Greener Route for Synthesis of aryl and alkyl-14H-dibenzo [a,j] xanthenes using Graphene Oxide-Copper Ferrite Nanocomposite as a Recyclable Heterogeneous Catalyst

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A facile, efficient and environmentally-friendly protocol for the synthesis of xanthenes by graphene oxide based nanocomposite (GO-CuFe2O4) has been developed by one-pot condensation route. The nanocomposite was designed by decorating copper ferrite nanoparticles on graphene oxide (GO) surface via a solution combustion route without the use of template. The as-synthesized GO-CuFe2O4 composite was comprehensively characterized by XRD, FTIR, Raman, SEM, EDX, HRTEM with EDS mapping, XPS, N2 adsorption-desorption and ICP-OES techniques. This nanocomposite was then used in an operationally simple, cost effective, efficient and environmentally benign synthesis of 14H-dibenzo xanthene under solvent free condition. The present approach offers several advantages such as short reaction times, high yields, easy purification, a cleaner reaction, ease of recovery and reusability of the catalyst by a magnetic field. Based upon various controlled reaction results, a possible mechanism for xanthene synthesis over GO-CuFe2O4 catalyst was proposed. The superior catalytic activity of the GO-CuFe2O4 nanocomposite can be attributed to the synergistic interaction between GO and CuFe2O4 nanoparticles, high surface area and presence of small sized CuFe2O4 NPs. This versatile GO-CuFe2O4 nanocomposite synthesized via combustion method holds great promise for applications in wide range of industrially important catalytic reactions.

Xanthenes are important heterocycles with a variety of applications in the field of pharmaceutical chemistry1. Notable pharmaceutical properties of xanthene derivatives are antibacterial2, analgesic, antiviral3, anti-inflammatory4, antimalarial5 and anticancer6. These compounds have found wide use in dyes,7 laser technologies and as pH-sensitive fluorescent materials8. Because of their usefulness, research on the catalytic preparation of xanthenes has attracted great attention. Mainly, condensation of aldehyde and 2-naphthol is the usual procedure for library synthesis of xanthenes, and its structural variants. A wide variety of catalysts have been reported in literatures for the synthesis of xanthenes such as pTSA9, sulfamic acid10, molecular iodine11, tungsten heteropoly acid, silica sulphuric acid12, NaHSO4-SiO213, TiO2-SO414, amberlyst-1515, wet cyanuric chloride16, K2CoW12O40.3H2O, acrylic acidic ionic liquids17, cellulose-sulphuric acid18, boric acid19 and Yb(OTf)320. However, these catalysts suffer from one or more disadvantages, such as long reaction times, unsatisfactory yields, harsh reaction conditions, time taking work-ups, high cost, toxic solvent and difficulty in separation, justifying considerable scope for development of a noble catalyst for the synthesis of xanthenes via facile, energy efficient, easy separable and environmentally benign process.

Nanocatalysis, involving nanoparticles as catalyst has shown tremendous applications for a variety of organic transformations. Upto now, many investigations have been done on nanocatalysis, but there still remains the challenge of recovery of nanocatalyst from the reaction mixture. For this reason, magnetic nanoparticles have recently emerged as a useful group of nanocatalyst. The separation of magnetic nanoparticles is found to be simple and...
economical which diminishes the loss of catalytic activity, resulting in enhanced reusability. In addition, they exhibit high catalytic activity due to their large surface area and have relatively low preparation costs and toxicity. All these properties make them desirable and promising catalysts for industrial applications.

Among various magnetic nanoparticles, the copper ferrite, CuFe2O4 with a spinel structure, has been widely used in sensors, electronics and catalysis owing to its unique advantages such as environmental compatibility, moisture insensitive, high dispersion, high reactivity, low cost and easy separation by an external magnet. In catalysis, they are found to be a promising material for a variety of catalytic applications. For example, Amini et al. investigated the low temperature CO oxidation over mesoporous CuFe2O4 nanopowders synthesized by a novel sol–gel method. Parella et al. explored the catalytic application of CuFe2O4 nanoparticles for the Friedel–Crafts acylation. Feng et al. investigated the catalytic activity of CuFe2O4 nanoparticles for the reduction of 4-nitrophenol to 4-aminophenol with an excess amount of NaBH4. To further improve the application efficiency of nanoparticles, various strategies have been employed over the years. One of the effective strategies is depositing nanoparticles on various carbon supports. These carbon hybrids are found to be highly active and selective catalysts as the result of the synergistic combination of both nanoparticle and carbon supports.

Graphene oxide, a two-dimensional sheet of sp2 hybridized carbon has received increasing attention as it possesses similar properties to that of graphene. Because of its high surface area, mechanical and electrical properties and thermal stability it has been used as a significant supporting material and has been found as a promising material for fuel cells, sensors, solar cells, lithium batteries and organic synthesis. In the catalysis front, owing to its large specific surface area, high chemical stability, good adsorption capacity, highly active and highly selective GO-based nanocatalysts have been designed by decorating GO surface with nanoparticles. The combination of the NPs and the graphene oxide sheets affords the composite better performance due to the synergistic interaction between the NPs and the graphene oxide sheets. These GO-based nanocatalyst mimic both homogeneous (high surface area and easily accessible) as well as heterogeneous (stable and easy to handle) catalyst systems. In addition to this, the presence of polar oxygen-containing functional groups, such as hydroxyl, epoxy, and carboxyl groups around GO prevents metal oxide nanoparticles from aggregation and leaching. Various metal oxides nanoparticles such as Fe3O4, CoFe2O4, ZnFe2O4, TiO2, SnO2, SnO, ZnO and SnO2 were loaded on graphene oxide (GO) sheets, generating highly active and selective catalysts. Recently, our group designed graphene oxide–SnO2 nanocomposite (GO–SnO2) and used it as an efficient catalyst for the β-enaminones synthesis. Considering the benefits associated with both CuFe2O4 nanoparticles and GO, the combination of GO with CuFe2O4 would form a potential catalytic material and more recently, few studies have corroborated this fact. However, to our best knowledge, there has been no report yet on the use of graphene oxide-copper ferrite (GO-CuFe2O4) magnetic nanocomposite as a catalyst for biologically important xanthene derivatives syntheses.

