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# Highly efficient microwave assisted synthesis of magnetically separable GO-CoFe<sub>2</sub>O<sub>4</sub> nanocomposite for visible light induced oxidative coupling of benzyl amines

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### **Graphical Abstract**



#### Highlights

- An efficient, rapid and energy saving microwave assisted synthesis magnetic GO-CoFe<sub>2</sub>O<sub>4</sub> nanocomposite
- Use of enviro-economic molecular oxygen as primary oxidant
- Photocatalytic oxidative coupling of amines to imines under ambient conditions
- Heterogeneous photocatalyst with facile recovery by using an external magnet

#### Abstract

The present paper describes an efficient microwave-assisted synthesis of magnetic CoFe<sub>2</sub>O<sub>4</sub> and its nanocomposite with graphene oxide (GO-CoFe<sub>2</sub>O<sub>4</sub>) for photocatalytic oxidative coupling of benzylamines to the corresponding imines using molecular oxygen. The surface morphologies and structures of both CoFe<sub>2</sub>O<sub>4</sub> and GO-CoFe<sub>2</sub>O<sub>4</sub> nanocomposites were investigated by various spectroscopic techniques including powder X-ray diffraction (XRD), Transmission electron microscopy (HR-TEM), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption– desorption isotherms, X-ray photoelectron spectroscopy (XPS) and Raman Spectroscopy. Photocatalytic oxidative coupling experiments demonstrated that GO-CoFe<sub>2</sub>O<sub>4</sub> exhibited significantly higher efficiency than CoFe<sub>2</sub>O<sub>4</sub> nanoparticles, suggesting that GO played an important role in the reaction. Moreover, the magnetic nature of the synthesized nanocomposite provided facile recovery of the material by the influence of an external magnet.

Keywords: Photocatalysis, hybrid material, oxidative coupling, molecular oxygen, magnetic separation

#### **1. Introduction**

Exploitation of solar light to induce organic transformations in the presence of a photo-active catalyst is the subject of immense scientific interest and importance owing to the transparency of most of the organic molecules in the visible spectrum [1-6]. Use of this renewable energy (sunlight) not only makes the synthesis cost efficient but also provides an ideal solution for environment related issues originated by energy intensive chemical processes [7-9]. Imines are the important building blocks that have extensively used as intermediates in the synthesis of biologically important compounds and as liquid crystals in the field of analytical and polymer chemistry [10-11]. Conventionally imines are synthesized by the condensation of an aldehyde with an amine in an organic solvent under reflux conditions [12-13]. Oxidative coupling of amines over photoactive catalyst using molecular oxygen is a green and energy efficient approach for the synthesis of imines under mild reaction conditions [14-21]. In this context, Chen et al demonstrated a carbonyl modified carbon nitride photocatalyst for the oxidative coupling of amines using molecular oxygen [22]. Su et al reported oxidative coupling of amines to imines using mesoporous graphitic carbon nitride as a photocatalyst under visible light irradiation [23]. Lang and co-workers reported the visible light conducted selective oxidation of amines to imines using dye sensitized titania and TEMPO with atmospheric air pressure [16]. In a most recent approach, a porphyrinic based metal organic framework (PCN 222) was utilized efficiently as a photocatalyst for oxidative coupling of diverse amines upon visible light irradiation at ambient conditions [20]. Kumar et al demonstrated the use of iron bipyridine- graphitic carbon nitride as a hybrid catalyst for the photoactivity of aerobic oxidative coupling for benzylamines [14].

Cobalt ferrite, one kind of spinel ferrite ( $MFe_2O_4$ , M = metal cation) is a chemically and thermally stable magnetic material having high magnetic hardness and magneto crystalline anisotropy [24-

28]. Owing to its activity in the visible light, it has been extensively applied in photo-catalytic reactions [29-30]. Recently Li and co-workers developed a magnetically separable photo-catalyst TiO<sub>2</sub>/CoFe<sub>2</sub>O<sub>3</sub> by the sol gel and electro-spinning methods for photocatalytic degradation of methylene blue under UV-Vis light [31]. In an another approach by Wang et al degradation of methylene blue, methyl orange, rhodamine etc was achieved by a highly visible light active cobalt ferrite/graphene nanocomposite with different degree of graphene content [32]. The graphene oxide plays a significant role in improvement of photo-catalytic activity of cobalt ferrite under visible light irradiation. In an another development, Haw and co-workers reported a novel magnetically recoverable TiO<sub>2</sub>-cobalt ferrite nanocomposite for the photo-degradation of methylene blue [30]. Inspired by these reports, we synthesized a nanocomposite containing graphene oxide and cobalt ferrite (GO-CoFe<sub>2</sub>O<sub>3</sub>) for oxidative coupling of amines to corresponding imines under visible light. Owing to the presence of oxygen functionalities in GO, the synthesized nanocomposite offered better dispersion in organic solvents. So far, a number of methods such as solvothermal, ultrasonic have been explored for the synthesis of nanocomposites of CoFe<sub>2</sub>O<sub>4</sub> with GO for various applications [29, 33-35].

