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# Facile and single-step route towards the ZnO@C core-shell nanoparticles as oxygen vacancy induced visible light active photocatalyst using the thermal decomposition of Zn(an)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> complex†

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Zinc oxide-carbon (ZnO@C) core-shell nanoparticles were synthesized using a facile and single-step method, which involved the thermal degradation of a zinc aniline nitrate complex in methanol. The formation of ZnO and carbon was observed at the early stages of synthesis (> 200 °C), whereas a further increase in the temperature determines the level of the carbon coating. Transmission electron microscopy confirmed that the ZnO@C nanoparticles obtained at 600 °C were ~100 nm in size with a uniform 5-20 nm thick carbon coating. The nano-coating of carbon on ZnO along with the presence of oxygen vacancies promoted its photocatalytic activity under visible light with higher efficiency for the photodegradation of rhodamine B than bare ZnO. The two probable pathways for the visible activity and the enhanced photodegradation capacity of ZnO@C core-shell nanoparticles are also discussed. The synthesized ZnO@C core-shell nanoparticles exhibited very good stability and recyclability, highlighting their potential use as an efficient visible light driven photocatalyst for pollutant degradation.

# Introduction

In the 21<sup>st</sup> century, water pollution is the major environmental issue and a leading cause of diseases and deaths of thousands of people daily.<sup>1</sup> The effluent from the textile industry, which contains various organic dyes, is one of the major point source of water pollution and significant cause of eutrophication and perturbation in aquatic ecosystems. Among the various techniques of water pollution remediation, such as adsorption,<sup>2</sup> flocculation<sup>3</sup> and reverse osmosis,<sup>4</sup> heterogeneous photocatalysis<sup>5,6</sup> has been considered as a promising economical technique owing to its advantages of complete organic carbon mineralization and ambient operating conditions.

Zinc oxide (ZnO) with exceptional electrical, optical and piezoelectric properties is an important semiconductor material for applications in the areas of optics, solar cells and gas sensors, and it has also considered as a promising photocatalyst owing to its direct and wide band gap of 3.3 eV.<sup>7</sup> Over the past few years, various ZnO based materials with different shapes and sizes have been synthesized and attempted for the photodegradation of organic dyes. On the

other hand, its applications are still limited because of its inherent defects involving a wide band gap, which restricts the absorbing wavelength just in the ultraviolet light range and results in low light utilization efficiency. Photo-corrosion is also one of the obstacles impeding the practical maximization of photocatalytic performance. To overcome these disadvantages several methods including noble metal deposition,<sup>8</sup> creation of structural defects<sup>9</sup> and semiconductor coupling<sup>10</sup> have been developed. The photocatalyst composite with different materials including graphene, carbon-based carbon nanotubes, fibers, and fullerene provides an efficient means of overcoming these drawbacks with enhanced photocatalytic activity.<sup>11</sup> Because of the high cost and complex preparation process of these carbon materials, researchers have developed the methods to fabricate ZnO-carbon (ZnO@C) composites using the thermal degradation of carbon precursors in the presence of zinc oxide or zinc salt.<sup>12-14</sup> If the surface of the nanostructure ZnO is modified with carbon, the good properties of ZnO and carbon will be integrated into the hybrids, which is advantageous for overcoming some of the intrinsic defects of ZnO. Thermal degradation of the zinc complex is a promising simple methodology that requires less expensive and simple instrumental facilities to fabricate ZnO@C composites. Ma et al.<sup>15</sup> and Cho et al.<sup>16</sup> reported the synthesis of ZnO@C composites using citric acid and vitamin C as the carbon source, respectively. Most papers reported the multi-step synthesis or use of commercial ZnO.<sup>17-19</sup> Xue et al.<sup>20</sup> performed the single stage synthesis of ZnO@C composite using zinc citrate as the carbon source, which exhibited

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<sup>†</sup> Electronic Supplementary Information (ESI) available: XPS survey spectra of ZnO and ZnO@C-2, XRD pattern of ZnO@C composite, Pseudo-first order kinetics plots of RhB degradation using ZnO and ZnO@C, and Uv-visible absorption spectra of rhodamine B after photodegradation. See DOI: 10.1039/x0xx00000x

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efficient photocatalytic activity for methylene blue (MB) degradation under UV irradiation.