The methods to synthesize GO-based nanocomposites are diverse, such as hydrothermal, solvothermal, and co-precipitation method. However above mentioned methods had some disadvantages such as time consuming, expensive, pollution causing and low yields. One method which has attracted a great deal of research in generating various metal oxide nanostructures is solution combustion synthesis (SCS). SCS is a time and energy-saving method as compared with other routes, especially for the preparation of complex oxides which can be easily adapted for scale-up applications. This method is economical both in terms of energy consumption and time. It is a simple, safe and rapid fabrication process for easily affordable porous materials due to their inherent characteristics. Many oxide nanostructures such as TiO2, ZnO, SnO2, BiVO4, ZrO2, Co3O4 and WO3 have been synthesised via SCS route. Various nanocomposites including ZnO–Fe2O3, TiO2–SnO2, TiO2–ZrO2 and TiO2–Al2O3 were also prepared by this method. Therefore, we envisioned that this quick, straightforward process can be used to synthesise highly porous GO-CuFe2O4 nanocomposite that can enhance the catalytic activity of a reaction by providing more adsorption and reaction sites during the reaction.

Herein, we report the successful synthesis of highly porous GO-CuFe2O4 nanocomposite through a solution combustion route and subsequently, for the first time the use of this material as a promising heterogeneous catalyst for xanthene synthesis have been demonstrated. The xanthene synthesis was obtained via two-component coupling of aromatic aldehyde and 2-naphthol in the presence of GO-CuFe2O4 nanocatalyst and the same protocol was applied to other xanthene derivatives syntheses. All the reactions proceeded in a shorter period of time compared to traditional catalysts. Moreover, the catalyst can be recycled and reused up to five cycles with minimal loss in activity in a solvent free system. Our methodology may provide insight into the design of nanocatalysts using combustion route for its use in many more industrially important catalytic applications.

Results and Discussion

Structure and morphology characterization. Compared to the techniques employed for the preparation of nanocomposites such as solvothermal, hydrothermal and wet impregnation method, SCS is both energy and time efficient. Moreover, it can easily afford porous materials during the combustion process which is advantageous for adsorption of organic reactants on the nanocatalyst. During the synthesis, hydrated nitrates as metal precursors due to the efficient oxidizing power of NO3− groups and its lower decomposition temperature and good solubility in water. Urea (CO(NH2)2) was used as a common fuel due to its low cost, good availability, high exothermicity, as well as their high coordination ability toward nitrates which help in controlling the size of nanoparticles. The samples obtained after the SCS synthesis was then characterized by various characterization techniques as outlined below.

FTIR spectra were recorded to study the effective incorporation of CuFe2O4 nanoparticles on GO matrix and presence of different functional groups present in the nanocomposite material. Figure 1(i) displays FTIR spectra of the GO-CuFe2O4 nanocomposite. As shown in Fig. 1(i), the broad absorption band at 3400–3500 cm−1 in the FT-IR spectra of GO sample is associated with the stretching vibration of the –OH group. The peak at 1728 cm−1 corresponds to the stretching of the –C=O and –COOH groups on GO sheets. The peak at 1616 cm−1 (aromatic C=C) can be ascribed to the skeletal vibrations of un-oxidized graphene domains. The C–O bond is
associated with the band at 1047 cm\(^{-1}\). These observations are in good agreement with previous literatures\(^{60,61}\). In the FTIR spectrum of GO-CuFe\(_2\)O\(_4\), the presence of two absorption bands at 562 cm\(^{-1}\) and 480 cm\(^{-1}\) can be noticed. The absorption band at around 529 cm\(^{-1}\) belongs to the stretching vibration of Cu\(^{2+}\) in octahedral site and the absorption band at around 436 cm\(^{-1}\) belongs to the stretching vibration of Fe\(^{3+}\) in the tetrahedral site of CuFe\(_2\)O\(_4\) nanoparticles, respectively\(^{62}\). It is interesting to find that after the composite synthesis, the peaks at 1047 cm\(^{-1}\) are still present in the spectrum which suggests the minor reduction of functional groups after the composite synthesis.

XRD is a powerful technique to analyze the phase purity and crystal structure of the material. Figure 1(ii) displays the XRD spectrum of GO and GO-CuFe\(_2\)O\(_4\) composites, wherein all the peaks can be assigned to cubic CuFe\(_2\)O\(_4\) spinel structure. It is interesting to find that no impurity peaks of copper oxides (Cu\(_2\)O or CuO) were observed in the spectrum\(^{27,41,63,64}\). A series of characteristic diffraction peaks observed at 30.5, 35.2, 57.0, 62.8 and 74.1 correspond to (220), (311), (511), (440) and (533) crystal planes of CuFe\(_2\)O\(_4\), respectively (JCPDS card no: 85-1326). Moreover, no typical diffraction peak of GO (001) or RGO (002) was observed in the XRD spectrum suggesting that the GO in the GO-CuFe\(_2\)O\(_4\) composite was fully exfoliated due to the crystal growth of CuFe\(_2\)O\(_4\) nanoparticles between the interlayer of GO sheets, which results in the low diffraction intensity of GO\(^{41}\). The presence of broad peaks suggests the formation of smaller nanoparticles and particle size was found to be around 10 nm calculated using Debye-Scherrer formula\(^{65-67}\). All the above results demonstrate that during the composite synthesis GO sheets help in the controlled synthesis and the stabilization of the NPs.

