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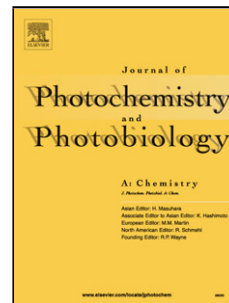
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Visible light assisted oxidative coupling of benzylamines using heterostructured nanocomposite photocatalyst

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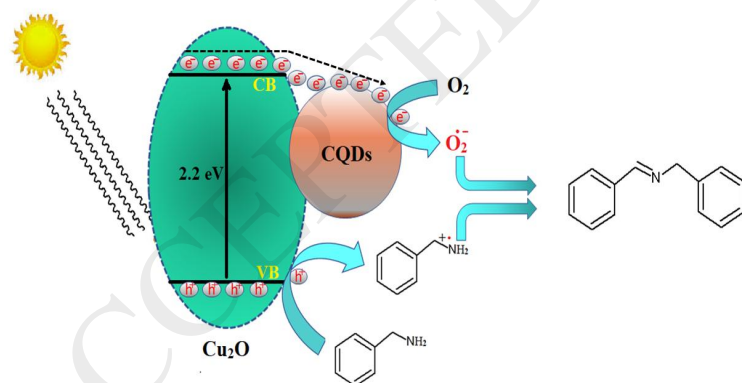
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Graphical Abstract



Highlights of the research

- Facile synthesis of hybrid nanocomposite consisting of copper (I) oxide and carbon quantum dots.
- Heterogeneous photocatalyst for organic transformation
- Visible light assisted oxidative coupling of benzyl amine
- A green, economical and efficient photochemical approach
- Higher activity and robustness of hybrid photocatalyst than neat Cu₂O and CQDs.
- Facile recovery and efficient recycling of the photocatalyst.

Abstract

The present paper describes a simple and direct synthesis of heterostructured nanocomposite consisting of copper(I) oxide and carbon quantum dots (Cu₂O/CQD). The structure and composition of the photocatalyst were determined by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–Vis diffuse reflectance spectroscopy and Raman spectroscopy. The synthesized photocatalyst was used for coupling of benzylamines using molecular oxygen as oxidant and house hold white LED as light emitting source under mild reaction conditions. The developed photocatalyst exhibited excellent activity, robustness and efficient recycling without any significant loss in activity for several runs.

Keywords: Photocatalysis; oxidative coupling; quantum dots; hybrid catalyst; benzylamine.

1.0 Introduction

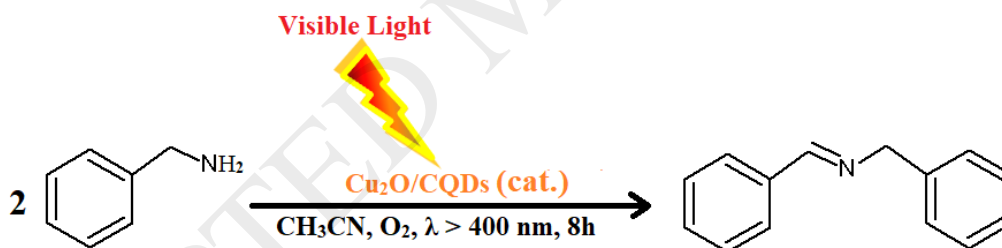
Sunlight is a unique natural energy source which is inexpensive, nonpolluting and abundantly available. Hence, the replacement of high-energy synthetic processes with clean, cost effective and green photochemical approaches has become an area of tremendous importance in recent decades [1]. So far, many semiconductor photocatalysts have been reported for organic transformations [2]; however, less efficiency, limited visible light absorbance and poor conversion rates are certain drawbacks associated with these methodologies [3]. Copper(I) oxide (Cu_2O) is a promising visible light active semiconductor which possesses some unique properties such as narrow band gap (2.2 eV), low cost, non-toxicity, better environmental acceptability and good adsorption of molecular oxygen [4]. Owing to these physical and chemical properties, Cu_2O has extensively been investigated in solar conversion processes and catalysis [5]. Furthermore, the coupling of Cu_2O with other semiconductors to form heterostructured composites is a promising approach for enhancing the charge separation as well as photo-activity [6]. In this regard, a number of heterostructured composites consisting of Cu_2O and semiconductors like TiO_2 , CdS , ZnO and CuO have been reported for numerous photocatalytic applications [7].

In the recent years, carbon quantum dots (CQD), novel nanosized carbon materials with less than 10 nm, have gained significant interest in the area of catalytic and photocatalytic applications. Owing to their excellent optical and electronic properties including higher absorbance and superior charge transfer, these materials have widely used in photocatalytic applications [8]. In addition, low cost, non-toxicity, facile functionalization, good biocompatibility and chemical inertness make CQD as the material of choice in place of commonly known inorganic semiconductor and organic dye photocatalysts [9].

