Original Article

Synthesis of g-C$_3$N$_4$/N-doped CeO$_2$ composite for photocatalytic degradation of an herbicide

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In photocatalysis, surface engineered CeO$_2$ could be vital due to oxygen vacancies arise from multiple valency, i.e. Ce$^{3+}$ and Ce$^{4+}$. This study reports photocatalytic properties of g-C$_3$N$_4$/CeO$_2$ composite synthesized by a facile method in the presence of l-arginine. Physicochemical properties of g-C$_3$N$_4$/CeO$_2$ material were analyzed through various characterization techniques such as XRD, UV–Vis, physisorption, etc., and correlated with its photocatalytic activity. Observed bandgap of the synthesized composite material was in the visible region, around 2.8 eV which is less than that of typical ceria, but higher than bandgap of exfoliated g-C$_3$N$_4$. On the further side, N doping into CeO$_2$ was confirmed through XPS analysis. It is estimated that synthesis method aided for the N doping, which further played key role in lowering the bandgap of g-C$_3$N$_4$/CeO$_2$ composite. Finally, Photocatalytic activity of g-C$_3$N$_4$/CeO$_2$ composite was analyzed through degradation of an herbicide i.e. diuron, and the study revealed the good performance of the catalyst.

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1. Introduction

Worldwide increasing trends of energy consumption and removal of toxic chemicals from air, soil and water, are some of the major concerns for scientific community, and one common solution is to develop efficient photocatalytic materials [1]. Till date several materials, such as TiO$_2$ [2,3], MoS$_2$ [4], ZnO [5], BiO [6,7] etc., have been studied for this purpose. Among them photocatalytic studies on g-C$_3$N$_4$ have been increased due to its eco friendliness, low cost and extraordinary properties, such as, its band gap lies in visible region and it is the stable allotrope of carbon nitride due to the existence of strong covalent bond between carbon and nitrogen [8]. Moreover, it possesses high surface area due to 2D stacking of $\pi$ conjugated planes analogous to graphite. The main disadvantage of g-C$_3$N$_4$ is high rate of recombination of photo induced electron-hole pairs [9–11], and several modification endeavors have been reported such as doping nonmetal into g-C$_3$N$_4$ [12] creating heterojunction with other semiconductor materials, etc. Among various possibilities, photocatalysis by forming heterojunction between two semiconductors, known as z-scheme photocatalysis [13–15], have been attracted interest as they will allow to utilize large portion of the solar spectrum and reduce the recombination rate by driving the reduction and oxidation reactions at different sites of the catalyst.

On the other hand, cerium is more abundant among the rare earth elements, and its oxide form, i.e. ceria, became most important material in wide variety of applications such as drug delivery [16], fuel cell [17], and one of the most widely used co-catalysts, due to its properties. Co-existence of Ce$^{3+}$ and Ce$^{4+}$ states makes ceria very attractive, and changing their ratio, thereby oxygen vacancies, will provide the opportunity to tune surface properties for its use in various applications especially in catalysis. In addition to the size of the particles, the ratio of ceria oxide states depends on the synthesis method and conditions [18,19], and therefore final g-C$_3$N$_4$/CeO$_2$ composite properties specific to synthesis method or process. Till date, few studies have been reported on g-C$_3$N$_4$/CeO$_2$ composite developed through different methods, such as, mixing-calciation route [20,21], co-pyrolysis [22], ultrasonic deposition [23], template-assisted synthesis [24], hydrothermal synthesis [25,26] towards photocatalytic applications such as degradation of dyes, CO$_2$ reduction, etc. However, to our knowledge, studies on effect of doping and/or degradation of pesticide/herbicides are limited for g-C$_3$N$_4$ based materials. In this study, we developed ceria nanoparticles on exfoliated g-C$_3$N$_4$ nanosheets in a facile in-situ synthesis process without using any complex equipment and toxic raw materials. For the first time, this paper reports the nitrogen doping into ceria in g-C$_3$N$_4$/CeO$_2$ composite. Also, an herbicide i.e. diuron, was employed as model contaminant for testing photocatalytic properties of the synthesized heterojunction material and further correlated with its physico-chemical properties.