During the present study, a novel microwave assisted methodology adopted for the synthesis of GO-CoFe<sub>2</sub>O<sub>4</sub> nanocomposite that make its synthesis simple, rapid, cost effective and energy efficient. The synthesized nanocompoiste was used as a visible light active photocatalyst for the oxidative coupling of benzylamines to corresponding imines using molecular oxygen as an oxidant in high to excellent yields (Scheme 1).







Scheme1. Oxidative coupling of benzyl amine using GO-CoFe<sub>2</sub>O<sub>4</sub> as a photocatalyst

#### 2. Experimental

#### 2.1 Materials used

Cobalt nitrate hexahydrate ( $\geq$ 98%), iron (III) nitrate nonahydrate ( $\geq$ 98%), ethylene glycol (99.8%), 4-fluoro benzylamine (97%), 4-bromobenzylamine (96%), aniline ( $\geq$ 99.5%) were purchased from Sigma Aldrich and used without further treatment. Benzylamine (98+%), 4-methoxy benzylamine (98+%), 4-chloro benzylamine (97+%), 4-methyl benzylamine (98%), 3-chloro benzylamine (97+%), 4-chloro3-fluoro benzylamine (98%), 4-bromo aniline (98+%), 4-chloro aniline (98%) were purchased from Alfa Aesar and urea (99.5%) was procured from Rankem, Ranbaxy India and used as received.

#### 2.2 Techniques used

X-ray diffraction of the sample was recorded over a Bruker D8 advanced diffractometer, with a voltage of 40 kV with Cu K $\alpha$  radiation of a wavelength of 1.5418 A°. The FT-IR spectra of the samples were recorded by Perkin Elmer Fourier Transform Infrared spectrophotometer in which potassium bromide was used to make the transparent pellet for analysis. UV-Visible spectroscopic analyses of the samples were done by Perkin Elmer Lambda-19 UV-VIS-NIR spectrophotometer where barium sulfate was used as a baseline of standard reflectance. The surface area and pore analysis were done by a Micrometrics ASAP2010 instrument in which nitrogen adsorption and desorption isotherm using liquid nitrogen at 77 K. XPS measurements were done by a system (ESCA<sup>+</sup> omicron nanotechnology, Oxford instruments Germany). HR-TEM and FE-SEM were used to analyze the morphology of the sample. HR TEM images of the samples were recorded by high-resolution transmission electron microscopy (JEM 2100), an operating voltage of 200 kV and LaB<sub>6</sub> was used as an electron source in it. In field emission scanning electron microscopy (Quanta

200F, FEI) a range of detectors including Secondary Electron (SE) and Energy Dispersive X-ray analysis (EDS), etc were used with accelerating voltage of 15kv. Raman spectra of the samples were recorded by HR 800 Jobin-Yvon Raman spectrometer with a spectral range of 4000 cm<sup>-1</sup> to 100 cm<sup>-1</sup>. Thermal gravimetric analysis of the photocatalyst was done by a Perkin Elmer TG-DTA instrument over a temperature range of 30 °C to 800 °C with a rise of 10 °C per minute under a nitrogen atmosphere.

#### 2.3 Synthesis of CoFe<sub>2</sub>O<sub>4</sub>

The desired nanocomposite was synthesized by a microwave-assisted approach. In a typical synthesis, ferric nitrate (3.85g, 16mmol) and cobalt nitrate (5.82g, 32 mmol) were dissolved in a minimum amount of deionized water followed by the addition of 3 g of urea and the resulting mixture was allowed to stir for 20-30 min. Further, 50 ml of ethylene glycol and 30 ml water were added and the mixture was refluxed in a Milestone microwave reactor at 110 °C with an energy input of 1000 W for 4 h. After completion of the reaction, the solid was separated by centrifugation and washed with distilled water, followed by ethanol. Finally, the obtained material was dried and calcined at 300 °C for 4 h.