In recent years, photocatalytic oxidation processes using visible light irradiation are gaining considerable interest for the maximum utilization of solar energy as it consists of nearly 45% of the solar spectrum [10]. In addition, most of the photo-catalytic transformations occur under ambient conditions which are advantageous over thermocatalytic processes, which require higher reaction temperatures [11]. Among the various oxidation processes, oxidative coupling of amines to corresponding imines is an important chemical transformation in organic synthesis. These compounds have found wide applications as synthetic intermediates in the preparation of bioactive molecules of therapeutic interest [12]. Conventional oxidation methods involve the use of stoichiometric oxidants such as 2-iodoxybenzoic acid, *N*-*tert*-butylphenylsulfonimidoyl chloride, which produce copious amounts of undesirable waste and are detrimental to the environment. Subsequently, catalytic methods using ruthenium based catalysts such as RuCl_3 , $[\text{RuCl}_2(\text{RCH}_2\text{NH}_2)_2(\text{PPh}_3)_2]$, ruthenium (II) porphyrin, ruthenium-hydroxyapatite, $\text{Ru}_2(\text{OAc})_4\text{Cl}$ and $\text{Ru}/\text{Al}_2\text{O}_3$ in conjunction with molecular oxygen as oxidant have been reported for this transformation [13]. However, very few reports are known on the photocatalytic oxidation of benzylic amines to the corresponding imines using O_2 as an oxidant. In this context, Su and co-workers reported mesoporous graphite carbon nitride (mpg- C_3N_4) for the oxidation of benzylic alcohols and amines with O_2 under visible light [14]. Higher pressure (0.5 MPa) and need of halogenated solvent (trifluorotoluene) make this methodology of limited applicability. Furukawa et al. [15] described niobium oxide/ O_2 system for the photo-oxidation of amines. Apart from these semiconductor photocatalysts, recently, Berlicka et al. [16] investigated porphyrin or porphycene-mediated photo-oxidation of primary amines to *N*-benzylidene benzylamines in excellent conversion yields. Despite the excellent activity of these dyes under visible light, homogeneous nature and non-recyclability are the obvious drawbacks associated with this system. Hence, the development of heterogeneous photocatalyst along with the use of low cost

metals under visible light irradiation is highly desired from both environmental and economic viewpoints. Raza et al. [17] studied oxidative coupling reactions of amines by photoactive WS₂ nanosheets. More recently, Kumar et al. [18] reported an efficient semiconductor-metal complex hybrid photocatalyst, namely, graphitic carbon nitride (g-C₃N₄) and iron (III) bipyridine complex for the oxidation of the benzylic amines with molecular oxygen under visible light irradiation. However, the multi-step synthesis of the hybrid photocatalyst makes the developed methodology of limited practical applicability.

In this paper, we report an efficient and simple visible light assisted heterostructured nanocomposite consisting of cuprous oxide (Cu₂O), carbon quantum dots (CQD) i.e. Cu₂O/CQD catalyzed photo-oxidation of benzylamines using molecular oxygen as an oxidant to the corresponding imines under ambient conditions (Scheme 1).



Scheme 1: Photo-oxidation of benzylamines.

Experimental Section

2.1 Materials

Fructose, sodium hydroxide (NaOH), and copper perchlorate (Cu(ClO₄)₂) were obtained from Sigma Aldrich (France) and used as received.

2.2 Techniques used

SEM images were obtained using an electron microscope Hitachi S4700 equipped with a cold field emission emitter and two different detectors (high efficiency In-lens SE detector, Everhart-Thornley Secondary Electron Detector). The samples were prepared by casting 50 μL aqueous of Cu_2O -CQDs composite on a clean silicon wafer followed by drying in an oven at 80 $^\circ\text{C}$ to remove adsorbed water. Transmission electron microscopy (TEM) imaging was performed on a FEI Tecnai G2-F20 microscope operating at an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 advance diffractometer (Cu-K α radiation, 1.54056 \AA) with an applied voltage of 40 kV and an anode current of 40 mA in the 2θ range of 10-80 $^\circ$. UV/Vis absorption spectra were recorded using a Perkin Elmer Lambda UV/Vis 950 spectrophotometer in quartz cuvettes with an optical path of 10 mm. The wavelength range was 200–800 nm. X-ray photoelectron spectroscopy (XPS) experiments were performed in a PHI 5000 VersaProbe - Scanning ESCA Microprobe (ULVAC-PHI, Japan/USA) instrument at a base pressure below 5×10^{-9} mbar. Monochromatic AlK α radiation was used and the X-ray beam, focused to a diameter of 100 μm , was scanned on a 250×250 μm surface, at an operating power of 25 W (15 kV). Photoelectron survey spectra were acquired using a hemispherical analyzer at pass energy of 117.4 eV with 0.4 eV energy step. Core-level spectra were acquired at pass energy of 23.5 eV with 0.1 eV energy step. All spectra were acquired at 90 $^\circ$ between X-ray source and analyzer and with the use of low energy electrons and low energy argon ions for charge neutralization. After subtraction of the Shirley-type background, the core-level spectra were decomposed into their components with mixed Gaussian-Lorentzian (30:70) shape lines using the CasaXPS software. Quantification calculations were performed using sensitivity factors supplied by PHI. The sample was prepared by casting a concentrated aqueous solution of the material onto silicon substrate followed by drying at 100 $^\circ\text{C}$ for 1 h.