2. Materials and methods

2.1. Synthesis of g-C$_3$N$_4$

Synthesis of bulk g-C$_3$N$_4$ using melamine (Sigma–Aldrich, 99% AR) as precursor involves a process of polycondensation with simultaneous elimination of ammonia [27]. In typical synthesis process, 10 g of melamine was taken into an alumina crucible with lid, then placed in a muffle furnace and heated at 550 °C for 2 h with a ramp of 9 °C. Then the obtained product was made into fine powder using a mortar.

2.2. Exfoliation of bulk g-C$_3$N$_4$ via thermal oxidation

Thermal oxidation method was employed to exfoliate bulk g-C$_3$N$_4$ to develop nanosheets [28] and thereby increasing surface area. 1 g of bulk g-C$_3$N$_4$ was placed in open ceramic container and was heated at 550 °C for 3 h with ramp 9 °C/min. After this process, huge decrease in weight and the density of material was observed which confirm the exfoliation.

2.3. Synthesis of g-C$_3$N$_4$–Ceria composite

100 mg of thermal exfoliated g-C$_3$N$_4$ was dispersed in 50 mL of ethanol by ultrasonication, and then 100 mg of L-arginine was added which turns pH of the reaction mixture to 8.5. Then 200 mg of CeCl$_3$.7H$_2$O was introduced into it and stirred on magnetic stirrer for 30 min. Then the reaction mixture was placed in a hot air oven overnight at 70 °C. Then the reaction mixture was centrifuged and washed thrice with ethanol and dried in oven for 3 h at 90 °C.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns for the samples were collected using Bruker D8 advance eco diffractometer. Chemical states of the sample were identified using X-ray photoelectron spectrum (XPS), which was recorded using K-Alpha spectrometer from Thermo Scientific. Transmission Electron Microscopic (HR-TEM) images were taken using JEOL JEM 2100. The nitrogen physiosorption experiments were carried out in a Micromeritics TriStar II, at −196.2 °C. The samples were degassed at 300 °C for 2 h with nitrogen gas. The surface area was calculated using the standard BET method. Pore size distributions were obtained from the BJH method using the adsorption of the isotherms. UV–Vis adsorption spectra were recorded in a Varian CARY 300, at room temperature with a range of 200–800 nm. Scanning electron microscopic images were recorded using JEOL JSM-IT 500 instrument.

2.5. Photocatalytic activity tests

The photocatalytic activity of g-C$_3$N$_4$, exfoliated g-C$_3$N$_4$ and the g-C$_3$N$_4$/CeO$_2$ composite were identified via degradation of diuron using benchtop xenon lamp unit “suntest CPS+” solar
simulator equipped with air-cooled 1500W xenon lamp. In a typical experiment, 30 mg of photocatalyst was dispersed in 200 mL of 25 ppm diuron solution and kept under dark for 60 min with stirring to establish adsorption–desorption equilibrium. During the irradiation, 3 mL solution was collected using a syringe with a filter for every 20 min and analyzed using UV-Vis spectrophotometer. The rate of degradation of diuron was calculated by C/C_0 where C was the concentration of the sample collected after specified time interval and C_0 was that of the diuron after dark adsorption–desorption equilibrium. The cyclic runs for g-C_3N_4/CeO_2 composite were carried out by collecting the catalyst through centrifugation, dried and then used in the next cycle. Superoxide radicals (O_2^-·), active holes (h^+·) and hydroxyl radicals (·OH) are the major reactive oxidative species in photodegradation experiments. The role of these attacking species were determined through in-situ trapping experiments using p-benzoquinone, ammonium oxalate and isopropanol as scavengers for O_2^-·, h^+· and ·OH radicals, respectively [29].