To further confirm the effective reduction of GO during the composite synthesis and possible electronic interaction between GO and CuFe\(_2\)O\(_4\) NPs, Raman measurements were carried out and are shown in Fig. 2(a). Similar to GO, GO-CuFe\(_2\)O\(_4\) has two prominent D and G bands at 1354 and 1606 cm\(^{-1}\), respectively. A small shifting of the bands in comparison to that of GO suggest the increase in disorderness on the GO surface. It is well known

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**Figure 1.** (i) FTIR spectra of GO and GO-CuFe\(_2\)O\(_4\) nanocomposite and (ii) XRD powdered spectra of GO and GO-CuFe\(_2\)O\(_4\) nanocomposite.

**Figure 2.** (a) Raman spectra of GO and GO-CuFe\(_2\)O\(_4\) nanocomposite, and (b) Hysteresis loops of pure CuFe\(_2\)O\(_4\) and GO-CuFe\(_2\)O\(_4\). The inset is the magnetic separation property of GO-CuFe\(_2\)O\(_4\) nanocomposite.
that the D band arises due to the defects in the graphene sheets whereas the G band arises due to the E_{2g} mode arising due to the sp^{2} hybridised carbon domains. The D/G band intensity ratio (I_{D}/I_{G} = 0.97) of GO-CuFe_{2}O_{4} was found to be larger than that of GO (I_{D}/I_{G} = 0.86). This suggests the possible electronic interaction between the GO and CuFe_{2}O_{4} NPs which results in the reestablishment of conjugated graphene oxide network (sp^{2}) after loading of CuFe_{2}O_{4} nanoparticles.

In order to check the magnetic properties of the as-obtained pure CuFe_{2}O_{4} and GO-CuFe_{2}O_{4} nanocomposite, magnetic measurement was carried out by VSM technique at room temperature and the results are shown in Fig. 2(b). The magnetic hysteresis loops of CuFe_{2}O_{4} and GO-CuFe_{2}O_{4} are an S-like curve that confirms the strong magnetic response to a varying magnetic field. The specific saturation magnetization (M_{s}) was found to be 13.0 emu/g for CuFe_{2}O_{4} and 8.1 emu/g for GO–CuFe_{2}O_{4} composite revealing the superparamagnetic behavior of both the samples. It should be pointed out that the saturation magnetization (M_{s}) values decreased after the loading of GO. The values of coercivity and remanence are summarized in Table 1. When an external magnetic field was applied for 20 s, rapid aggregation of the catalysts can be observed from their homogeneous dispersion (as shown in the inset of Fig. 2b). This observation suggests that the GO-CuFe_{2}O_{4} nanocatalyst can be easily separated from the solution phase using an external magnet, which is important in practical applications.

A non-monochromatic Mg Kα (hv = 1253.6 eV) X-ray source and PHOIBOS 150 electron energy analyzer from SPECS GmbH, Germany was used to acquiring X-ray photoelectron spectroscopy (XPS) measurements with the base pressure below 1 × 10^{-9} mbar. We have investigated the chemical composition and electronic structure of the GO-CuFe_{2}O_{4} nanocomposite. The presence of the core-level peaks in XPS survey spectra, as shown in Fig. 3(a,b), indicates the existence of Fe, Cu, O, and C elements in CuFe_{2}O_{4} and GO samples. In Fig. 4(a,b), we show the C 1s XPS spectrum of GO and GO-CuFe_{2}O_{4} nanocomposite samples. For GO, the main peak positioned at around 284.5 eV, is assigned to non-oxygenated ring carbon molecules, while alternate peaks at 286.7, 287.8 and 289.1 eV are assigned to the oxygen-containing groups (C–OH), (C=O), and (O=C–OH), respectively (Fig. 4a).

The C 1 s core-level spectrum of GO-CuFe_{2}O_{4} sample demonstrates that there is no significant change in intensity of the oxygenated functionalities in comparison to that of GO (Fig. 4b). This suggests the minor reduction of functional groups during the nanocomposite synthesis which is essential for the anchoring of metal nanoparticles on GO surface. In Fig. 4(c,d) we show the core-level spectra of Fe 2p and Cu 2p, respectively. The Fe 2p core-level spectrum shows two strong peaks at 710 and 722.8 eV, which are associated with Fe 2p_{1/2} and Fe 2p_{3/2} spin-orbit splitting, respectively. These are compared well with the Fe^{3+} octahedral species and the Fe^{3+} tetrahedral species. We also observed peaks at about 3 eV below the respective Fe 2p_{1/2} (Fe 2p_{3/2}) core-level peaks most probably due to FeO. Additionally, the satellite structure between the two peaks at 718 eV was the fingerprint of the electronic structure of Fe^{3+}. Figure 4d shows the Cu 2p core-level spectrum, which appears at 932.7 eV and is in accordance with Cu^{2+} states as reported in literatures. A satellite peak is observed at 940.8 eV, which can be attributed to the formation of CuO. Overall, the XPS spectra of Cu 2p and Fe 2p show that Cu is in the +2 and Fe is in the +3 oxidation state in the nanocomposite, which is in good agreement with literatures on CuFe_{2}O_{4} particles. These results indicate successful incorporation of CuFe_{2}O_{4} nanoparticles (NPs) on graphene oxide sheets.

| Samples         | M_{s} (emu g^{-1}) | H_{c} (Oe) | M_{r} (emu g^{-1}) |
|-----------------|---------------------|------------|--------------------|
| CuFe_{2}O_{4}   | 13.0                | 824        | 16.21              |
| GO-CuFe_{2}O_{4}| 8.1                 | 1246       | 8.46               |