The synthesis of 1D ZnO@C core-shell structures and their field emission studies have been reported by several researchers.<sup>21,22</sup> To the best of the authors' knowledge, there are no reports available on the synthesis of the ZnO@C coreshell nanoparticles and their applications as photocatalyst. This paper reports the facile single stage synthesis of ZnO@C coreshell nanoparticles via the thermal degradation of zinc-aniline nitrate complex. The obtained ZnO@C core-shell nanoparticles were utilized further as a photocatalyst for the degradation of rhodamine B (RhB) under visible light irradiation.

# **Experimental**

#### Synthesis of ZnO@C core-shell nanoparticles

Zinc nitrate hexahydrate was procured from Duksan chemicals Company, South Korea. Aniline and RhB were purchased from Sigma Aldrich. All chemicals were used as received. In a typical procedure, zinc nitrate hexahydrate (2 mmol) was dissolved in methanol (2 mL) followed by the addition of aniline (4 mmol) in a porcelain crucible. The resulting zinc aniline nitrate  $(Zn(an)_2(NO_3)_2)$  complex was heated to 500, 600 and 700 °C in a muffle furnace to obtain ZnO@C-1, ZnO@C-2 and ZnO@C-3, respectively. For a comparative study, the synthesis of bare ZnO was carried out in a similar manner without aniline. **Characterization** 

X-ray diffraction (XRD, PANalytical, X'pert PRO-MPD, Netherland) with Cu K $\alpha_1$  ( $\lambda$  = 1.54056 Å) radiation was used for crystallographic phase identification of the sample. Field emission scanning electron microscopy (FE-SEM, S-4200; Hitachi, Ltd.) and transmission electron microscopy (TEM, JEM-2100 JEOL) with an accelerating voltage of 15 and 200 kV, respectively, were used to examine the morphology of the samples. The optical properties of the materials were analyzed by UV-VIS-NIR diffuse reflectance spectrophotometer photoluminescence (VARIAN, Cary 5000, USA) and spectroscopy (PL) using a wavelength of 325 nm and a power of 50 mW (Kimon, 1 K, Japan), respectively. Attenuated total reflection - infrared (ATR-IR) was performed on a Thermo Scientific Nicolet Smart iTR iS10. Raman spectra were collected using the XploRa Plus instrument (Horiba, Jobin Yvon, Germany) coupled to an optical microscope. A laser having a wavelength of 532 nm was used for excitation. The samples were investigated with a grating having 1200 grooves/mm and using a HORIBA Scientific CCD detector (1024 × 256-pixel, TE air cooled). With this configuration the wavenumber and wavelength resolution are approx. 3.26 cm<sup>-1</sup>/CCD pixel and 0.09 nm/CCD pixel, respectively. The calibration of wavenumber shifting was also performed before the sample characterization using silicon wafer (< 1cm<sup>-1</sup>). The peak fitting of recorded Raman spectra using Lorentzian function showed the maximum error of 0.05. The elemental composition of the samples was determined using a CHN/O analyzer (Perkin-Elmer, Optima 8300). The chemical states of the samples were characterized by X-ray photoelectron spectroscopy (XPS,

Thermo Fisher Scientific Escalab 250) with monochromatized AlK $\alpha$  excitation (h = 1486.6 eV). Electrochemical impedance spectroscopy (EIS) was performed in a three electrode cell with a 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as the electrolyte using a potentiostat (VersaSTAT 3, Princeton Research, USA). The working electrodes were prepared by coating a paste of the sample with 10 wt% Nafion as the binder on a FTO glass electrode using the doctor-blade method. A Ag/AgCl (3M KCl) and platinum gauge were used as the reference and counter electrodes, respectively.