### 2.4 Synthesis of the GO-CoFe<sub>2</sub>O<sub>4</sub>photocatalyst

The graphene oxide was prepared by modified Hummers method [36]. The nanocomposite was synthesized by placing 2g of graphene oxide and 0.2 g of  $CoFe_2O_4$  in a round bottom flask with a mixture containing 80 ml water and ethylene glycol (in a 1:1 volume ratio). The reaction mixture was refluxed by microwave irradiation in a microwave reactor at 160 °C by an energy input of 900 watts for 5 h. After completion of the reaction, the mixture was cooled and the nanocomposite was filtered off, collected and washed with deionized water. Finally, the material was dried at 80 °C in

a vacuum oven for 12 hrs. Similarly, other GO-CoFe<sub>2</sub>O<sub>4</sub> samples were prepared by varying the loading of CoFe<sub>2</sub>O<sub>4</sub> with GO

#### 2.5 Photocatalytic oxidative coupling of benzylamines

Benzylamine (90.5 mmol, 0.054g), 3 ml of acetonitrile and 50 mg of photocatalyst were charged into a 50 ml round bottom flask. The reaction mixture was allowed to stir at room temperature in the presence a source of visible light under 1 atm pressure of molecular oxygen for 12 h. A 20watt LED lamp (Model No. HP-FL-20W-F-Hope LED Opto-Electric Co., Ltd (Shenzhen, China,  $\lambda \ge 420$  nm) was used for the photocatalytic experiments. Intensity of the light at vessel was found to be 75 W/m<sup>2</sup> as measured by intensity meter. The formation of product and completion of the reaction was confirmed by thin layer chromatography (TLC). At the end of the reaction, the photocatalyst was separated out by an external magnet. The photocatalyst did not show any leaching as confirmed by ICP-AES analysis of the recovered material. The product was isolated and purified by column chromatography over silica gel. The pure products were confirmed by GC-MS and <sup>1</sup>H NMR analysis.

#### 3. Results & Discussion

### 3.1 Synthesis and characterization of the photocatalyst

GO-CoFe<sub>2</sub>O<sub>4</sub> nanocomposite was synthesized by the microwave heating of a mixture of GO and CoFe<sub>2</sub>O<sub>4</sub> as illustrated in Scheme 2.



Scheme 2: Preparation of GO-CoFe<sub>2</sub>O<sub>4</sub>

The changes in the chemical functionalities during the synthesis of nanocomposite were determined by FT-IR spectroscopy. The FT-IR spectra of GO, CoFe<sub>2</sub>O<sub>4</sub> and GO-CoFe<sub>2</sub>O<sub>4</sub> are displayed in figure 1. The FT-IR spectrum of GO reveals characteristic vibrational bands at 1072 cm<sup>-1</sup>, 1614 cm<sup>-1</sup>, 1733 cm<sup>-1</sup>, 2911 cm<sup>-1</sup> and 3397 cm<sup>-1</sup> corresponding to the C-O stretching, OH bending, C=O stretching (carboxyl or carbonyl), C-H stretching and OH stretching modes of vibration respectively. The emergence of an intense peak between 550 cm<sup>-1</sup> to 600 cm<sup>-1</sup> in the FT-IR spectrum of CoFe<sub>2</sub>O<sub>4</sub> attributed to the Co-O and Fe-O stretching vibration modes of metal-oxygen bonds. Absorption bands appeared at 1618 cm<sup>-1</sup> and 3411 cm<sup>-1</sup> are ascribed to the –OH of the absorbed water moieties on the surface of the nanocomposite. In the spectrum of GO-CoFe<sub>2</sub>O<sub>4</sub> at 2927 cm<sup>-1</sup>(C-H stretching), 1711 cm<sup>-1</sup> (stretching vibration of C=O) and 555 cm<sup>-1</sup> (Co-O, Fe-O) suggested the interaction of GO with cobalt ferrite. A slight shifting in the frequency values of the final nanocomposite compared to characteristic bands of the pure samples such as GO and CoFe<sub>2</sub>O<sub>4</sub> [29] indicated the changes in the chemical behavior during the microwave irradiation.