Table 1. Magnetic properties of CuFe_{2}O_{4} and GO-CuFe_{2}O_{4} nanocomposite.
The structural composition of GO and GO-CuFe$_2$O$_4$ was then ascertained by FESEM which are presented in Fig. 5. It is found from Fig. 5a that the GO exhibits thin sheet structure with wrinkled or folded morphology with a few stacked layers. Furthermore, the GO nanosheets appear as an isolated lamellar structure which is convenient for magnetic CuFe$_2$O$_4$ particle to anchor on its surface. Unlike graphene, GO sheets are expected to be "thicker" due to the presence of carbonyl, carboxyl, hydroxyl and epoxy groups above and below the original graphene planes. Figure 5b,c shows the morphology of GO-CuFe$_2$O$_4$ nanocomposite. The crumpled and layered structure of GO can be easily seen in the FESEM images (5b-c). Spherical CuFe$_2$O$_4$ nanoparticles of larger size (~121 ± 2 nm) are found to be homogeneously distributed on the GO surface indicating the agglomeration of synthesized nanoparticles.

Furthermore, the energy dispersive X-ray (EDX) analyses were recorded and are shown in the Fig. 5d. Elements such as C, O, Cu and Fe can be detected in the sample of GO-CuFe$_2$O$_4$. From EDX analysis it was confirmed that SCS could be an excellent and efficient route for the synthesis of graphene oxide based spinel nanocomposite. The EDX analysis showed that the distribution of the elements in the product was Cu = 14.28%, Fe = 28.95% and O = 56.77% (Table 2), thereby confirming the iron/copper ratio as 2.02 which is very much close to the atomic ratio in the formula CuFe$_2$O$_4$. Later on, TEM and HRTEM with EDS mapping and scan were carried out. TEM images further demonstrate the layer structure of GO in the nanocomposite. From (Fig. 6a) TEM image, it can be seen that several individual CuFe$_2$O$_4$ particles seems to be agglomerated to form a bigger particle (size of 110 ± 2 nm) which sizes are found to be similar (~121 ± 2 nm) nm) to that obtained from FESEM images. The size of the individual CuFe$_2$O$_4$ nanoparticles is of 10 ± 2 nm which can be clearly seen from Fig. 6b. This agglomeration and interconnection of individual CuFe$_2$O$_4$ nanoparticles can be attributed to the powerful inherent magnetic interaction of magnetic particles.

Moreover, the NPs were not observed outside the GO sheets indicating very good interactions between NPs and GO sheets. This homogeneous distribution of the CuFe$_2$O$_4$ NPs can possibly be one factor for the enhanced catalytic activity as described later. The crystalline nature of the composite was further confirmed by SAED analysis which depicts a ring-like structure (Fig. 6f). The (220), (311), (400), (511) and (440) rings are indexed to the tetragonal CuFe$_2$O$_4$. These patterns indicated that the nanoparticles are polycrystalline. HRTEM analysis (Fig. 6d) demonstrates the crystalline structure of CuFe$_2$O$_4$ nanoparticles. The HRTEM image of the composite shown in Fig. 6d can be resolved into lattice fringe of 0.25 nm which can be indexed to (311) plane of spinel CuFe$_2$O$_4$. Later on, elemental mapping was carried to determine the elemental distribution of the individual components on the surface of CuFe$_2$O$_4$ nanoparticles, and the results are displayed in Fig. 7a. Energy-dispersive X-ray spectrometry (EDS) mapping analysis shows that the Cu, Fe and O elements are uniformly distributed in the CuFe$_2$O$_4$ nanoparticles, indicating the formation of spinel nanoparticles without phase segregation, as shown in Fig. 7 (red, Cu).
(green, Fe) and (blue, O). No traces of other impurities were seen in the spectra, suggesting that the synthesized composite are pure. The line scan along the direction derived in Fig. 7b demonstrated that all the elements are mixed well in the NPs. This further shows the high compositional uniformity of the GO-CuFe₂O₄ composite.

The surface area of the nanocomposite play an important role in the enhancement of catalytic activity by providing more adsorption and reaction sites during the reaction. To find the possible impact of SCS method on surface area and porosity, N₂ adsorption-desorption isotherm of CuFe₂O₄ and GO–CuFe₂O₄ composite were carried out and are shown in Fig. 8a. The BET surface area of CuFe₂O₄ and GO–CuFe₂O₄ nanocomposite exhibit type IV isotherm based on the IUPAC classification. The composite had a higher specific surface area (90 m²·g⁻¹) than that of CuFe₂O₄ (22 m²·g⁻¹). The surface area is found to be higher than other reported system synthesized by solvothermal method (35 m²·g⁻¹). The average pore diameters in GO–CuFe₂O₄ composite were found to be 12 nm (Fig. 8b). This observed increase in the surface area could be one of the factors responsible for the enhanced catalytic activity of the GO–CuFe₂O₄ composite discussed later in detail.

TGA analysis is a useful analytical tool to study thermal stability of materials and to determine the composite composition. Therefore, TGA measurements of GO and GO-CuFe₂O₄ composites were measured in air atmosphere and are shown in Fig. 9. The GO has two weight losses of 41.4% and 59.2% at around 200 °C and 520 °C, respectively, which can be assigned to the degradation of GO and oxidation of carbon, respectively. In comparison, GO-CuFe₂O₄ shows a total mass loss of 33.2% when the temperature reaches 800 °C illustrating a much higher thermal stability than GO. According to the weight losses of GO-CuFe₂O₄, the amount of CuFe₂O₄ in the GO-CuFe₂O₄ is estimated to be about 33.5 wt %. Later on, the actual elemental composition and percentage

| Element | Weight % | Atomic % | Atomic ratio |
|---------|----------|-----------|--------------|
| O       | 56.77%   | 82.6      |              |
| Fe      | 28.95%   | 11.8      | 2.02         |
| Cu      | 14.28%   | 5.6       | 1            |

Table 2. EDX compositions of GO-CuFe₂O₄ nanocomposite.
Iodine loading for GO-CuFe$_2$O$_4$ nanocomposite were further analysed by ICP-OES study. ICP analysis of 10 mg sample showed 1.96, 3.47 mg of Cu and Fe elements (i.e. 19.6% and 34.7%), respectively which means 7.43 mg of CuFe$_2$O$_4$ was loaded on graphene oxide sheets (i.e. 25.7% GO content). This 25.7% GO loading was in agreement with the TGA analysis as described above. ICP findings further confirmed that Cu and Fe are present in 1:2 molar ratios which are consistent with stoichiometry of CuFe$_2$O$_4$ structure.