#### Photodegradation of rhodamine B under Visible light

In a typical process, the catalyst (500 mg /L) was suspended in the dye solution (5 ppm) using an ultrasonication treatment for 10 min. The adsorption-desorption equilibrium of the dye on the catalyst was achieved by stirring the suspension in the dark for 30 min. Under ambient conditions and stirring, the solution was exposed to visible light placed 12 cm away from the solution. A 400 W visible light lamp with an intensity of 31 mW/cm<sup>2</sup> and  $\lambda$  > 500 nm obtained from 3M USA was used as the light source for the photocatalytic studies. A sample solution was taken at certain time intervals during the experiments, and centrifuged to remove the catalyst completely. The solution was analyzed by UV-Vis spectrophotometer (Optizen 2120UV; Mecasys Co., Ltd., South Korea). The percentage degradation is reported as  $C/C_0$ , where C and  $C_0$  are the absorbance of the dye solution after each irradiated time interval and the initial absorbance dye solution at the  $\Lambda_{max}$ , respectively.

# **Results and discussion**

#### Characterization of ZnO@C core-shell nanoparticles

Though the formation of complex was clearly intimated by the quick precipitation, it was further confirmed using XRD and ATR-IR analysis. The crystallographic changes occurred in the zinc nitrate salt was recorded by XRD pattern of  $Zn(an)_2(NO_3)_2$  complex (Fig. S1†) showing the numbers of comparatively less intense peak instead of sharp peaks of zinc nitrate hexahydrate. The transmittance band observed at 515 and 425 cm<sup>-1</sup> in ATR-IR spectrum of  $Zn(an)_2(NO_3)_2$  complex (Fig. S2†) attributed to Zn–O and Zn–N bond and also evidenced the formation of complex. Fig. 1(a) shows the XRD pattern of the as-prepared samples from the thermal degradation of the



**Fig. 1** XRD pattern of the as-obtained ZnO and ZnO@C coreshell nanoparticles (a) XRD of the samples obtained at different temperatures. (b) Enlarged area of 31° to 37°  $2\theta$  in (a).

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Zn(an)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> complex at different temperatures, which shows the characteristic XRD peaks of ZnO corresponding to the (100), (002), (101), (102), (110), (103), (112), and (201) planes of the typical wurtzite ZnO structure (JCPDS 36-1451), while no other peaks from Zn(NO<sub>3</sub>)<sub>2</sub> and ZnO<sub>2</sub> impurities were observed.<sup>23</sup> The mean crystallite size calculated from the X-ray line broadening of the 002 peak using the Scherrer's equation were 59, 32, 33 and 47 nm for ZnO, ZnO@C-1, ZnO@C-2 and ZnO@C-3, respectively. Although, all samples were nanocrystalline in nature, the ZnO prepared without complex formation showed the highest crystalline size, whereas the crystalline size increased with increasing temperature. Similar observations were also noted by Zhang et al.<sup>24</sup> in case of a ZnO@C composite, where carbon plays an important role in XRD peak broadening. No peak was observed in the 20-30° 20 range, possibly due to the lower contribution of carbon as well as its amorphous nature. Hence, the obtained samples were analyzed further by elemental (CHN) analysis for determining the carbon content. The carbon and hydrogen contents (wt %) of the ZnO@C-1, ZnO@C-2 and ZnO@C-3 were 0.410 (C), 0.043 (H); 0.181 (C), 0.027 (H); and 0.024 (C), 0.002 (H), respectively. In contrast, carbon and hydrogen were not detected in ZnO.

The distinguished peaks of ZnO for the shoulder of Zn-O bending and Zn–OH vibrations were observed in all samples at ~500 and 900 cm<sup>-1</sup>, respectively, in the ATR-IR spectra (Fig. 2a).<sup>6,25,26</sup> In the case of ZnO@C-1 and ZnO@C-2, the sharp peaks at 2902 and 2981 cm<sup>-1</sup> were assigned to the stretching vibration of the C-H bond, which also confirms the presence of the carbon structure.<sup>27,28</sup> The peaks observed at 1050 and 1400 cm<sup>-1</sup> were attributed to the C-O and C=C stretching vibrations, respectively. The absence of such peaks in the case of ZnO is due to the lack of aniline, as the carbon precursor during synthesis. In case of ZnO@C-3, however, the absence of such peaks reflects the absence or presence of very minute quantities of carbon due to its oxidation at such a high calcination temperature (700 °C). The intensity of the peaks, representing the presence of carbon in ZnO, also decreased with increasing calcination temperature. A peak at 3400 cm<sup>-1</sup> which is generally assigned to the -OH stretching mode and is present in the current spectra, might be due to the carbon bonded –OH groups or surface Zn–OH groups.<sup>29</sup> Raman spectroscopy has been used to examine the carbon incorporation and defects, mainly the oxygen vacancies in the



Fig. 2 (a) ATR-IR and (b) FT-Raman spectra of the as-obtained ZnO and ZnO@C core-shell nanoparticles. The inset in 2b shows the enlarged area of Raman shift from 400 to 500 cm-1 of 2b.