2.3 Synthesis of carbon dots

Carbon quantum dots (CQDs) were synthesized by a one-pot method at a relatively low reaction temperature [19]. In a typical procedure, fructose (500 mM) and sodium hydroxide (500 mM) were added to 20 mL water. The resulting solution was placed into a Teflon-lined stainless-steel autoclave and heated at 50 °C for 1 h. The solution turned from a colorless into brown.

2.4 Synthesis of Cu₂O/CQDs

Copper perchlorate (1.35 g) was dissolved in 10 mL of previously prepared CQDs solution and heated at 80 °C for 3 h. The formed precipitate was separated by centrifugation, washed with water three times and annealed at 120 °C overnight [19]. For comparison, Cu₂O was prepared by the same procedure using copper chloride and sodium hydroxide without adding fructose as mentioned above. The Cu content in the Cu₂O/CQDs was determined by ICP-AES which was found to be 38.04 wt% (2.9 mmol Cu/g catalyst).

2.5 Photocatalytic oxidative coupling of benzylamines

All the photocatalytic experiments were carried out by using a 20 watt white cold LED light (Model No. HP-FL-20W-F-Hope LED Opto-Electric Co., Ltd, $\lambda > 400$ nm) as a light source. In a typical experiment, benzylamine (1 mmol) and photocatalyst (25 mg) were mixed in acetonitrile (10 mL). The resulting mixture was irradiated with visible light with stirring for 8 h in the presence of molecular oxygen. The progress of the reaction was monitored by TLC. After completion of the reaction, the photocatalyst was separated by filtration and the obtained residue was concentrated under reduced pressure to obtain a crude product. The pure product was obtained via purification using column chromatography on silica gel by using ethyl acetate: hexane (9:1) as eluent.

3.0 Results and Discussion

3.1 Synthesis and characterization of photocatalyst

The $\text{Cu}_2\text{O}/\text{CQDs}$ investigated in this work was prepared according to a previous protocol published by some of us [19]. The morphology of the synthesized $\text{Cu}_2\text{O}/\text{CQD}$ nanocomposite was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM image of the synthesized nanocomposite as shown in Figure 1a revealed nanoparticles in the aggregated form.