Catalytic Reactions. Till now many acid catalyst had been reported and it was found that they are showing an efficient path for synthesis of xanthenes and its derivative. But they suffer a lot of disadvantage notably due to their prolonged reaction time, tedious work condition, use of VOCs and hazardous reaction conditions. To overcome this problem the use of ILs as solvents as well as promoter in the synthesis have been reported, but high cost of imidazole, thiazole and pyridine based IL and use of costly catalyst for the synthesis have been the essential drawbacks. To overcome this drawback use of graphene oxide based nanocomposite can be promising catalytic material. Towards this objective the reaction of 2-naphthol (2 mmol) with benzaldehyde (1 mmol) was chosen as a model reaction at 125 °C under solventless condition to assess the catalytic performance of GO-CuFe$_2$O$_4$ nanocatalyst. The effects of various reaction parameters on reaction of 2-naphthol with benzaldehyde were also investigated. The products were characterized by FT-IR, $^1$H-NMR and $^{13}$C-NMR spectroscopy.

To obtain the optimal reaction conditions, the effect of type of catalyst and catalyst dosage were initially investigated. Table 3 shows the yield of 14-phenyl-14H-dibenzo [$a$, $j$] xanthene (10a) in the presence and absence of catalyst. The reaction did not proceed in the absence of catalyst, but it increased in the presence of GO (20% yield) and CuFe$_2$O$_4$ nanoparticles (72% yield) (Table 3, entries 2 and 3). However, the combination of CuFe$_2$O$_4$ with appropriate amount of GO results in a dramatic enhancement of the catalytic activity of GO-CuFe$_2$O$_4$ (98% yield) (Table 3, entry 4). Since the support material takes an important role in catalysis, the impact of GO content on the catalytic activity of the GO-CuFe$_2$O$_4$ nanostructures was also investigated. The conversion rate of the reaction increased from 10 to 98% with increasing the loading amount of GO in GO-CuFe$_2$O$_4$ from 10–20% (Table 4, entries 1–5) and then decreased to 84% with further increase in loading.

This increase in catalytic activity of GO-CuFe$_2$O$_4$ composite can be attributed to the synergistic effect between the CuFe$_2$O$_4$ and the graphene oxide sheets. The presence of GO in the composite could enhance the adsorption of reactant molecules onto the catalytic sites of the GO-CuFe$_2$O$_4$ through π-π stacking and electrostatic interactions, leading to a high conversion rate. Additionally, the introduction of CuFe$_2$O$_4$ NPs into GO matrix results in its uniform dispersion on GO sheets and prevent them from agglomerating, thus increasing the number of active centers on CuFe$_2$O$_4$ nanoparticles. However, with further increase in GO amount beyond 20 wt% led to the lowering of active centres in the composite, which promoted less yield of the desired product. Therefore, 20 wt% was chosen as the required amount to carry out the reaction.

Figure 6. (a–e) TEM image of GO-CuFe$_2$O$_4$ nanocomposite at different magnification, (f) SAED image of GO-CuFe$_2$O$_4$ nanocomposite.
Later on, the effect of different dosages of GO-CuFe$_2$O$_4$ on xanthenes synthesis was examined (Table 5, Entry 1–7). The conversion rate increased from 60 to 98% with the rise of GO-CuFe$_2$O$_4$ doses from 5 to 20 mg. However, no significant difference was observed when the amount of catalyst was increased from 10 to 20 mg and yield lie above 90%. Theoretically, the amount of active sites on GO-CuFe$_2$O$_4$ rise with increasing dosage of catalyst, which increased the formation rate of xanthene, and would promote the reaction to reach a higher conversion rate.

**Figure 7.** EDS mapping of (a) GO-CuFe$_2$O$_4$ nanocomposite and (b) EDS line scan of GO-CuFe$_2$O$_4$ nanocomposite.

**Figure 8.** (a) Nitrogen adsorption/desorption isotherm and (b) pore size distribution of pure CuFe$_2$O$_4$ and GO-CuFe$_2$O$_4$ nanocomposite.
Figure 9. Thermogravimetric analysis (TGA) curves of GO, and GO-CuFe₂O₄ nanocomposite.