ZnO structure. Fig. 2b presents the typical Raman spectra recorded for ZnO and ZnO@C core-shell nanoparticles. The more intense peaks at ~100 and ~440 cm<sup>-1</sup> were assigned to the  $E_2^{low}$  and  $E_2^{high}$  modes of wurtzite ZnO, respectively, due to the vibration of the zinc sub lattice in ZnO and oxygen vibrations.<sup>6</sup> The transition at 334 cm<sup>-1</sup> was attributed to a ZnO multiple-phonon-scattering process,  $E_2^{high} - E_2^{low}$ . The mode at 384 cm<sup>-1</sup> was associated with the A1 (TO) phonon frequency.<sup>30</sup> The peak observed for the  $E_{1LO}$  mode at ~ 580 cm<sup>-1</sup> was attributed to the formation of defects, such as oxygen vacancy, zinc interstitial, or their complexes.<sup>31</sup> The inset in Fig. 2b shows the peak shift from higher frequency to lower frequency (red shift) of about 5 cm<sup>-1</sup>, which also confirms the presence of oxygen vacancies and the incorporation of the carbon.  $^{\rm 32\text{-}34}$  The presence of carbon in the case of ZnO@C-1 and ZnO@C-2 was also confirmed by its characteristic peaks at 1355 (D-band) and 1575 cm<sup>-1</sup> (G-band) associated with defects or disorder due mainly to  $sp^3$  hybridization and stretching of the  $sp^2$  bonded carbon atoms, respectively.35,36 The D- and G-band, representing the presence of carbon were not observed in case of ZnO and ZnO@C-3, whereas the intensity of the peaks decreased with increasing the calcination temperature, which is also in accordance with the ATR-IR results.

The morphology of the obtained materials was investigated by FE-SEM. The ZnO synthesized from the thermal degradation of zinc nitrate hexahydrate salt showed the formation of diamond shaped particles with an average size of 10  $\mu$ m and possessing a six-faced pyramidal structure at both sides (up and down). The formation ZnO with similar morphological features from the thermal decomposition of zinc nitrate hexahydrate has been reported previously.37 ZnO obtained from the thermal degradation of Zn(an)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> complex resulted in the formation of nanoparticles, which might be due to the sudden decomposition of the complex at ~180 °C into ZnO and carbon. The thick layer of carbon on the ZnO nanoparticles can be visualized by FE-SEM (Fig. 3b) for ZnO@C-1, whereas in the case of ZnO@C-2, agglomerated ZnO nanoparticles with a smooth surface were observed (Fig. 3c).



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**Fig. 4** TEM images of ZnO@C-2 showing (a) agglomerated ZnO@C-2 nanoparticles, (b) close view of a cluster of ZnO@C-2 nanoparticles coated with the carbon shell (as shown in inset), (c) individual ZnO@C-2 particle with a clear view of carbon shell, (d) HR-TEM image representing the ZnO core, carbon shell and their interface, (e) SAED pattern of ZnO@C-2, and elemental mapping showing the distribution of (f) zinc, (g) oxygen and (h) carbon.