3. Results and discussion

Through this synthesis process, we successfully synthesized CeO_2 nanoparticle from CeCl_3 with the help of L-arginine and they are anchored in-situ on to the nanosheets of g-C_3N_4. The following are the purpose of using arginine in the reaction (i) it modifies the exfoliated g-C_3N_4 sheets surface and (ii) It helps in formation of ceria nanoparticles and (iii) excellent coordination between ceria nanoparticles and the guanidine group of arginine protects the ceria from agglomeration and hence making them to distribute uniformly on the exfoliated g-C_3N_4 sheets. Similar observation was made by Gadhari et al. in the synthesis of copper-cobalt ferrite on graphene oxide [30].

3.1. XRD analysis

The crystalline phase of synthesized materials was analyzed using XRD technique and presented in Fig. 1. Characteristic peaks for g-C_3N_4 around 13° and 27.8° correspond to (002) and (004) crystalline planes, respectively, are observed. According to JCPDS 87-1526, peaks at 13.0 and 27.8° indicate the formation of hexagonal phase of g-C_3N_4. The later peak shifted to slightly higher diffracted angle, i.e. 28.2°, for exfoliated g-C_3N_4 and thus indicating successful exfoliation [31]. The peaks in X-ray diffraction pattern of g-C_3N_4/CeO_2 composite synthesized using L-arginine developed the broader peaks at 47.3°, 56.0° and 76.67° correspond to (220), (311) and (331) of CeO-np respectively, in accordance to JCPDS. No. 00-034-0394 and indicates the cubic structure of ceria. Diffraction peak around 28.5° corresponds to Ceria (111) plane is not apparent, as it is overlapped by higher intensity peak of carbon nitride (002) plane. Similar overlapping of peaks is also observed elsewhere [25]. From above discussion, the formation of g-C_3N_4/CeO_2 composite is established.

3.2. UV visible

Understanding optical properties, absorption ability and bandgap, is important as they will affect the photocatalytic performance of the catalyst. Fig. 2(a) shows UV-Visible absorption spectra of the synthesized materials measured at room temperature. From Fig. 2(a) following points are observed: (1) all samples showed absorption response in the visible region of the spectrum; (2) bulk g-C_3N_4 absorption edge is at around 500 nm; (3) all other samples showed a red shift in

Fig. 1 – XRD patterns of the synthesized materials.

Fig. 2 – (a) UV–vis absorption spectra of the synthesized material and (b) (αhv)^0.5 vs hν of bulk g-C_3N_4, exfoliated g-C_3N_4 and CeO_2/g-C_3N_4 composite.
their absorption edge w.r.t bulk g-C3N4 in the following order; bulk g-C3N4 < the composite < exfoliated g-C3N4. Following the equation \((\alpha \nu) = A(\nu - \nu_0)^n\), where \(\alpha\), \(\nu\), \(\nu_0\), \(E_g\), \(A\) and \(n\) are absorption coefficient, Planck constant, light frequency, band gap energy, a constant and a variable dependence on the type of bandgap, respectively, band gap values were determined through Tauc plot by extrapolating the curve to zero of the x-axis from the graph of \((\alpha \nu)^{1/2}\) vs \(\nu\), as shown in Fig. 2(b). The calculated band gap values are 2.71, 2.86 and 2.8 eV for bulk g-C3N4, exfoliated g-C3N4 and the composite samples, respectively and it is well known that the increase in the bandgap values for exfoliated g-C3N4 is due to quantum confinement effect. However, composite showed blue shift in the band gap compared to that of the exfoliated and typical ceria [32]. The lower bandgap of the composite is due to Nitrogen doping into ceria, as it leads to bandgap narrowing by forming intermediate energy levels by mixing of 2p orbital of N with 2p orbital of O. [33,34]. It is also established that the presence of Ce³⁺ and oxygen defects affects the band gap value of ceria [35–37].

