in an oven at 80°C for overnight and the yellowish solid obtained was then calcined in the presence of air, at 450°C for 4 h to obtain the white powder of undoped TiO$_2$. Different wt% of the ceria doped on titania materials were synthesised following the similar protocol, but using 36 ml of water with requisite amounts cerium acetylacetonate hydrate precursor dissolved in it. The resultant catalyst materials were denoted as bare TiO$_2$, 0.1 wt% CeO$_2$/TiO$_2$, 0.5 wt% CeO$_2$/TiO$_2$ and 1.0 wt% CeO$_2$/TiO$_2$. Materials and methods section is provided in the supporting information (SI-I).

2.2. Photocatalysis experiments

Photo-degradation experiments of caffeine were carried on lab scale using a 32 W / 480 Osram dulux F378 daylight – Compact fluorescence lamp. The lamp was fitted into a cylindrical Pyrex jacket used to cover the lamp. Reaction was conducted in a 1 L Pyrex beaker, and the vessel was set on a magnetic stirrer together with a lamp in the jacket. 300 ml of caffeine solutions containing 5, 10 or 15 mg L$^{-1}$ were used in the experiments. In a typical run, 50 mg of catalyst was added to the caffeine solution. Then the solution was ultra-sonicated for 10 min and stirred in the dark for 60 min before light illumination. After 1 h, the solution was an irradiated with 32 W day light fluorescence lamp for 2 h. To monitor the progress of the reaction, 4 ml aliquots of reaction mixture was withdrawn at 20 min intervals. Samples were centrifuged using a Mikro 120 micro centrifuge for 2 min at 140 rpm and filtered using 0.45 micron. The extent of degradation of caffeine was monitored spectrophotometrically by recording the absorbance values at its absorption maxima 271 nm as function of reaction progress.
2.3. Products analysis
The product analysis was done using Shimadzu, LC-MS TOF mode. System was equipped with an electrospray ionization source ESI. An injection volume was kept at 10 µL. Isocratic elution using a reverse phase, in which mobile phase was made of 65% v/v acetonitrile and 35% v/v methanol. The chromatogram was recorded for 15 min run and the product peaks appeared between retention times of 3 and 4 minutes. Samples were analyzed after 20 minutes starting of the caffeine degradation reaction.

3. Results and discussion
3.1. Catalyst characterisation

3.1.1. BET analysis. Figure 1 shows the N\textsubscript{2} isotherms of the synthesized materials. The BET surface areas of the material are tabulated in table 1. All the catalyst materials were observed to be type IV with H1 hysteresis loop [19]. Type IV isotherms are usually associated with mesoporous materials and H1 hysteresis loop is caused by agglomerates in the materials. Further, it is also characteristic of material with high pore size uniformity. The calculated BET surface area of all four catalysts exhibited the similar pattern, which is a commonly observed trend in doped materials, when the metal dopant possess larger surface area than TiO\textsubscript{2}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{n2isor.png}
\caption{N\textsubscript{2} sorption/desorption isotherms of (a) bare TiO\textsubscript{2} (b) 0.1% Ce/TiO\textsubscript{2} (c) 0.5% Ce/TiO\textsubscript{2} and (d) 1.0% Ce/TiO\textsubscript{2} as prepared material.}
\end{figure}
Table 1. Summary of the textural characterizations, XRD and band gap analysis for the prepared materials.

| Sample          | BET Surface area/ m²g⁻¹ | BJH adsorption pore volume/ cm³g⁻¹ | BJH adsorption pore size/ nm | FWHM (101) / rad | Anatase crystal size (101) / nm | Band gap energy / eV | EDX / Wt. % |
|-----------------|-------------------------|----------------------------------|-------------------------------|------------------|--------------------------------|---------------------|-------------|
| Bare TiO₂       | 15.955                  | 0.0841                           | 18.012                        | 0.01556          | 8.92                           | 3.14                | --          |
| 0.1% Ce/TiO₂    | 36.754                  | 0.1762                           | 17.232                        | 0.01829          | 7.58                           | 3.12                | 0.098       |
| 0.5% Ce/TiO₂    | 57.884                  | 0.2229                           | 12.613                        | 0.01902          | 7.29                           | 3.05                | 0.481       |
| 1.0% Ce/TiO₂    | 66.048                  | 0.3342                           | 16.475                        | 0.01831          | 7.54                           | 2.88                | 1.025       |

3.1.2. SEM & TEM analysis. SEM and TEM micrograph of CeO₂/TiO₂ (wt% 0.1, 0.5, and 1.0) and bare TiO₂ are shown in the figures 2 and 3 below. An examination of the micrographs indicates that particles have irregular shapes and agglomerated. XRD spectra shows that ceria doping decreases the crystalline size by inhibiting growth, but this does not affect the morphology of the material. The presence of ceria was established by EDX analysis of the catalyst material. The results suggest that ceria is well dispersed throughout the TiO₂ surface. EDX revealed the presence of Ti, O and Ce.