FESEM did not show any changes in the morphological features when the calcination temperature was increased from 600 to 700 °C (ZnO@C-3, Fig. 3d). ZnO@C-2 was examined further by TEM analysis based on its higher photocatalytic activity. Similar to that observed by FE-SEM, TEM of ZnO@C-2 also showed the agglomerated form of ZnO nanoparticles (Fig. 4a), a separated bunch of a few ZnO particles and individual ZnO particles (Fig. 4b and c). A closer view showed that the ZnO nanoparticles, which reflect the smooth surface

morphology in FE-SEM, possessed a shell of carbon (inset of Fig. 4b). Fig. 3c clearly shows the nanosized coating of carbon layer on the ZnO particle. The coating of the carbon material on ZnO varied in thickness from 5-20 nm, which resulted from the oxidation of the excess carbon material with a higher calcination temperature, e.g. 600 °C. The interaction of ZnO core with the carbon shell at their interfaces with a disturbance in the ZnO lattice (Fig. 4d), was also helpful in the easy transfer of excited electrons from ZnO to carbon, which extended the time for electron hole pair recombination.<sup>38</sup> These stacking faults and lattice defects could be attributed to the substitution of larger C anions for the O sites in the ZnO lattice.<sup>16,39</sup> The spacing between the lattice of the ZnO core was 0.26 nm (Fig. 4d), which corresponds to the distance between the (002) planes of ZnO crystal lattice.<sup>24</sup> Fig. 4e depicts the typical SAED pattern of ZnO. Elemental mapping by TEM also reflects the formation of the ZnO@C core-shell structure (Fig. f, g and h).

In semiconductor materials, a reduction of the band gap and the response of a catalyst to visible light can be achieved either by the formation of oxygen vacancies or carbon doping.<sup>40,41</sup> In both cases, optical characterization provides crucial information regarding its electronic interaction with light, which is a more important factor in the case of photocatalysis. The optical properties of the obtained samples were analyzed by UV-Visible DRS and PL spectroscopy. Surprisingly, ZnO obtained from zinc nitrate hexahydrate showed the lowest band gap as compared with the other synthesized ZnO@C core-shell nanoparticles (Fig. 5a and b). The red shift observed in the absorbance of ZnO under UV-Visible light can be explained by oxygen vacancies in the ZnO due to the shortage of oxygen in the environment during the decomposition of nitrate ions in zinc nitrate hydrate and its large grain size.<sup>24,42,43</sup> The shoulder peak observed at ~500 nm in the absorbance spectrum of ZnO (Fig. 5a) compared to the



**Fig. 5** Optical properties of the obtained ZnO and ZnO@C core-shell nanoparticles (a) UV-Visible absorbance spectra, (b) corresponding Tauc plot and (c) room temperature PL spectra (Inset in Fig. 3c shows a the plot of the  $I_{DL}/I_{NBE}$  ratios of the different synthesized ZnO@C core-shell nanoparticles).

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other samples also reflects the formation of extensive oxygen vacancies.<sup>37</sup> The trend of the band gap energy of obtained sample was as ZnO < ZnO@C-1 < ZnO@C-2 < ZnO@C-3. As shown in the Tauc plot (Fig. 5b), all samples exhibited lower binding energies ( $\leq$  3.1 eV) than typical ZnO (3.3 eV) and were expected to show photocatalytic activity in the visible region of light. Fig. 5c presents the room temperature PL spectra of the as-synthesized ZnO and ZnO@C core-shell nanoparticles obtained at different temperatures. As shown in the PL spectra (Fig. 5c), all samples exhibited two major peaks, first at ~ 390 nm, which was assigned to the near band gap emission (NBE) resulting from the recombination of free charge carriers, whereas the second at ~530 nm broad deep-level (DL) emission, also called green emission, was mainly because of the radial-recombination of a photo-generated hole with a singly ionized charge state of the specific defect (oxygen vacancies) in the ZnO crystal.44,45 In the case of ZnO@C-1, the defects due to oxygen interstitials (as observed by peak in red orange region and positioned at ~610 nm) were more dominant than oxygen vacancies. The intensities of the peak for oxygen vacancies increases with increasing calcination temperature compared to the intensities of peak for oxygen interstitials.<sup>46</sup> A plot of the ratio of intensities of peak DL (in case of ZnO@C-1, peak at ~ 610 nm was considered) and NBE, i.e.,  $I_{DI}/I_{NBF}$  (inset of Fig. 5c) provides a clear understanding of the crystalline structure of the obtained photocatalysts. ZnO obtained from zinc nitrate (without aniline) showed the highest  $I_{DL}/I_{NBE}$  ratio depicting the larger number of defects, mainly oxygen vacancies, which were also correlated with the DRS results. In the case of the ZnO@C core-shell nanoparticles, the ratio was decreased further with increasing calcination temperature, i.e., from 500 to 700 °C, suggesting the enhancement in the crystallinity of the ZnO. The characterization suggests that the ZnO@C-1 obtained at 500 °C contains a comparatively larger amount of carbon and a higher defective structure associated mainly with oxygen