3.4. XPS analysis

Surface chemistry of the composite was analyzed by employing XPS technique. XPS survey scan is shown in Fig. S1 of the supplementary material and demonstrates that composite mainly consists Ce, O, N and C elements with no other impurity peaks. High-resolution spectrum of C 1s, N 1s, O 1s and Ce 3d peaks presented in Fig. 4(a)–(d), respectively. Core level spectrum of C 1s peak can be fitted with 3 peaks with peak positions around 293.6, 287.9 and 284.4 eV which can be ascribed to two-coordinated C atoms (C2), three-coordinated C atoms (C≡C) and carbon contamination, respectively as shown in Fig. 4(a). Deconvoluted N 1s spectrum is shown in the Fig. 4(b) with five peaks occurring at 404.2, 400.9, 399.8, 398.8 and 397.1 eV which are corresponding to N–N bonds, C–N–H bonds, three coordinated (N(N=C)) nitrogen, two coordinated (N(N=C)) nitrogen in the sp²-hybridized nitrogen and Ce–N bond [38], respectively. With the above information, it is concluded that sp²-bonded graphitic carbon nitride is presented in the composite. Ammonia [39] from C3N4 during the preparation of the composite or nitrogen functionalization from arginine, could be reason behind the formation of Ce–N bond by incorporation of nitrogen into ceria and thereby resulting the lower band gap material as observed in the UV–Vis spectra analysis. Peak fitting for O 1s is shown in Fig. 4(c) and peaks around 533, 531.7, 530.7 and 529.0 eV are assigned to surface –OH group, oxygen vacancies, O₂ in Ce³⁺ and O₂ in Ce⁴⁺, respectively.

Dependent on the reaction process during the synthesis, but in general, presence of Ce³⁺ ions and oxygen vacancies reduce the co-ordination number to seven from eight in case of Ce⁴⁺ based fluorite structure. The co-existence of Ce³⁺ and Ce⁴⁺ can be analyzed by deconvoluting the high-resolution Ce 3d spectra as shown in Fig. 4(d). Following the convention established by Burroughs et al. [40], 3d⁵/₂ spin-orbit states labeled as µ and 3d⁷/₂ states as ν. Full spectrum can be deconvoluted into eight peaks with peak centered at 318.8, 316.6, 313.9, 308.9, 306.4, 302.5, 299.8 and 297.8 eV, respectively. The first three peaks at 318.8, 316.6 and 313.9 eV are attributed to five-coordinated Ce³⁺ states, whilst the other five peaks at 308.9, 306.4, 302.5, 299.8 and 297.8 eV are attributed to seven-coordinated Ce⁴⁺ states.

### Table 1 – Surface area, pore volume and pore sizes of various catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C3N4</td>
<td>18.19</td>
<td>0.08</td>
<td>156.05</td>
</tr>
<tr>
<td>Exfoliated g-C3N4</td>
<td>198.16</td>
<td>0.68</td>
<td>149.70</td>
</tr>
<tr>
<td>Ceria-exfoliated g-C3N4</td>
<td>51.42</td>
<td>0.24</td>
<td>255.28</td>
</tr>
</tbody>
</table>

Materials Fig. 3(b) shows Barrett-Joyner-Halenda (BJH) curves, which are obtained from the desorption branch of the BET isotherm. Variation in surface area between the samples listed in Table 1, along with average pore volume and average pore size. From the table, the surface area of exfoliated g-C3N4 was higher by one order of magnitude to that of bulk g-C3N4. On the other hand, surface area of the composite is in between those of exfoliated g-C3N4 and bulk g-C3N4. Hence surface area of the samples showed the following trend g-C3N4 < composite < Exfoliated g-C3N4 and is in agreement with the previous reports [26]. The decrease in surface area of the heterojunction material is because of the probable change in the dimensions due to occupation of pores by the ceria nanoparticles.