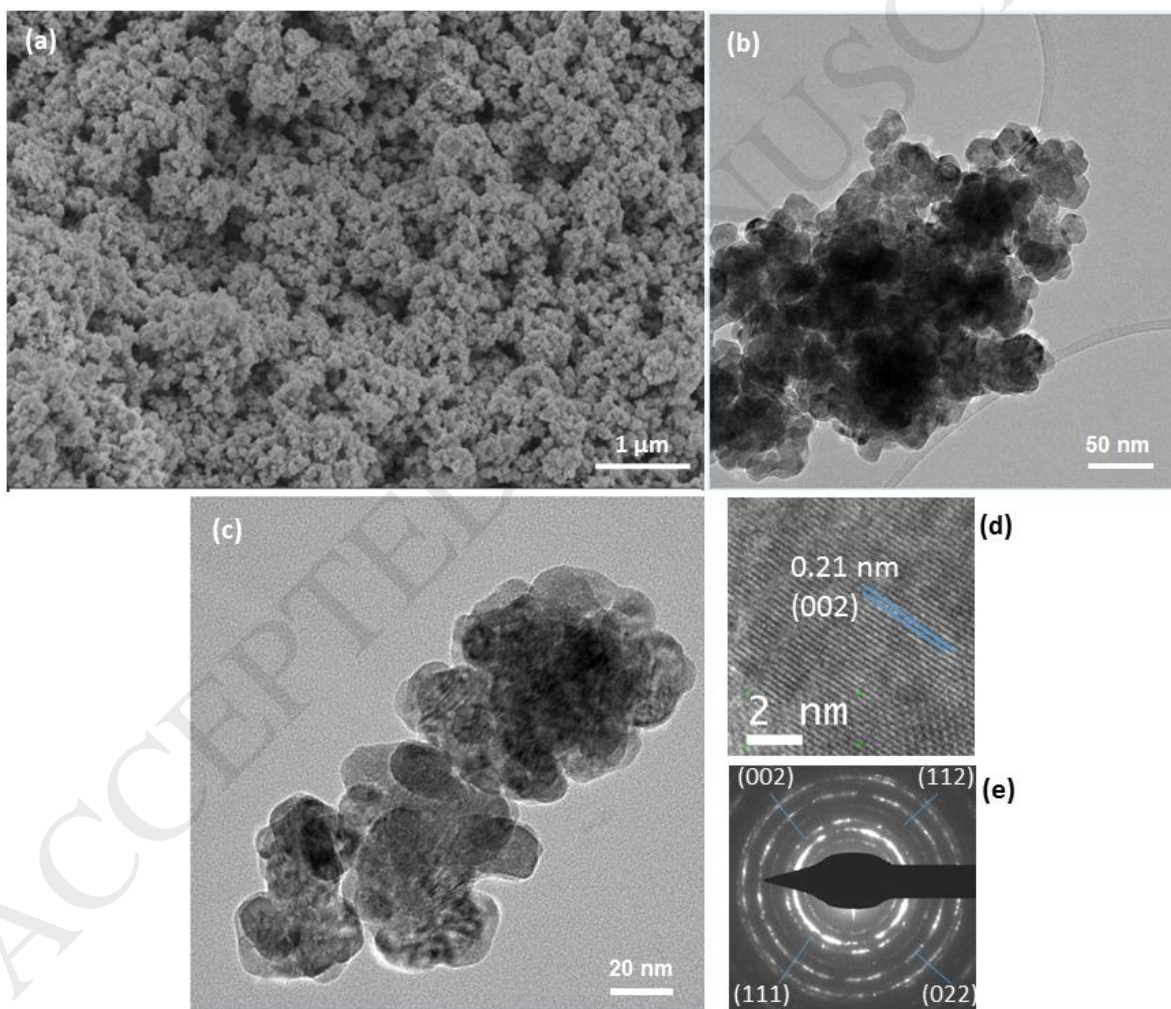


Figure 1. SEM (a), low (b) and high (c) resolution TEM images, (d) HR-TEM of a nanoparticle and (e) SAED of $\text{Cu}_2\text{O}/\text{CQD}$.

The TEM image of the prepared nanocomposite indicated Cu_2O NPs of 20-30 nm in size (Fig. 1b, c). In addition, in the HR-TEM image of a single Cu_2O NP an interplanar distance of 0.21 nm between adjacent planes, related to the interplanar spacing of the (002) plane of Cu_2O was observed (Fig. 1d). The appearance of five diffraction rings in the selected-area electron diffraction (SAED) pattern corresponding to the (022), (112), (002), (111), and (011) planes of Cu_2O suggested the poly crystalline nature of the sample (Fig. 1e).

X-ray diffractogram of $\text{Cu}_2\text{O}/\text{CQD}$ composite as shown in Figure 2 exhibited several reflections having at least two different crystalline phases of Cu (ICDD No. 65-9026) and Cu_2O (ICDD No. 78-2076). The diffraction planes of the Cu phase observed at 43.2° and 50.3° were corresponded to the Cu(111) and Cu(200), respectively. The other diffraction peaks at 29.5° , 36.5° , 42.2° , 61.3° , and 73.7° were related to the Cu_2O (110), Cu_2O (111), Cu_2O (200), Cu_2O (220) and Cu_2O (311) crystalline planes, respectively. Indeed, very weak peaks of Cu appeared in the XRD pattern of $\text{Cu}_2\text{O}/\text{CQD}$. However, the material is mostly Cu_2O and also the chemical transformation is a photochemical process, the contribution of Cu is believed to be negligible. Hence we have denoted active photocatalyst as $\text{Cu}_2\text{O}/\text{CQD}$. Additionally, a small peak at $\sim 22.8^\circ$ confirmed the presence of carbon from the CQD. These characterization results were found to be in good agreement with our previous reports on reduced graphene oxide modified with Cu_2O [20], and Cu_2O modified multi-walled carbon nanotube nanostructures [21] and CQD [22].

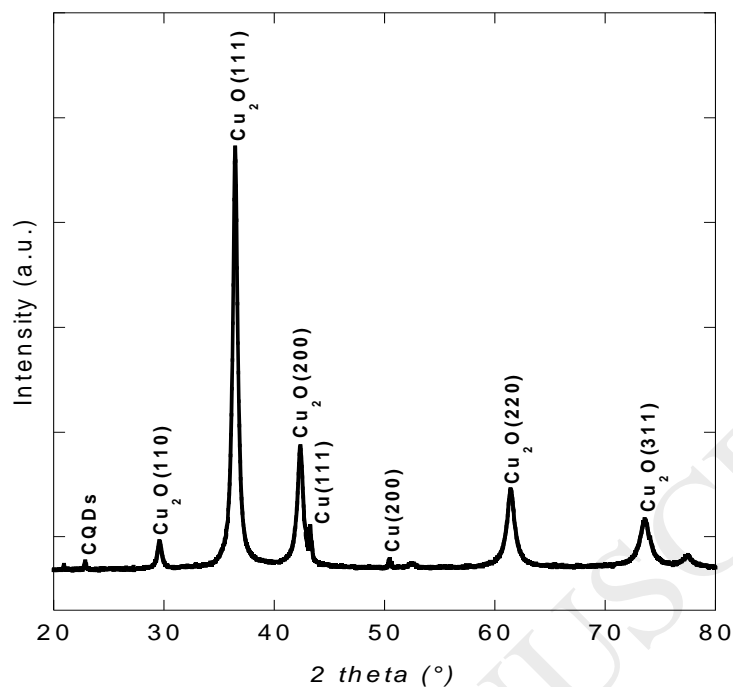


Figure 2. Powder X-ray diffraction pattern of Cu₂O/CQD.

The UV-Vis spectra of nanocomposite Cu₂O/CQD and its components are shown in Figure. 3. The UV-vis absorption spectrum of CQDs in water revealed a main absorption peak at 293 and a shoulder at 340 nm attributed to the π - π^* transition of the conjugated C=C and the n - π^* transition of the C=O, respectively [19]. Interestingly, both Cu₂O and Cu₂O/CQD absorb remarkably in the visible region, making these materials suitable for photocatalytic processes under visible light irradiation. The band gap of Cu₂O was determined with the help of Tauc plot which was found to be 2.2 eV (Fig. S3). According to the band gap, the absorption edge wavelength for Cu₂O was estimated to be 563 nm.