**Fig. 6** High-resolution XPS (a) O 1s spectrum of ZnO, (b) O 1s spectrum of ZnO@C-2 and (c) C 1s spectrum of ZnO@C-2.

interstitials. Although the overall defects in ZnO@C-2 decrease due to the higher calcination temperature, oxygen vacancies were dominant over oxygen interstitial, which might be due to the utilization of surface oxygen during the oxidation of carbon. In the case of ZnO@C-2, the surface oxygen is utilized for the oxidation of carbon, which leads to the dominance of oxygen vacancies over oxygen interstitials and a decrease in the carbon concentration. Further increase in the calcination temperature (700 °C) results no or negligible amount of carbon in ZnO@C-3, which tends to decrease in the oxygen vacancies because of the higher availability of oxygen on the ZnO surface. The appearance of the band in the near IR region (~770 nm) for ZnO@C-2 and ZnO@C-3 was due either to ZnO defects or the second-order feature of NBE.<sup>47,48</sup>

The detail structural features of the ZnO and ZnO@C-2 were examined by XPS. The peaks representing the presence of Zn, O and C (in case of ZnO@C-2) can be seen clearly from the survey spectra of ZnO and ZnO@C-2 (Fig. S3a†). The two peaks observed in the high resolution XP spectra of Zn 2p for ZnO (Fig. S3b†) and ZnO@C-2 (Fig. S3c†) were attributed to the spin-orbit splitting,  $Zn^{2+}\ Zn2p_{3/2}$  (~1022 eV) and  $Zn^{2+}\ Zn2p_{1/2}$ (~1045 eV) states. The high resolution O1s spectrum of ZnO (Fig. 6a) and ZnO@C-2 (Fig. 6b), de-convoluted into three peaks using the XPS peak fitting program, clearly indicates the presence of the different oxygen bonding in the respective samples. The major band (~530.8 eV) observed in both the O 1s spectra was attributed to the  $O^{2-}$  ions on the wurtzite structure of the hexagonal Zn<sup>2+</sup> ion array, which indicates the Zn-O bonds in ZnO crystal. On the other hand, the peak located at higher binding energy (~532.5 eV) could be assigned to the chemisorbed oxygen, such as H<sub>2</sub>O, CO<sub>3</sub> and so on. The peak at the intermediate binding energy (~531.5 eV) was attributed mainly to the presence of the oxygen vacancies in the ZnO crystal. In the case of ZnO, the relative intensity or the area of the peak defining the oxygen vacancies was higher than the peak associated with chemisorbed oxygen. In contrast, a reverse trend was noticed for ZnO@C-2. This suggests that oxygen vacancies are prominent in the case of ZnO, whereas the larger amount of chemisorbed oxygen in ZnO@C-2 might be due to the presence of the more oxygen bonded to the carbon layer. Fig. 6c shows the high resolution C1s spectrum of ZnO@C-2 showing the presence of the carbon with various chemical states. The major peak at 284.6 eV was assigned to the sp<sup>3</sup> hybridized C-C bond.<sup>24</sup> The peaks observed at relatively lower and higher binding energies, i.e., at ~282.6 and 288.9, were attributed mainly to the presence of Zn-C bonds and carbonate species, respectively.<sup>39</sup> The broad band at 286.2 eV depicts the presence of the O-C-O complex.<sup>24,49</sup> XPS provides further support of the doping of carbon with a ZnO crystal and also a clearer view on the oxygen vacancies in both samples.

Fig. 7 presents a schematic representation of the different stages involved in the current photocatalyst synthesis, as observed by different characterization techniques and literature support. The  $Zn(an)_2(NO_3)_2$  complex was stable up to < 180 °C under atmospheric pressure and exothermic degradation occurred with further increases in temperature.<sup>50</sup>



Fig. 7 Schematic diagram of different stages involved in the synthesis of ZnO@C core-shell nanoparticles using the  $Zn(an)_2(NO_3)_2$  complex.