Table 3. Effect of different catalysts on the reaction of 2-naphthol and benzaldehyde. a. Reaction conditions: 2-naphthol (2 mmol) and benzaldehyde (1 mmol). b. Isolated yield.

| Entry | Catalyst | Catalyst loading | Yield (%) |
|-------|----------|------------------|-----------|
| 1.    | Graphite |                  | 10        |
| 2.    | GO       |                  | 20        |
| 3.    | CuFe₂O₄ nanoparticle | 72      |
| 4.    | GO/CuFe₂O₄ |                  | 98        |
| 5.    | CuO      |                  | 52        |
| 6.    | Fe₃O₄    |                  | 40        |
| 7.    | Cu(NO₃)₂  |                  | 12        |
| 8.    | Fe(NO₃)₃ |                  | 4         |
| 9.    | Without catalyst | traces     |
| 10.   | GO + CuFe₂O₄ physical mixing | 74   |
| 11.   | CuFe₂O₄ powder |                | 52        |

Table 4. Effect of different amount of catalyst loading on the reaction of 2-naphthol and benzaldehyde. a. Reaction conditions: 2-naphthol (2 mmol) and benzaldehyde (1 mmol). b. Isolated yield.

| Entry | Amount of catalyst (mg) | Time (min)/% yield |
|-------|-------------------------|--------------------|
| 1.    | Nil                     | 60/nil             |
| 2.    | 5                       | 30/60              |
| 3.    | 10                      | 20/90              |
| 4.    | 15                      | 15/92              |
| 5.    | 20                      | 10/98              |

Table 5. Synthesis of 14H-dibenzo[a. j] xanthene using different amount of catalysts. a. Reaction conditions: 2-naphthol (2 mmol) and benzaldehyde (1 mmol). b. Isolated yield.
Increasing of reaction temperature and the best result was obtained at 125 °C (Table 7, entries 5 and 10). It was found that the conversion rate gradually increased with solvent less conditions (Table 7, entries 6–10). In addition, the reaction was carried out in very shorter reaction time and in higher yield under solventless condition (Table 6, entry 9).

Later on, a wide range of aldehydes containing electron-withdrawing and electron donating groups were investigated. Aldehydes containing electron withdrawing groups such as chloro, bromo, and nitro underwent condensation in short reaction times with excellent isolated yields under both conditions (Fig. 10, entries 10h to 10 m). Aldehyde containing electron-donating groups such as methyl, methoxy and hydroxyl required longer reaction time (Fig. 10, entries 10c to 10g). Therefore, the presence of electron-withdrawing and electron donating groups on the phenyl ring had affected the rate of reaction which indicates that there is clear electronic role of substituent. Also, for meta and para substituted groups, the rate of the reaction was affected which explain steric effect of substituents.

The presence of acidic site on catalyst surface plays an important role in the overall catalytic activity of chemical reaction. In general, xanthene syntheses are carried out conventionally with the use of Lewis and Brönsted acid catalysts. In our GO-CuFe2O4 catalyst, the acidic site in both GO and CuFe2O4 can therefore control the overall catalytic cycle. Numerous oxygen containing functionalities (e.g., alcohols and carboxylates) generated during the synthesis of GO via exhaustive oxidation provide Brönsted acidic sites to GO. At the same time, CuFe2O4 has strong Lewis acid character which originates primarily from the presence of tripositive Fe3+ and dipositive Cu2+ ions. The Lewis acidity of Fe3+ can be attributed due to its higher electronegativity while for Cu2+ this is due to acquisition of a stable and completely filled d-subshell on receiving an electron. As our GO-CuFe2O4 system has two acidic sites (GO as Brönsted site and CuFe2O4 as Lewis acid site) one would expect that Lewis and Brönsted acid site can play a synergistic role in the overall catalytic reaction.

### Table 6. Effect of solvent on the condensation of 14H-dibenzo [a, j] xanthene using GO-CuFe2O4 nanocatalyst.

| Entry | Solvent | Catalyst | Catalyst loading | Temp (°C) | Yield (%) |
|-------|---------|----------|-----------------|----------|-----------|
| 1.    | H2O     | GO-CuFe2O4 | 20 wt %        | 125      | 92        |
| 2.    | Methanol | GO-CuFe2O4 | 20 wt %        | 125      | 88        |
| 3.    | Ethanol  | GO-CuFe2O4 | 20 wt %        | 125      | 84        |
| 4.    | DCM     | GO-CuFe2O4 | 20 wt %        | 125      | 42        |
| 5.    | Acetonitrile | GO-CuFe2O4 | 20 wt %    | 125      | 50        |
| 6.    | Toluene | GO-CuFe2O4 | 20 wt %        | 125      | 60        |
| 7.    | DMSO    | GO-CuFe2O4 | 20 wt %        | 125      | 68        |
| 8.    | Hexane  | GO-CuFe2O4 | 20 wt %        | 125      | 20        |
| 9.    | Solvent less | GO-CuFe2O4 | 20 wt %       | 125      | 98        |

*Reaction conditions: 2-naphthol (2 mmol) and benzaldehyde (1 mmol). Isolated yield.*
In order to confirm the importance of synergistic interaction between GO and CuFe₂O₄, we compared the activity of GO-CuFe₂O₄ to that of a physical mixture of GO and CuFe₂O₄. It can be found that the catalytic activity of the reaction system containing physical mixture of GO and CuFe₂O₄ (74% yield) is similar to those observed for pure CuFe₂O₄ nanoparticles (72% yield), which is lower than that of GO-CuFe₂O₄ (98% yield) as shown in Table 3. These results indicated the possibility of synergism between GO and CuFe₂O₄ acidic sites in the xanthene synthesis. Similar synergistic effects in the final catalytic activity were reported in the literatures. Moreover, in GO-CuFe₂O₄ nanocomposite which was obtained by chemical method, the CuFe₂O₄ nanoparticles would exhibit strong interactions with graphene oxide sheets, thereby, strongly influencing the catalytic behaviour of the nanocomposite. On the other hand, a simple physical mixing cannot create effective interfacial contacts between the CuFe₂O₄ nanoparticles and graphene oxide sheets. As a result, slower diffusion and decrease of mass transfer of reactant molecules take place which would be the cause for the decrease in yield in case of physically mixed GO and CuFe₂O₄ NP system.

In addition, the crucial role of CuFe₂O₄ nanoparticles as good catalyst was also demonstrated. As can be seen from Table 3, CuFe₂O₄ nanoparticles which provide smaller particle size and higher surface area showed higher activity to that of powder CuFe₂O₄ samples. Moreover, in comparison to Fe₃O₄ samples, pure CuFe₂O₄ nanoparticles showed higher activity, demonstrating the active role of Cu²⁺ in the catalytic reaction.