Figure 1. FT-IR spectra of samples (a) GO, (b) CoFe<sub>2</sub>O<sub>4</sub> and (c) GO- CoFe<sub>2</sub>O<sub>4</sub>

The crystalline phases of GO, CoFe<sub>2</sub>O<sub>4</sub> and GO-CoFe<sub>2</sub>O<sub>4</sub> were examined by powder X-ray diffraction (XRD) pattern as depicted in Figure 2. A characteristic peak at 20 value of 11.16 corresponding to the 001 crystal plane of GO. Peak position in the XRD pattern of CoFe<sub>2</sub>O<sub>4</sub> at 20 values of 18.10, 30.5, 35.22, 43.08, 50.02, 57.4 and 62.9 are assigned to (111), (220), (311), (400), (422), (511) and (440) crystal planes respectively with reference to JCPDs card no. 22-1086 [37]. The absence of characteristic peak of GO in the XRD pattern of GO-CoFe<sub>2</sub>O<sub>4</sub> suggested the crystalline growth of cobalt ferrite between the stacked layers of GO resulted in the destruction of systematic stacking of GO sheets [37]. Moreover, the emergence of a new broad peak at 20 value

of 25.4° related to the 002 plane suggested the reduction of GO to rGO during the synthesis under microwave irradiation [38-39].



Figure 2. XRD patterns of samples a) GO, b) CoFe<sub>2</sub>O<sub>4</sub> and c) GO-CoFe<sub>2</sub>O<sub>4</sub>

UV-Vis spectra of the CoFe<sub>2</sub>O<sub>4</sub> and GO-CoFe<sub>2</sub>O<sub>4</sub> are illustrated in Figure 3. The UV-Vis absorption spectra of both CoFe<sub>2</sub>O<sub>4</sub> and GO-CoFe<sub>2</sub>O<sub>4</sub> exhibited absorption band from UV to visible region. It can be seen clearly that neat CoFe<sub>2</sub>O<sub>4</sub> exhibits the absorption in a broad range

from 200 nm to 400 nm. However, after the incorporation of GO into the CoFe<sub>2</sub>O<sub>4</sub>, the nancomposite shows high absorbance in both near UV and visible light region credited to the  $\pi$ - $\pi^*$  and n- $\pi^*$  transitions. The increased intensity of absorption band at 220-280 nm region in GO-CoFe<sub>2</sub>O<sub>4</sub> might be due to the additional transition of aromatic C-C bonds of GO. This is a clear indication of the presence of extensive conjugated sp<sup>2</sup> carbon network in the final material. The less intense absorption band around 300-350nm was assigned to the n- $\pi^*$  transitions of C=O bonds present in the GO-CoFe<sub>2</sub>O<sub>4</sub> nanocomposite. Moreover, GO-CoFe<sub>2</sub>O<sub>4</sub> showed little humps at 400-550 nm regions and long absorption band in comparison to pure CoFe<sub>2</sub>O<sub>4</sub>, which indicated the higher visible light activity of the nanocomposite.



Figure 3.UV- Vis spectra of the samples.

The band gap energy of the  $CoFe_2O_4$  and  $GO-CoFe_2O_4$  were determined by tauc plots as depicted in figure 4. The value of band gap energy of ~2.4 eV was observed for  $CoFe_2O_4$ ; whereas 2.11 eV

was estimated for the GO-CoFe<sub>2</sub>O<sub>4</sub>. The lower band gap along with the higher absorption in visible region for GO-CoFe<sub>2</sub>O<sub>4</sub> confirmed the higher photocatalytic efficiency of the nanocomposite.



Figure 4. Tauc plot of the a) CoFe<sub>2</sub>O<sub>4</sub> and b) GO-CoFe<sub>2</sub>O<sub>4</sub>.

Elemental composition of the synthesized nanocomposite was studied by using X-ray photoelectron spectroscopy (Fig. 5) The complete survey scan of XPS analysis confirms the presence of desired elements  $C_{1s}$ ,  $O_{1s}$ ,  $Fe_{2p}$  and  $Co_{2p}$  as shown in Figure 5a. Four characteristic XPS peaks of carbon C1s at binding energy values of 284.26 eV, 285.17 eV, 286.32 eV and 288.66 eV are attributed to a sp<sup>2</sup>carbon atom, C-C, C-O, and C=O respectively (Fig. 5b). The  $O_{1s}$  exhibits three key peaks at binding energy values 527.92 eV (Co-O, Fe-O/C-O-C), 529.11 eV (C-OH) and 531.05 eV (C=O) as displayed in Figure 5c. The  $Fe_{2p}$  (Fig.5d) and  $Co_{2p}$  (Fig.5e) peaks are observed near to 711 eV and 782 eV respectively. The  $Fe_{2p}$  spin-orbit split peak observed at 709.12 eV (Fe  $2p_{3/2}$ ) and 723.0 eV(Fe  $2p_{1/2}$ ) with a difference of 13.22 eV while the spin-orbit split peaks of  $Co_{2p}$  are found at 781.30 eV(  $Co_{2p3/2}$ ) and 796.52 eV( $Co_{2p1/2}$ ) with separation energy of 15.2 eV. These values are in well agreement with the reported literature [40-41].