Figure 2. Scanning electron micrographs of (a) bare TiO₂ (b) 0.1% Ce/TiO₂ (c) 0.5% Ce/TiO₂ and (d) 1.0% Ce/TiO₂ as prepared material.
Figure 3. Transmission electron micrographs of (a) bare TiO$_2$ (b) 0.1% Ce/TiO$_2$ (c) 0.5% Ce/TiO$_2$ and (d) 1.0% Ce/TiO$_2$ as prepared material.

Figure 4. IR Spectra of the prepared material.

3.1.3. FTIR analysis. Figure 4 displays the FTIR spectrum of CeO$_2$ doped TiO$_2$ samples and bare TiO$_2$. The absorption bands found in the low range of 500–800 cm$^{-1}$ for correspond to Ti–O and Ti–O–Ce bands [20,21]. The broad absorption peaks appeared at 3300 cm$^{-1}$ due to the physisorbed OH group at the surface of the material [4]. The Ti–O–Ti bands are seen in the region of 380–1130 cm$^{-1}$ [20].
The bands that appears in the range of 2200–2400 cm\(^{-1}\) are assumed to be due to Ce–O bands. There are no peaks attributed to organic compounds because of the fact that they were removed when the material was calcined. The peaks appeared at 1627 cm\(^{-1}\) and 3388 cm\(^{-1}\) are characteristic of \(\text{H}_2\text{O}\) bending and vibration of hydroxyl groups [22-25].

3.1.4. **UV-DRS analysis.** Figure 5 illustrates the optical absorption spectra of the synthesized catalyst materials. The results obtained indicate significant red shift in all doped samples. The red shift is caused by CeO\(_2\) energy levels in the band gap [16], which is to the transitions of the dopant ceria electrons between the conducting and valance bands of titania [17]. The optical band gap of the prepared material was calculated from the Tauc plot in figure 5 using this equation.

\[(\alpha h\nu)^2 = A (h\nu - E_g),\]

where \(h\nu\) the energy of photon and \(\alpha\) denotes the absorption coefficient.

\[\alpha = \frac{4\pi k}{\lambda};\]

where \(k\) = absorption index/ absorbance; \(\lambda\) = wavelength and \(A\) = constant related to the material.

![Figure 5. UV/ Vis – DRS and Tauc plot of the prepared material.](image)

The calculated values from the Tauc plot display that all the catalyst materials had a reduced band gap compared to bare TiO\(_2\) or commercial material, Degussa P25. It was seen that the band gap reduced with the increase in the metal loading of the dopant. Reduction in band gap suggest that e\(^-\)h\(^+\) can be generated using visible light. The band gaps of different catalyst materials are summarised in table 1.

3.1.5. **XRD and Raman spectra analysis.** Figure 6 represents the powder XRD patterns and the summary of Raman spectra of bare TiO\(_2\), and CeO\(_2\) doped TiO\(_2\) catalysts materials. Figure 6(a) indicates that all the materials peaks characteristic of polycrystalline nature. It suggests that all the samples possess high crystallinity with anatase structure only \((2\theta = 25.2, 37.76, 48.02, 54.05, 55.03, 62.80, 68.85, 70.19\) and 75.07) corresponds to the JCPDS file no: 21-1272. No ceria diffraction peaks observed in the spectra, which could be due to either CeO\(_2\) is incorporated in the crystal structure of TiO\(_2\) or it may be that the wt\% of dopant is too minor. An observation of the diffraction patterns, indicate that doping of ceria on titania caused a marginal shift only suggest that no significant structural changes. The average crystallinity size for the anatase diffraction peak (101) was calculated using Debye–Scherrer equation [26].
\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where \( D \) = crystallite size in nm; \( k \) = Scherrer’s constant \( \approx 0.9 \); \( \lambda \) = wavelength of the X-ray radiation (\( \text{CuK}_{\alpha} = 0.15406 \text{ nm} \)); \( \beta \) = full width at half-maximum of the diffraction peak; and \( \theta \) = the diffraction angle.

**Figure 6.** (a) X-ray diffraction and (b) Raman spectra.

As shown in table 1, there is a decrease in crystalline size with addition of cerium dopant from 8.92 nm to 7.29 nm with the exception of 7.54 for ceria (1.0 wt%). This result indicates the presence of ceria, to an extent inhibit the growth of crystalline anatase phase.

Raman spectra was applied to study the physical modifications of all the prepared materials. According to symmetry group analysis anatase TiO\(_2\) has six mode of vibrations. Four of these vibration modes are indicated in figure 6(b). 146 (E\(_g\)), 197 (E\(_g\)), 399 (B\(_{1g}\)), 515 (A\(_1g\)), 519 (B\(_{1g}\) is superimposed with the A\(_1g\)), and 639 cm\(^{-1}\) (E\(_g\)) and the other three modes are IR active and one mode is inactive [27-29].