From all the results discussed above, a plausible mechanism for xanthene synthesis using GO-CuFe₂O₄ catalyst has been outlined in Fig. 11. The presence of strong acidic sites (both Lewis and Brønsted acid) in GO-CuFe₂O₄ nanocatalyst initially facilitates the efficient chemical adsorption of reactant molecules and favours the interaction of carbonyl group of aldehyde (IA) to the acidic sites. Because of this interaction, the carbonyl group of aldehyde was protonated/activated for nucleophilic attack in the subsequent steps and forms an intermediate form (IB). The Lewis acid site, Cu²⁺ and Fe³⁺ of CuFe₂O₄ nanoparticle that anchored onto the GO surface also co-ordinate with the intermediate by bonding with the –OH group, which further increases its electrophilic nature and helps in the stabilisation of intermediate. Finally, the intermediate (II) undergoes nucleophilic attack by a second molecule of β-naphthol to produce intermediate (III). The desired product is then formed by the cyclodehydration of intermediate (III) followed by dehydration. The coordination of CuFe₂O₄ NPs with the hydroxyl groups of intermediate help in increasing the electrophilicity of the intermediate and for subsequent nucleophilic attack of the β-naphthol molecule and in the cyclization process. It can be concluded that the Cu²⁺ and Fe³⁺ of CuFe₂O₄ nanoparticle help in activation and stabilization of substrate molecules during xanthenes synthesis.

**Reproducibility of catalyst.** Recovery of catalysts is important for the re-usage and application cost of a catalyst. Since GO-CuFe₂O₄ composite are found to be magnetic they can be easily removed from reaction solution with a magnet. Therefore, the catalytic stability of the GO-CuFe₂O₄ nanocomposite for the reaction of benzaldehyde with 2-naphthol (2 mmol) and benzaldehyde (1 mmol) was studied to give the desired product. After completion of the reaction (monitored by TLC), the catalyst was separated by applying an external magnetic field, washed with deionized water and acetone, and then vacuum dried at 60 °C for 3 h before being used in the subsequent recycling experiment. As shown in Table 7, GO-CuFe₂O₄ nanocomposite was still stable even after being recycled five times. The composite showed very high activity (yield 87 and 93%) even after 5th cycle without any accountable loss of activity. The recovered catalyst was

![Chemical structure](image)

**Table 7.** Effect of temperature on the condensation of 14 H-dibenzo [a. j] xanthene using GO-CuFe₂O₄ nanocatalyst. Reaction conditions: 2-naphthol (2 mmol) and benzaldehyde (1 mmol). Isolated yield.

| Entry | Solvent | Catalyst | Catalyst loading | Temp (°C) | Yield (%) |
|-------|---------|----------|-----------------|----------|-----------|
| 1.    | Water   | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | r.t      | 8         |
| 2.    | Water   | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | 35       | 30        |
| 3.    | Water   | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | 70       | 58        |
| 4.    | Water   | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | 100      | 78        |
| 5.    | Water   | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | r.t      | 10        |
| 6.    | Solventless | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | 125      | 92        |
| 7.    | Solventless | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | 70       | 75        |
| 8.    | Solventless | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | 100      | 88        |
| 9.    | Solventless | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ | 125      | 98        |
| 10.   | Solventless | GO-CuFe₂O₄ | 20 wt % GO/CuFe₂O₄ |          |           |
characterized by powder XRD which showed similar pattern with fresh sample indicating stability of spinel structure (see Fig. S1). Further, FESEM image (Fig. S1) showed similar morphology after 5th cycle. ICP analysis also showed very minute change in percentage loading (Cu: 1.91 and Fe: 3.34) as compared to original loading 1.96, 3.47 mg of Cu and Fe elements for copper ferrite NPs. This outstanding stability and recyclability of GO-CuFe2O4 nanocomposites can be ascribed to very good interaction between CuFe2O4 NPs and GO sheets which prevents agglomeration of the nanoparticles.

Comparison with other reported systems. Later on, to check the efficiency of our catalyst we have compared the activity of our catalyst with other reported catalysts. Table 8 shows the comparison of reported catalyst with our catalyst for the synthesis of xanthene under the same conditions. From Table 8, it can be seen that our catalyst exhibited higher yields in lesser time compared to the other reported system such as sulfamic acid10, [2-(sulfoxy)ethyl] sulfamic acid94, Fe(HSO4)3 95, functionalized mesoporous materials96, InCl3/P2O5 97, HY zeolite98 and K5CoW12O40.3H2O99. These results confirmed that our GO-CuFe2O4 catalyst is more effective and less time consuming for synthesis of xanthenes under solventless condition.

Methods
Graphite powder and CDCl3 were purchased from Sigma-Aldrich. Cu (NO3)2·3H2O, Fe (NO3)3·9H2O, H2O2 (30%), isopropanol, ethanol, NaNO3, H2SO4 (98%), HCl, KMnO4, urea and silica gel (100–200 mesh) were purchased from Hi-Media. All chemicals were used as received without further purification. 18 Milli-Ω water was used throughout the synthesis.
Figure 11. Plausible mechanism for the synthesis of xanthenes catalyzed by GO-CuFe₂O₄ nanocomposite.

Figure 12. Recyclability study of the catalyst for the one-pot synthesis of 14-(phenyl)-14H-dibenzo[a,j]xanthenes.
The combined ethyl acetate extracts were washed with water (2 × 10 mL) and dried over Na₂SO₄. The crude product thus obtained was washed with hexane and cold ethanol. The purified product was then obtained after column chromatography. All products were characterized by comparison of their physical constants and spectral data with those for authentic samples.