Although the synthesis of the ZnO@C photocatalysts was carried out at > 500 °C, the formation of ZnO nanoparticles and carbon occurred at ~180 °C due to exothermic degradation of the complex. XRD analysis of the product recovered at 200 °C (Fig. S4†) revealed the characteristics peaks of the typical wurtzite ZnO structure (JCPDS 36-1451). The product obtained at this early stage was completely black in color, showing the presence of a larger amount of carbon, which is described as ZnO@C composite. The product obtained at different calcination temperatures from 500 to 700 °C showed the decreasing carbon content was due to oxidation to CO2, which resulted in the ZnO@C core-shell structure (at 600 °C). The thermal degradation of zinc nitrate in methanol allows the formation of micron sized diamond shaped ZnO particles. The comparatively slower decomposition of zinc nitrate allows nucleation and agglomeration to form the diamond shaped micro particles, whereas in case of the  $Zn(an)_2(NO_3)_2$  complex, thermal decomposition of the complex resulted in nanoparticles formation.51,52

## Photocatalytic activity

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Based on a literature review and detailed characterization, the synthesized ZnO@C core-shell nanoparticles were expected to behave as a visible light active photocatalyst. Therefore, the photocatalytic degradation of RhB was performed in the presence of visible light as a test reaction (Fig. 8). As shown in Fig. 8, photolysis has no pronounced effect on the degradation of RhB (> 9%) under visible light, whereas ZnO showed the 45% of degradation of RhB under similar conditions. Although, ZnO possesses a lower band gap, it showed less photocatalytic activity for RhB degradation due mainly to the larger particle size, which provides fewer catalytic sites and less interactions with RhB. The carbon content or shell thickness on the photocatalyst is a crucial factor to enhance its photocatalytic activity. Among the ZnO@C photocatalysts synthesized, ZnO@C-2 exhibited the highest photocatalytic activity and showed 98% degradation of RhB after 150 min irradiation. The lower photocatalytic activity of ZnO@C-1 (82% degradation of RhB after 150 min) might be due to the presence of a large amount of carbon on ZnO, which leads to a blockage of optical



Fig. 8 Photocatalytic degradation of RhB using ZnO and different Zn@C core-shell nanoparticles under visible light.



**Fig. 9** Effect of the catalyst amount on photodegradation of RhB using ZnO@C-2 under visible light.

adsorption and a decrease in the production of photo-charges. The excess of carbon deposited on the ZnO may also lead to poor contact between the photocatalyst and dye, which resulted in a decrease in photocatalytic activity. The order of the photocatalytic activity for the degradation of RhB under similar conditions was ZnO@C-2 > ZnO@C-3 >ZnO@C-1 > ZnO, which further confirms that the loading or thickness of the carbon shell plays a crucial role in the photocatalytic properties.<sup>53</sup> After the photodegradation of RhB, no new absorption band was observed in its UV-visible spectra (Fig. S5†), indicating the complete degradation of RhB. Fig. 9 describes the effect of the catalyst loading on the photocatalytic degradation of RhB under similar conditions. As expected, the decrease in the catalyst amount from 500 mg/L to 250 mg/L and further to 100 mg/L leads to a decrease in the photodegradation of RhB from 98 to 88 % and further to 77%, respectively (Fig. 9). In contrast, an increase in catalyst loading (750 mg/L) allowed faster photodegradation of RhB (90 min) with similar efficiency (93%, Fig. 9).

Generally, the pseudo-first order kinetic model used to understand the kinetic properties of the photodegradation process suggests that the reaction takes place at the interface

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Fig. 10 (a) Pseudo-first order rate constant for the degradation of RhB using ZnO and ZnO@C core-shell nanoparticles (500 mg/L) and (b) recyclability of ZnO@C-2 for photodegradation of RhB under visible light.



Fig. 11 Schematic diagram of the proposed mechanism for the photodegradation of RhB using ZnO@C core-shell nanoparticles (ZnO@C-2) under visible light.