3.3. BET analysis

To understand the specific surface area and pore size distribution of the samples, Brunauer–Emmett–Teller (BET) technique was employed. Fig. 3(a) shows the N₂ adsorption-desorption isotherms of g-C3N4, exfoliated g-C3N4 and the composite. All samples showed type IV isotherms with H3 hysteresis loops indicate mesoporous structure of synthesized
### 3.6 Photocatalytic activity

The photocatalytic activity tests were carried by identifying diuron characteristic absorbance peak intensity at 250 nm. It is noteworthy to mention that there is diuron adsorption onto the tested photocatalysts after adsorption-desorption equilibrium. Degradation of diuron with time using the studied photocatalysts is shown in Fig. 6(a). Photolysis of diuron also carried under same conditions, as can be seen from Fig. 6 (a) almost no change in diuron concentration is observed after two hours of light irradiation. However, in the presence of photocatalyst, there is clear reduction in diuron concentration with time and concentration reduced by around 15, 34 and 46% for bulk g-C_3N_4, exfoliated g-C_3N_4 and the g-C_3N_4/CeO_2 composite, respectively. It was previously established by other authors that bulk g-C_3N_4 photocatalytic activity is lower compared to that of exfoliated g-C_3N_4 due to high recombination rate of electron hole pair and lower surface area of bulk g-C_3N_4. Following Langmuir–Hinshelwood pseudo first order kinetic equation: ln([C]/[C]) = -kt where k is rate constant (h^{-1}), first order rate constants determined, and are 0.20048 and 0.28308/h for exfoliated g-C_3N_4 and the composite, respectively. During the first 20 min of light irradiation, both exfoliated and the composite showed almost same concentration change. However, with progress in the time, the diuron concentration reduction slowed when compared to that of the composite. It is clear from UV–Vis analysis that in-situ preparation promoted nitrogen doping into ceria and thereby reduction of band gap of the resulting composite material. This relatively low band gap material helped in fast transfer of the electron from valence band to conduction band and relatively higher photocatalytic activity. Hence, diuron
Fig. 5 – (a)–(c) HR-TEM images of CeO$_2$/g-C$_3$N$_4$ composite at different magnifications with scale bars 100 nm, 50 nm and 20 nm, respectively (d) SEM image of CeO$_2$/g-C$_3$N$_4$ composite and (e) and (f) elemental mapping of Ce and O, respectively.

Fig. 6 – (a) Degradation of diuron with bulk, exfoliated and CeO$_2$/g-C$_3$N$_4$ composite. (b) Reusability of CeO$_2$/g-C$_3$N$_4$ composite sample. (c) Photocatalytic activity of CeO$_2$/g-C$_3$N$_4$ composite in the presence of scavengers.
photocatalytic degradation efficiency is higher for the composite than those of bulk and exfoliated g-C3N4.

Catalyst stability or reusability of g-C3N4/CeO2 composite was tested through four consecutive cycles as shown in Fig. 6(b). From the graph, the tested photocatalyst showed consistent performance over all cycles in degradation of diuron through photocatalysis. It is therefore g-C3N4/CeO2 composite is stable photocatalyst and will be good candidate for environmental protection through photocatalysis. On the other hand, the main radical responsible was tested through scavengers experiments as shown in Fig. 6(c). It is clear from the figure that diuron degradation is almost suppressed when employed p-benzoquinone as scavenger, but, in the presence of ammonium oxalate or isopropanol, degradation continues with slightly lower rate compared to that of scavenger. This indicates that O2− are dominating active species in oxidation of diuron using g-C3N4/CeO2 photocatalyst.

4. Conclusions

In summary, nitrogen doping into ceria was achieved while synthesizing CeO2/g-C3N4 composite material with no additional process steps. Morphological studies revealed excellent distribution of ceria nanoparticle with size around 3 nm on g-C3N4 nanosheets. Doping of Nitrogen into CeO2 resulted in lowering the bandgap of CeO2/g-C3N4. Photocatalytic properties through degradation of diuron showed improved performance of the composite when compared to that of bulk and exfoliated g-C3N4. This higher performance can be ascribed to improved separation efficiency of photo-induced electron-hole pair by forming heterojunction between ceria and g-C3N4.

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.2018.11.008.

References