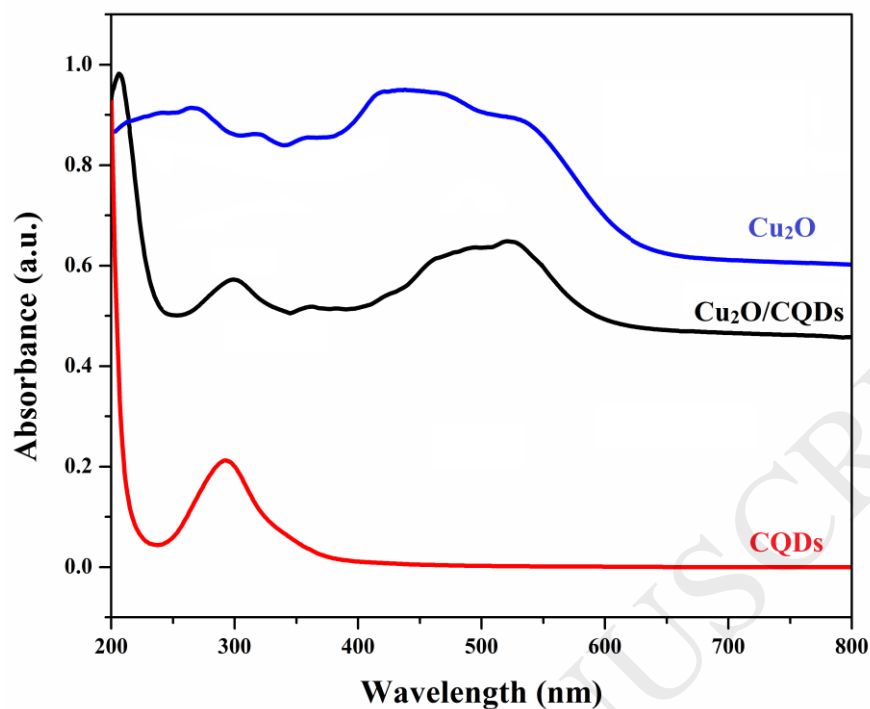


Figure 3. UV-Vis spectra of CQD, Cu₂O/CQD and Cu₂O

The chemical composition of the synthesized nanocomposite was examined by X-ray photoelectron spectroscopy (XPS). In survey scan as shown in Figure S1, the appearance the corresponding peaks of all the desired elements such as Cu_{3s} (75.0 eV), Cu_{3p} (122.5 eV), C_{1s} (285.0 eV), O_{1s} (531.5 eV) and Cu_{2p} (532 eV) confirmed the successful synthesis of the material. The high-resolution XPS spectrum of C_{1s} (Fig. 3) revealed the main peak at ~285 eV due to C-H, C-C and C=C bonds from the CQD along with two components at 286.2 and 288.6 eV assigned to C-O and C=O bonds, respectively.

The XPS high-resolution spectrum of Cu_{2p} displayed two peaks at 932.5 and 952.4 eV attributed to Cu_{2p3/2} and Cu_{2p1/2}, respectively from Cu₂O (Fig. 4). The XPS high-resolution spectrum of O_{1s} exhibited peaks at 530.7 and 531.8 eV respectively, due to the oxygen bonded to the carbon skeleton of the CQD and Cu-O in Cu₂O (Fig. S2).

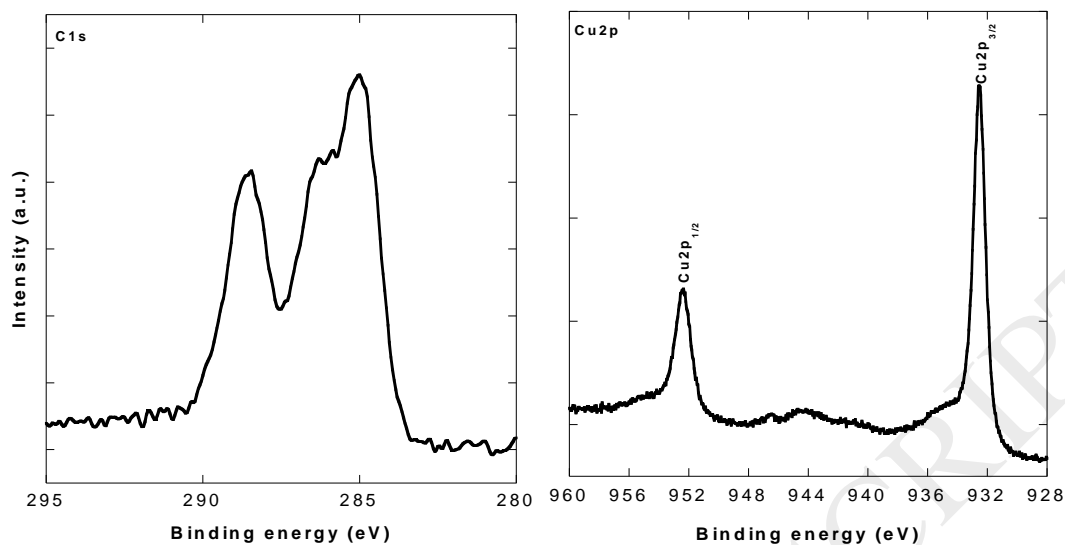


Figure 4. High-resolution XPS spectra of C_{1s} and Cu_{2p} of Cu₂O/CQD.