Figure 5. XPS of GO- CoFe<sub>2</sub>O<sub>4</sub>. Where a) survey scan, b) C1s, c) O1s, d) Fe 2p and e)Co 2p.

HR-TEM images of GO-CoFe<sub>2</sub>O<sub>4</sub> as shown in Figure 6 reveal spherical or oval shaped morphology and fine structure of the sample. Growth of nanomaterial with a uniform distribution

over the surface of graphene oxide layer can be seen clearly in the image at scale of 200 nm (Fig 6a) [32]. SAED pattern as shown in figure 6b further confirmed the formation of nanocomposite. Figure 6d provides the detailed view of crystalline fringes (0.259 nm) of interlayer spacing of  $CoFe_2O_4$  attributed to 311 crystal plane. The EDX elemental mapping composition of the nanocomposite is in good agreement with the synthesis of the final photocatalyst and showed the presence of all desired elements such as C, O, Co and Fe (Fig. 6e). The weight percentage of the elements in EDX was found to be carbon (89.1%), oxygen (8.2%), iron (1.6%) and cobalt (1.1%). The elemental mapping of GO-CoFe<sub>2</sub>O<sub>4</sub> showed a homogenous distribution of all elements throughout the nanocomposite at 500 nm scale, as represented in Figure 7.



**Figure 6**. HR –TEM images of GO-CoFe<sub>2</sub>O<sub>4</sub> a) at 200nm scale, b) SAED pattern, c) at 5 nm scale, d) Interplanar d-spacing observed at 5 nm scale, e) EDX pattern.



**Figure 7**. Elemental mapping of the GO-CoFe<sub>2</sub>O<sub>4</sub>, where a) Carbon, b) Oxygen, c) Iron and d) Cobalt

In order to understand the surface morphology of the synthesized fresh photocatalyst and recovered one scanning electron microscopy (SEM) analysis was carried out. The SEM images of both versions of nanocomopsite as shown in figures 8a and 8b revealed that the morphology remained intact in the recovered photocatalyst even after the six cycles.



Figure 8. SEM images of GO-CoFe<sub>2</sub>O<sub>4</sub>(a fresh catalyst and (b recycled catalyst.

Disorder in the nanocomposite in terms of  $sp^2$  carbon material was characterized by Raman spectroscopy. In the Raman spectrum of GO as shown in figure 9, the two peaks in the range of 1100-1400cm<sup>-1</sup> and 1500-1700 cm<sup>-1</sup> are attributed to D and G band respectively. The Raman shifts near the range of 230 - 300 cm<sup>-1</sup>, 400-500 cm<sup>-1</sup> and 500-750 cm<sup>-1</sup> in GO-CoFe<sub>2</sub>O<sub>4</sub> are attributed to the E<sub>g</sub>, T<sub>2g</sub> and A<sub>1g</sub> shifts of CoFe<sub>2</sub>O<sub>4</sub> respectively [29]. The ratio of ID/IG indicates the presence of disordered carbon ratio in the graphene oxide. The ratio of disorder in GO-CoFe<sub>2</sub>O<sub>4</sub> was found to be 1.03 while in GO it was 0.9. This implies that the reaction of cobalt ferrite with graphene oxide increases the total amount of defected carbon as well as a decrement in  $sp^2$  carbon. Raman spectra showed a clear image of changes from GO to GO-CoFe<sub>2</sub>O<sub>4</sub> nanocomposites.