3.1.6. **Photoluminescence analysis.** Photoluminescence (PL) is a tool employed in investigation of e-h\(^+\) pair relationship of the semiconductor and assess the ion trapping, migration and charge carrier transfers [30]. The exciton emission suggests that the catalyst materials possess huge exciton binding energies with extended exciton radiative period [31-33]. PL study is used to understand the oxygen vacancy, surface state and defects of metal doping using ceria. From the results obtained in the figure 7, it is clearly seen that with increase in the weight composition of ceria, there is a decrease in the emission intensity compared with bare TiO\(_2\). The decrease in emission intensity was attributed to oxygen vacancy or defects caused by the metal, which lead to an increase in optical properties. While, the three emission peaks at 376, 378, and 382 nm are attributed to the exciton recombination, the band at 485 nm corresponds to the self-trapped excitons. The longer wavelength peaks are attributed to the oxygen vacancies in the lattice of titania [23]. The signal seen around 530 nm is assumed to be caused by an increase oxygen vacancies on the surface of the catalyst [34]. Therefore, 0.5% CeO\(_2\)/TiO\(_2\) showed higher intensity compared to other catalysts.
3.1.7. **Photocatalytic degradation of caffeine.** Figure 8 shows degradation of CAF as a function of time using various synthesized materials and a commercial catalyst Degussa P25 under visible light after equilibrating in the dark for 60 min. Degradation of CAF was first done using a blank, in which light was used to degrade CAF without the catalyst.

Assessing the obtained results it is clear that BET surface area does not play much role in photo degradation of CAF. Although, 1.0% CeO$_2$/TiO$_2$ photocatalyst has the highest surface area and it had lower activity compared to 0.5% CeO$_2$/TiO$_2$, which possessed smaller surface area. The Tauc plot data shows that gap energy decreased with an increase in metal dopant. Further, there was no photo-degradation observed in absence of any catalyst (figure 8). This meant that visible light alone had no effect in degrading CAF. Better photocatalytic performance was observed with the commercial catalyst P25, which is assumed to comprise both the TiO$_2$ phases (anatase and rutile). As shown in the
figure, bare TiO$_2$ had low photocatalytic activity. However, ceria doped TiO$_2$ demonstrated photocatalytic activity. This also suggests that though the prepared materials had reduced band gap compared to P25, their lower efficiency is because of high electron-hole recombination. The increase in photocatalytic activity of ceria doped titania catalyst material compared to the bare titania and it can be also attributed to the redox pair of ceria. It has been reported to act as an effective electron scavenger, for majority of electrons from TiO$_2$, this leads to efficient adsorption of O$_2$ to generate superoxide (O$_2^-$) radicals, which increases photocatalytic activity [6,35].

3.1.8. Effect of pH. The variation in the solution pH results from the changes in H$^+$ and OH$^-$ ion concentrations. Hydroxyl radicals are widely known to play a vital role in photocatalytic degradation. Hence a change in pH to alkaline medium is expected to increase OH$^-$ ions in the reaction medium, which will then be transferred into hydroxyl radicals [36,37]. However, in caffeine is a weak base, it is more soluble in low pH aqueous medium in high pH medium. In low pH solutions, caffeine exists completely as a protonated salt, thus making it more hydrophilic.

In the aim of optimising the efficiency of Ce-0.5 wt. catalyst, degradation of caffeine was performed in different pH conditions and the results are displayed in figure 9. From the obtained results, it can be seen that degradation of caffeine is favoured in acidic conditions.

![Figure 9](image)

Figure 9. Effect of pH in degradation of caffeine over 120 min.

3.1.9. Detection of degradation products. Pure caffeine and its degradation products were analysed by LC-MS TOF by injecting the standard solution of caffeine and its reaction products under similar conditions for 5 min runs. The pure caffeine was characteristic of a long intensity at m/z 194. Samples of reaction mixture collected at 20 min intervals were collected and investigated. One intermediate and two reaction products, 6-amino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetradroymidin-5-ly)-methylcarbamic acid (ATCA) and N-methyl-N-(methylcarbomoyl)-2-oxoacetamide (MMO) were positively identified among the degradation products (Supporting information, SI-II). Scheme 1 illustrates the probable mechanistic scheme based the identified intermediate and reaction products.
Scheme 1. Plausible reaction mechanism of photocatalytic degradation of caffeine under visible light using Ce/TiO$_2$.

4. Conclusion
An efficient ceria doped TiO$_2$ materials were synthesised by using sol-gel procedure. It was seen from nitrogen isotherms that all as prepared materials were mesoporous and exhibited type IV isotherms. PXRD showed that all ceria doped TiO$_2$ were polycrystalline in nature and they were all anatase phase. Synthesized materials were showed excellent photocatalytic activity by the degradation of caffeine in the presence of visible light. An increase in pH showed a decrease in catalytic activity of the as prepared materials.

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