3.2 Catalytic Activity

The photocatalytic activity of the synthesized nanocomposite Cu₂O/CQD and its components were checked for the oxidation of benzylamine with O₂ in acetonitrile solvent under visible light irradiation at ambient temperature and pressure conditions (Scheme 1). At first, optimization experiments using variable reaction parameters were performed and the results of these experiments are summarized in Table 1. In a blank reaction, no product was formed even in the prolonged time (24h) in the absence of photocatalyst under otherwise identical conditions. (Table 1, entry 1). Similarly, in the absence of a visible light source, no reaction was occurred (Table 1, entry 2), suggesting that the reaction was truly photocatalytic in nature. However, in the presence of visible light irradiation, the oxidation of benzylamine (1 mmol) using 25 mg Cu₂O/CQD as a photocatalyst in CH₃CN under an oxygen atmosphere at an ambient temperature (25 °C) and pressure (1 atm) afforded an almost quantitative yield of the corresponding imine (Table 1, entry 3). Furthermore, the use of neat Cu₂O or CQDs as photocatalysts under identical conditions

afforded only 12 and 30% conversion, respectively (Table 1, entry 4-5). Furthermore, the effect of various solvents was studied to select the optimum reaction medium. Among the different solvents such as methanol, dimethylformamide, tetrahydrofuran, acetonitrile, and ethanol (Table 1, entries 3, 6-9) studied, acetonitrile (CH₃CN) was found to be the best solvent for the reaction (Table 1, entry 3). Molecular oxygen played an essential role and in its absence (irradiation under nitrogen atmosphere), a negligible conversion was achieved (Table 1, entry 10). Although the reaction occurred efficiently at room temperature (24 °C) at 1 atmospheric pressure, to check the effect of temperature, the reaction was performed at 50 °C under described conditions (Table 1, entry 3). A marginal enhancement in the conversion (97.5%) was observed at higher temperature; therefore we selected room temperature as the optimum temperature for the reaction.

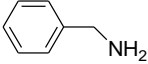
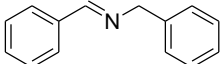
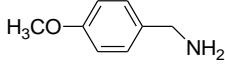
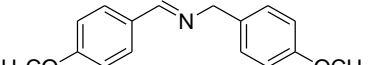
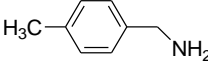
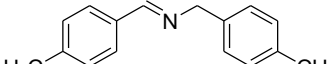
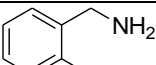
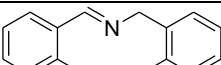
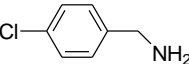
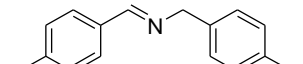
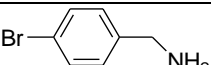
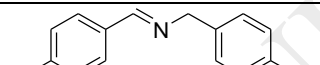
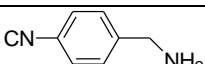
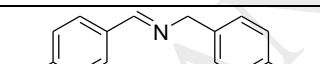
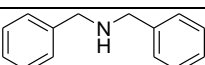
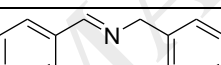
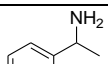
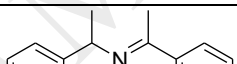
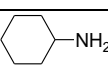
Table 1: Optimization of oxidative coupling of benzylamine with molecular oxygen under different reaction conditions^[a]

Entry	Visible light	Solvent	Photocatalyst	Time (h)	Conv. (%) ^[b]	TON ^[c]	TOF (h ⁻¹)
1	Yes	CH ₃ CN	No	24	-	-	-
2	No	CH ₃ CN	Cu ₂ O/CQDs	24	-	-	-
3	Yes	CH ₃ CN	Cu ₂ O/CQDs	8	97, 97.5 ^[d]	13.8, 13.9	1.7, 1.7
4	Yes	CH ₃ CN	Cu ₂ O	10	15	-	-
5	Yes	CH ₃ CN	CQDs	10	30	-	-
6	Yes	MeOH	Cu ₂ O/CQDs	10	74	10.6	1.1
7	Yes	DMF	Cu ₂ O/CQDs	10	92	13.1	1.3
8	Yes	THF	Cu ₂ O/CQDs	10	54	7.7	0.8
9	Yes	EtOH	Cu ₂ O/CQDs	10	75	10.7	1.1
10 ^[d]	Yes	CH ₃ CN	Cu ₂ O/CQDs	8	trace	-	-

^[a]Reaction conditions: benzylamine (1 mmol), photocatalyst (25 mg), solvent (10 mL), light source: white cold LED $\lambda > 400$ nm, time: 8-24 h under oxygen balloon; Power at reaction vessel: 70 W/m²; ^[b]determined by GC-MS; ^[c]TON is defined as the amount of product formed to that of the active site Cu in the photocatalyst; ^[d]at 50 °C temperature; ^[e]in the absence of molecular oxygen under N₂ atmosphere.