Figure 9. Raman spectra of the GO and GO-CoFe<sub>2</sub>O<sub>4</sub>

The specific surface properties such as BET surface area and total pore volume are examined by nitrogen adsorption-desorption isotherm. Both  $CoFe_2O_4$  and  $GO-CoFe_2O_4$  isotherms show type IV isotherm characteristic hysteresis loop and are represented in Figure 10 and 11 respectively. The type IV isotherm shows the mesoporous nature and multilayer adsorption capability of the material. The pore volume-pore diameter graph of the  $CoFe_2O_4$  (Inset in Fig. 10) shows the mesoporous (2 nm to 50 nm) nature of the material and the sharp peak indicates uniformity in the pore size. GO-CoFe<sub>2</sub>O<sub>4</sub> shows type IV isotherm and H4 hysteresis having internal voids and narrow slit-like pores. A broad peak in the pore volume-pore diameter graph of the GO-CoFe<sub>2</sub>O<sub>4</sub> (Inset in Fig.11) indicates the variable size of the pores in the nanocomposite. From CoFe<sub>2</sub>O<sub>4</sub> to GO-CoFe<sub>2</sub>O<sub>4</sub> the steepness of the isotherm decreased and the pore size of the material increased. The S<sub>BET</sub> and the total pore volume of the CoFe<sub>2</sub>O<sub>4</sub> are 134.18 m<sup>2</sup>/g and 2.60 cm<sup>3</sup>/g

while in GO-CoFe<sub>2</sub>O<sub>4</sub> the values are  $158.4 \text{ m}^2/\text{g}$  and  $1.75 \text{ cm}^3/\text{g}$  respectively. After the introduction of GO, a slight increment in the surface area and a modest drop in total pore volume was observed.



Figure 10. Adsorption-desorption isotherm of CoFe<sub>2</sub>O<sub>4</sub>



Figure 11. Adsorption-desorption isotherm of GO-CoFe<sub>2</sub>O<sub>4</sub>

Thermal behaviour patterns of GO,  $CoFe_2O_4$  and  $GO-CoFe_2O_4$  were examined and represented in Figure 12. Graphene oxide showed an initial weight loss around at 100 °C due to

the evaporation of adsorbed water molecules and ethanol. Another weight loss in the range of 168 to 300 °C attirbuted to the decomposition of organic moieties (COOH, OH etc) presented on the surface of GO. The TG-DTA curve of CoFe<sub>2</sub>O<sub>4</sub> showed a weight loss near 100 °C due to evaporation of water molecules. In case of GO-CoFe<sub>2</sub>O<sub>4</sub> nanocomposites a major weight loss in the range of 345 to 546 °C was attributed to the decomposition of oxygen containing organic moieties of GO.



**Figure 12**. DT-TGA curves of the samples a), b) and c) are the weight % and (d, (e and (f are the derivative weight % of GO, CoFe<sub>2</sub>O<sub>4</sub> and GO-CoFe<sub>2</sub>O<sub>4</sub> respectively.

#### **3.2 Photocatalytic activity**

Aerobic oxidative coupling of benzylamine to corresponding imine was selected as a model example to evaluate the photo-catalytic performance of the synthesized photocatalysts under the visible light illumination (20 W white LED light) at room temperature and 1atm pressure of molecular oxygen using acetonitrile as solvent. The results of these optimization studies are summarized in Table 1. The reaction did not take place both in the absence of the photocatalyst as well as in dark without light irradiation (Table 1, entries 1-2). These results confirmed that the reaction was truly photocatalytic and essentially required a photocatalyst to proceed. Further, the use of pure CoFe<sub>2</sub>O<sub>4</sub> under described reaction conditions exhibited poor efficiency and afforded lower conversion in comparison to the final photocatalyst (Table 1, entry 3). In order to screen out the best designed photocatalyst, a series of photocatalysts prepared by varying the loading of cobalt ferrite on graphene oxide, for example 2GO-0.2CoFe2O4, 2GO-0.1CoFe2O4, 2GO-0.05CoFe2O4. The conversion of benzylamine to corresponding imine was found to be increased with the loading of cobalt ferrite in the nanocomposite (Table 1, entry 4-6). Therefore, among the synthesized samples <sub>2</sub>GO-<sub>0.2</sub>CoFe<sub>2</sub>O<sub>4</sub> provided the highest conversion of 97% with 99% selectivity of the desired imine. After establishing the superior photocatalytic activity of 2GO-0.2CoFe2O4 nanocomposite over other two materials, its concentration/ amount used was optimized and on the basis of collected experimental data, 50 mg of the photocatalyst was found to be optimum (Table1, entry 6-7). Subsequently, among the different organic solvents studied acetonitrile afforded maximum conversion and therefore considered as most favorable reaction media for this oxidative coupling of benzyl amine (Table 1, entries 8-9). Moreover, in terms of reaction period, reduction in reaction time from 12 h to 6 h affected the reaction adversely (Table 1, entry 10). Hence, the optimized

conditions for the reaction were framed as 50 mg of photocatalyst (2GO-0.2CoFe2O4), acetonitrile as a reaction media under visible light irradiation for 12 h.