Fig. 12 Nyquist impedance plots of the ZnO and ZnO@C-2 in the dark and visible light.

between the catalyst and organic pollutants. The data obtained for the photocatalytic degradation of RhB using the synthesized photocatalysts at different time intervals was fitted to a pseudo-first order kinetic model (eq. 1) and the resulting rate constants are shown in Fig. 10a.

 $\ln(C_o/C) = kt$ (1)where  $C_{\alpha}$  and C are the concentration of RhB at time 0 and t, respectively; t and k are the reaction time and rate constant, respectively. A plot of  $ln(C_o/C)$  vs. t (Fig. S6†) shows that the photodegradation of RhB follows pseudo-first order kinetics. As ZnO@C-2 possessed the highest photocatalytic ability, it showed the highest pseudo-first order rate constant (0.0254),

which was ~7.5 times higher than the ZnO (0.0034), compared to the other photocatalysts. No photocatalytic system is practically applicable without recyclability. Therefore, the recyclability study of ZnO@C-2 was performed for up to four successive cycles after regenerating it by centrifugation followed by drying at 200 °C for 3 h. As shown in Fig. 10b, ZnO@C-2 exhibited very good stability and showed photocatalytic degradation of RhB up to ~96% after the 4<sup>th</sup> cycle without any significant decrease in activity. The overall study showed that the resulting ZnO@C core-shell nanoparticles (ZnO@c-2) could be recycled easily and reused multiple times for the photocatalytic degradation of organic pollutants under visible light irradiation.

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Based on the detail characterization and experimental evidence, the possible mechanism for the photodegradation of RhB using ZnO@C core-shell nanoparticles under visible light is shown in Fig. 11. Generally, the deposited carbon shell included two types of carbon species, one is the interfacial carbon attached chemically to ZnO and other is surface carbon. The highest occupied molecular orbital of amorphous carbon exists in the intermediate position between the conduction band and valence band of ZnO on the energy level diagram. Therefore, the interfacial carbon species are believed to play an important role in the more efficient charge separation and reducing the probability of photogenerated electron-hole recombination (Path Ib, Fig. 11). The prolonged charge separation leads to the production of more active free radicals, which are responsible for the oxidation of RhB to mineralized products, such as CO<sub>2</sub> and H<sub>2</sub>O. In this case, the absorption of visible light was attributed mainly to the lower band gap achieved by the presence of oxygen vacancies in the ZnO core (Path Ia, Fig. 11). The presence of a surface carbon layer with the appropriate thickness can also behave as a sensitizer and absorb the visible light. In this case the excited electrons transferred directly to the conduction band of the ZnO (Path II, Fig. 11) and the generated electron-hole pairs were utilized further for the degradation of RhB. The efficient transfer of charge carriers in the ZnO@C-2 core-shell nanoparticles over bare ZnO was also confirmed by EIS. Fig. 12 shows the EIS Nyquist plots of ZnO@C-2 and ZnO in the dark and under visible light. The arc radius of the EIS Nyquist plot, which reflects the interface layer resistance occurring at the surface, of the ZnO@C-2 electrode was smaller than that of the ZnO in the dark and under visible light. In particular, the interaction of the ZnO core with the carbon shell improves the transfer of photogenerated charge carriers and is responsible for the higher photoactivity of ZnO@C-2.

# Conclusions

Zn@C core-shell nanoparticles were synthesized using a simple, single-step process of thermal degradation of Zn(an)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> complex. The formation of ZnO nanoparticles was observed at lower temperatures, whereas a further increase in the temperature helps decorate the ZnO particles with a carbon shell with the oxidation of excess carbon. The ZnO@C core-shell structure obtained at 600 °C showed a

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uniform nanosized coating of the carbon layer with efficient photocatalytic activity for RhB degradation under visible light irradiation. The interaction of carbon with ZnO at the ZnOcarbon interface along with oxygen vacancies plays an important role in their higher photocatalytic activity and lowering the band gap to the visible active region. The present method shows the facile and fast synthesis of highly stable and recyclable visible active photocatalysts for pollutant removal.

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## Notes and references

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# **Graphical abstract:**

Zinc oxide/carbon core-shell nanoparticles, synthesized using thermal decomposition of zinc aniline nitrate complex, showed the excellent visible-light driven photocatalytic activity.