Furthermore, the reaction was generalized to variously substituted benzylamines under optimized reaction conditions using Cu₂O/CQD/O₂ system under visible light at room temperature. The results of these reactions are summarized in Table 2. All the substrates afforded corresponding imine products selectively without observing any by-product. Moreover, marginal substituent effect was observed and all the substrates containing either electron-releasing or withdrawing groups were smoothly and efficiently converted to the resultant *N*-benzylidene benzylamines in good to excellent yields (75-95%). The slightly higher activity of the electron rich amines might be due to the easy formation of an intermediate imine. Furthermore, *o*-substituted benzylamine displayed slightly poor product yield as compared to the *p*-isomer, which is mainly due to the obvious reason of steric hindrance (Table 2, entry 4). Secondary benzylamine (dibenzylamine) also showed high reactivity and afforded moderate product yield (Table 2, entry 8). However, cyclohexylamine was not reacted under the described conditions (Table 2, entry 10).

Table 2: Cu₂O/CQD-catalyzed oxidative coupling of benzylamines^[a]

Entry	Substrate	Product	Conv. (%) ^[b]	Yield (%) ^[c]
1			97	95
2			97.5	95
3			97	93
4			91	88
5			94	90
6			94	91
7			89	85
8			90	86
9			79	75
10		-	-	-

^aReaction conditions: benzylamine (1 mmol), Cu₂O/CQD (25 mg), acetonitrile (10 mL) under visible light irradiation with white cold LED $\lambda > 400$ nm for 8 h; Power at reaction vessel: 70 W/m²; ^bdetermined by GC-MS; ^cIsolated yield.

Further, to check the recyclability of the material, recycling experiments were performed by choosing benzylamine as a representative example. After completion of the reaction; the photocatalyst was separated by simple filtration, washed with acetonitrile, dried and reused in the subsequent experiments for six runs (Fig. 5). Almost similar conversion and product yield were obtained in all cases, suggesting that the synthesized photocatalyst was highly stable in nature. Furthermore, to ascertain the leaching of metal, selected filtrate samples of recycling

experiments were subjected to ICP-AES analysis. No metal trace was detected in the solution phase, indicating no leaching had occurred and the reaction was truly heterogeneous in nature.

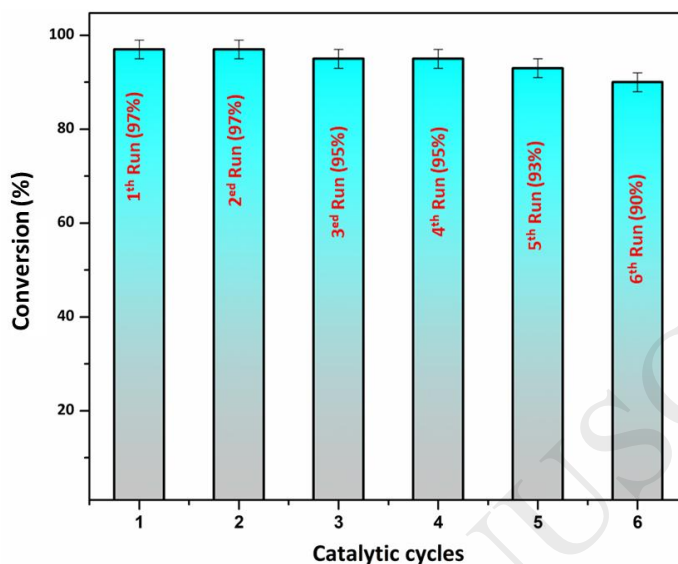
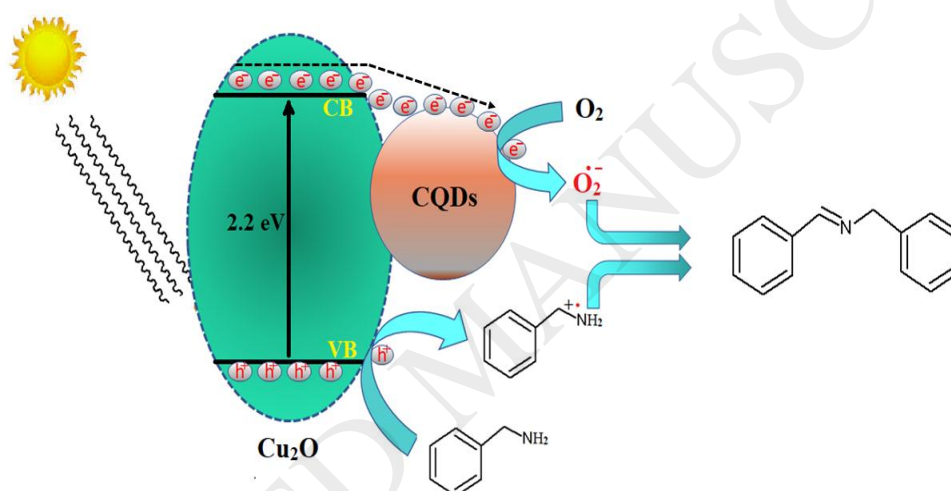


Figure 5. Results of recycling experiments.