Table 1. Optimization of reaction conditions for photocatalytic coupling of benzylamine<sup>a</sup>





Benzyl amine

N-benzylidenebenzylamine

Entry	Solvent	Catalyst	Reaction	Conv./Selec. <sup>b</sup>	TOF
			time, h	(%) <sup>b</sup>	( <b>h</b> -1)
1	Acetonitrile	-	12	0/0	_
$2^{c}$	Acetonitrile	2GO-0.2CoFe2O4	12	0/0	_
3	Acetonitrile	CoFe <sub>2</sub> O <sub>4</sub>	12	56/99	-
4	Acetonitrile	2GO-0.05CoFe2O4	12	34/99	2.8
5	Acetonitrile	2GO-0.1CoFe2O4	12	57/99	4.7
6	Acetonitrile	2GO-0.2CoFe2O4	12	97/99	8.1
7 <sup>d</sup>	Acetonitrile	2GO-0.2CoFe2O4	12	79 /99	6.5
8	Methanol	2GO-0.2CoFe2O4	12	91/99	7.5
9	Toluene	2GO-0.2CoFe2O4	12	82/99	6.8
10	Acetonitrile	2GO-0.2CoFe2O4	06	48/99	7.5

<sup>a</sup>Reaction conditions: 0.5 mmol of benzyl amine, 50 mg of catalyst (<sub>2</sub>GO-<sub>0.2</sub>CoFe<sub>2</sub>O<sub>4</sub>), 3ml of solvent, in presence of light for 12 hour at 1 atm pressure of O<sub>2</sub>, <sup>b</sup> Conversion and selectivity were determined by GC-MS analysis. <sup>c</sup>Experiment was conducted in the absence of light; <sup>d</sup>using 30 mg of the photocatalyst

After the optimization of reaction conditions, we extended the scope of the reaction for a variety of differently substituted benzylamines and the obtained data are tabulated in Table 2. The substrates having electron donating groups such as methoxy and methyl were found to be more reactive than the substrates with electron withdrawing groups (F, Cl, Br, etc).

Entry	Reactant	Product	Conv. <sup>[b]</sup> (%)	Select. <sup>[b]</sup> (%)
1	NH <sub>2</sub>		97	99
2	H <sub>3</sub> CO NH <sub>2</sub>	H <sub>3</sub> CO N OCH <sub>3</sub>	96	99
3	H <sub>3</sub> C NH <sub>2</sub>	H <sub>3</sub> C CH <sub>3</sub>	96	99
4	CI NH <sub>2</sub>	CI N CI	94	99
5	F NH <sub>2</sub>	F	94	99

**Table 2**.Photocatalytic coupling of differently substituted benzylamines<sup>[a]</sup>

<sup>a</sup>Reaction conditions: 0.5mmol of benzylamine, 3ml of acetonitrile, 50 mg of photocatalyst ( $_2$ GO- $_{0.2}$ CoFe $_2$ O<sub>4</sub>) under the visible light irradiation with an atmospheric pressure of O<sub>2</sub> for 12 h; <sup>b</sup>Conversion and selectivity were determined by GC-MS.

In addition, cross-coupling of benzylamine with aniline, substituted anilines and benzylamines was explored and the results of these experiments are summarized in Table 3. In cross-coupling reaction with aniline, the poor yield of the desired product was probably due to the self-coupling of benzylamine and lacking of alpha hydrogen atom in the aniline. In the case of different substrates of benzylamine the conversion was more efficient but the selectivity of the desired product reduced due to the self-coupling of the two benzylamine substrates.