Although, the exact mechanism of the reaction is not clear at this stage, based on our experimental findings and existing literature reports [17] a plausible mechanism of the reaction is depicted in Scheme 2. As shown in a controlled experiment that oxygen played a pivotal role and in its absence the reaction did not occur (Table 1, entry 10). It is believed that after absorbing the light, charge separation takes place in photocatalyst $\text{Cu}_2\text{O}/\text{CQD}$. The photogenerated electrons were excited from the VB to the CB of Cu_2O . Subsequently the photo-generated electrons were transferred to CQD, which act as electron collector, transporter to provide better mobility and charge separation. Furthermore, molecular oxygen gets excited under light and converted to the singlet oxygen which can accept an electron from the conduction band of nanocomposite to give superoxide radical. To confirm the formation of superoxide radical, the reaction was performed by adding a common radical scavenger, i.e. *p*-benzoquinone (BQ). A significant decrease in the

product yield was observed, which confirmed the formation of superoxide radical as an intermediate during the photo-oxidation reaction. In the subsequent step, benzylamine transferred an electron to the valence band of photocatalyst and converted to cation radical as shown in Scheme 2. In the final step, superoxide radical abstracts a hydrogen atom from the benzylic position of a benzylamine radical cation to produce benzylimine, which interacted with another benzylamine molecule to give the corresponding *N*-benzylidene benzylamine along with H₂O₂ as a by-product (Scheme 2).



Scheme 2: Plausible mechanism of photocatalytic oxidative coupling of benzylamine in the presence of Cu₂O/CQD.

3.3 Formation of singlet oxygen in Cu₂O/CQD system under visible light irradiation

The formation of singlet oxygen (¹O₂) during the photocatalytic oxidative coupling of benzylamine was investigated by adding sodium azide (NaN₃), a quencher of ¹O₂. For this study, a comparison was made between the original photocatalytic experiment and that obtained after the addition of sodium azide (NaN₃) at different time intervals (Fig. 6). As shown in Fig. 6, the

conversion of benzylamine using $\text{Cu}_2\text{O}/\text{CQDs}$ photocatalyst with oxygen under visible light irradiation was found to be 21, 58, 87.4 and 97.5% after 2, 4, 6 and 8h, respectively in the absence of NaN_3 . However, the conversion was reduced significantly, and maximum conversion reached only up to 12.5% after 8h when NaN_3 was added into the system. These experimental results confirmed the generation of singlet oxygen ($^1\text{O}_2$) in the photocatalytic system under visible light irradiation.

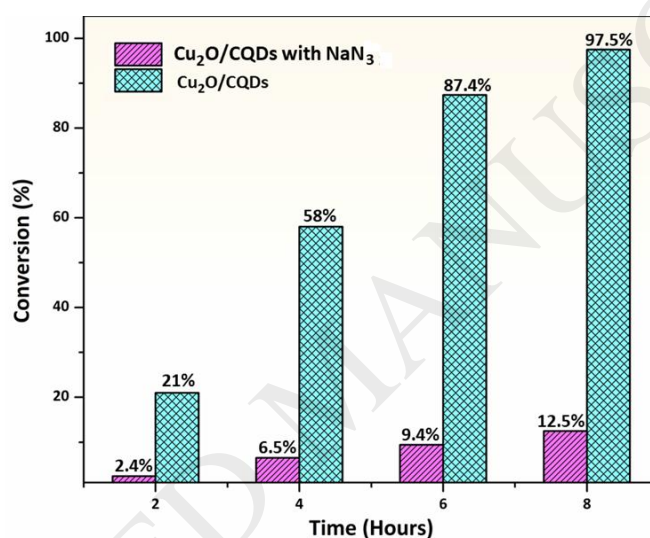


Figure 6. Conversion of benzylamine using $\text{Cu}_2\text{O}/\text{CQD}$ photocatalyst with and without adding NaN_3 as a quencher.

4.0 Conclusions

We have demonstrated an efficient, readily synthesized and cost effective photocatalyst i.e. heterostructured nanocomposite consisting of cuprous oxide and carbon quantum dots ($\text{Cu}_2\text{O}/\text{CQD}$) for the oxidative coupling of benzylamines using molecular oxygen as oxidant under visible light at ambient conditions. The developed nanocomposite $\text{Cu}_2\text{O}/\text{CQD}$ exhibited superior activity as compared to bare Cu_2O and CQD . In addition, the nanocomposite showed

excellent stability and efficient recyclability without any detectable leaching during the reaction. The superior performance of Cu₂O/CQD was mainly attributed to the enhanced charge transportation, effective separation of the photogenerated electron-hole pair and improved contact between photocatalyst and substrate molecules. Owing to the low cost and better efficiency, such Cu₂O/CQDs nanocomposite can be used as a promising alternative to the noble metals (Au, Pd, Pt etc) in improving the photocatalytic ability of semiconductor photocatalysts.

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Graphical Abstract**Visible light assisted oxidative coupling of benzylamines using heterostructured nanocomposite photocatalyst**

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