Entry	Benzylamine Rr	Amine 2	Product	Conv. <sup>[b]</sup> (%)	Select. <sup>[b]</sup> (%)
1	NH <sub>2</sub>	NH <sub>2</sub>	N	89	95
2	NH <sub>2</sub>	CI NH <sub>2</sub>	CI N	77	95
3	NH <sub>2</sub>	Br NH <sub>2</sub>	Br	65	95
4	NH <sub>2</sub>	H <sub>3</sub> CO NH <sub>2</sub>	OCH3	96	90
5	NH <sub>2</sub>	H <sub>3</sub> C NH <sub>2</sub>	C CH3	95	90
6	NH <sub>2</sub>	CI NH <sub>2</sub>	C N C I	92	89

### Table 3. Cross-coupling of benzylamine with other amines<sup>[a]</sup>

<sup>[a]</sup>Reaction conditions: 0.5 mmol of reactant1, 1.2 mmol of reactant 2 (1 to 3 reaction), 0.7 mmol of reactant 2 (4 to 6 reaction), 3 ml of acetonitrile, 50 mg of catalyst ( $_2GO_{-0.2}CoFe_2O_4$ ) under the visible light irradiation with an atmospheric pressure of O<sub>2</sub> for 12 h; <sup>[b]</sup>Conversion and selectivity were determined by GC-MS analysis.

Further, the recyclability of the photocatalyst was evaluated by performing the oxidative coupling of benzylamine under optimized reaction conditions. The photocatalyst was isolated from the reaction mixture with the help of an external magnet and washed with ethanol followed by deionized water, dried and used further for next experiments with fresh reactant. The activity of the photocatalyst was observed almost similar in terms of conversion and selectivity for six recycle experiments as represented in Figure 13.



Figure 13. Recycling experiments of the reaction

The mechanism for the photocatalytic oxidative coupling of benzylamines with oxygen is well documented in the literature [11,23]. In analogy to the existing reports a plausible mechanism of the reaction is depicted in Scheme 3. Under the light irradiation, charge separation occurred on the surface of the cobalt ferrite and transfer of the excited electrons form valance band to conduction

band occurs. These electrons in the CB are captured by the molecular oxygen to generate the superoxide radicals ( $O_2^{-}$ ) that is the key component in this coupling reaction. Holes are transferred to amine to give the amine radical cation that forms an intermediate imine on reaction with superoxide radical ( $O_2^{-}$ ). Further, this imine is get activated by another hole and furnish the desired coupling product upon interaction with second amine molecule with formation of ammonia as a byproduct [42-43]. In case of GO supported CoFe<sub>2</sub>O<sub>4</sub>, owing to the presence of unsaturated sp<sup>2</sup> carbon framework in the GO/ or rGO, photogenerated electrons can flow on the surface with minimum resistance and therefore inhibits the recombination of the electron-hole pairs [44]. Because of the diminished recombination, the photogenerated charge carriers are readily available for the reaction in GO-CoFe<sub>2</sub>O<sub>4</sub> and therefore it provided higher photocatalytic efficiency as compared to the pure CoFe<sub>2</sub>O<sub>4</sub> that afforded very low yield of the desired product imine under identical experimental conditions. In addition, presence of graphene enhances the surface area of the photocatalyst that increases the adsorption of the substrate on the surface because of the interaction between the conjugated  $\pi$ -electron system of GO with the substrate [45].

In order to confirm the involvement of superoxide radical, we added superoxide scavenger (benzoquinoe, 2%) to the reaction mixture and continued the reaction under described conditions. The product yield was found to be decreased remarkably (20%) that confirmed the generation of superoxide radical during the photocatalytic coupling of amines under developed protocol. The generated hydrogen peroxide might have decomposed to oxygen in the presence of cobalt ferrite catalyst as reported in the literature [46].



Scheme 3: Plausible mechanism for the oxidative coupling of benzylamine using  $GO-CoFe_2O_4$  as photocatalyst

#### Conclusions

The present paper demonstrated the application of a magnetically separable graphene oxide–cobalt ferrite nanocomposite, readily synthesized by a novel, rapid and energy efficient microwave assisted approach as photocatalyst for the oxidative coupling of amines to imines using molecular oxygen as oxidant under mild conditions. The photocatalyst was characterized by a number of analytical tools including XRD, FT-IR, Raman etc to elucidate the crystallinity and loading of cobalt ferrite on GO. Surface topography and morphology of the GO-CoFe<sub>2</sub>O<sub>4</sub> was determined using FE- SEM and HR-TEM techniques. The photo catalytic experiments of self-coupling and cross-coupling of amines to imines showed good conversion and selectivity with GO-CoFe<sub>2</sub>O<sub>4</sub>. The photocatalyst could easily be separated by external magnetic effect and showed consistent activity for several recycles. The developed protocol represented an efficient photocatalyst and can be used for the selective one-pot synthesis of imines under mild reaction conditions.

#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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