### Preparation of GO

GO was prepared from natural graphite powder through modified Hummers’ method[100–102]. In brief, 1 g of graphite was mixed to 25 ml to concentrated H₂SO₄ (98% w/w), followed by stirring at room temperature for 24 h. To the resulting pre-oxidized product, 100 mg of NaNO₃ was added to the mixture and stirred for 30 min. Subsequently, the mixture was kept below 5 °C using an ice bath and 3 g of KMnO₄ was slowly added to the mixture and the mixture was stirred for 2 h under the ice-water bath. After that about 250 ml distilled water and 20 ml H₂O₂ (30%) was added to dilute the solution at room temperature. After 10 min, a bright yellow solution was obtained and resulting solution was precipitated for 12 h, and the upper supernatant was collected and centrifuged. Successively, the GO powders were washed with 10% HCl and distilled water three times. The obtained GO was dispersed in distilled water to get a stable brown solution.

### Preparation of the GO-CuFe₂O₄ nanocatalyst

The GO–CuFe₂O₄ nanocomposite materials were synthesized by a solution combustion synthesis. Initially solution A was formed by adding 0.242 g (0.001 mol) sample of Cu(NO₃)₂.3H₂O and 0.808 g (0.002 mol) of Fe(NO₃)₃·9H₂O to 20 mL of water and kept for stirring for 30 min at room temperature to form a homogeneous solution. Later on, solution B was prepared by dispersing 0.150 g of GO in deionized water (1.48 mL) and ethanol (18 mL), followed by 30 min ultrasonic treatment. Then, solution B was added dropwise to solution A under vigorous stirring. After 1 h stirring, area was added as fuel to prepare the precursor solution. Finally, the precursor solution was heated on a hot plate at 100 °C to remove the solvent until a gel-like precursor was obtained. This precursor was introduced into a preheated muffle furnace at temperature of 400 °C in air and maintained for 10 min, during which combustion reaction took place. A black foam type GO–CuFe₂O₄ nanocomposite materials was obtained which was characterised by various analytical techniques and used as novel catalyst for xanthene synthesis (Fig. 13).

### General procedure for the synthesis of xanthenes under solventless condition

A mixture of the aldehyde (1 mmol), β-naphthol (2 mmol), and GO-CuFe₂O₄ (10 mg) nanocomposite was stirred at 125 °C for 10–15 min. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and solid obtained was dissolved in EtOAc (20 mL), followed by stirring the mixture for 10 min. Then, this was filtered to separate the catalyst. The catalyst was washed with ethyl acetate (2 × 10 mL). The combined ethyl acetate extracts were washed with water (2 × 10 mL) and dried over Na₂SO₄. The crude product thus obtained was washed with hexane and cold ethanol. The purified product was then obtained after column chromatography. All products were characterized by comparison of their physical constants and spectral data with those for authentic samples.

### General procedure for the synthesis of xanthenes in water media

A mixture of the aldehyde (1 mmol), β-naphthol (2 mmol), and GO-CuFe₂O₄ (10 mg) nanocomposite was stirred at 125 °C for 10–20 min in water as solvent. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and solid obtained was dissolved in EtOAc (20 mL), followed by stirring the mixture for 10 min. Then, this was filtered to separate the catalyst. The catalyst was washed with ethyl acetate (2 × 10 mL). The combined ethyl acetate extracts were washed with water (2 × 10 mL) and dried over Na₂SO₄. The crude product thus obtained was washed with hexane and cold ethanol. The purified product was then obtained after column chromatography. All products were characterized by comparison of their physical constants and spectral data with those for authentic samples.

### Catalyst Characterizations

The catalyst was analysed by X-ray diffraction study using PHILIPS PW 1830 X-ray diffractometer with CuKα source. The compositional information of the products was performed using EDX (JEOL JSM-6480 LV). Raman spectra were recorded using a BRUKER RFS 27 spectrometer with 1064 nm wavelength incident laser light. Field emission scanning electron microscopy (FESEM) of the sample was recorded by Nova Nano SEM/FEI. Transmission electron micrographs (TEM) of the sample were recorded using PHILIPS CM 200 equipment using carbon coated copper grids. The contents of Cu and Fe in the catalyst were analysed using ICP-OES made by Perkin Elmer, USA, ALPHA ATB. Nitrogen adsorption/desorption isotherm was obtained at 77 K on a Quanta chrome Autosorb 3-B apparatus. The specific surface area and pore size...
distribution were acquired by emulating BET equation and BJH method, respectively. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a Bruker spectrometer at 400 MHz using TMS as an internal standard. FTIR spectra of the product were recorded using a Perkin-Elmer FTIR spectrophotometer using NaCl support. Magnetic properties of the sample were measured by vibrating sample magnetometer (Lakeshore VSM) at room temperature. A commercial electron energy analyzer (PHOIBOS 150 from Specs GmbH, Germany) and a non-monochromatic Mg K\(_\alpha\) x-ray source (hv = 1253.6 eV) have been used to perform XPS measurements with the base pressure of \(< 1 \times 10^{-9}\) mbar. Catalytic reactions were monitored by thin layer chromatography on 0.2 mm silica gel F-254 plates. All the reaction products are known compounds and have been identified by comparing their physical and spectral characteristics with the literature reported values.

Conclusions

In conclusion, an inexpensive and magnetically recyclable GO-CuFe\(_2\)O\(_4\) nanocatalyst was synthesized by a simple combustion method. Using this nanocomposite, a facile, efficient and environmentally-friendly protocol for the synthesis of xanthenes was reported. The catalyst was thoroughly characterized by a set of analytical techniques. The formation of spinel nanoparticles was comprehensively demonstrated by EDS mapping and scan techniques. We have for the first time demonstrated the use of GO-CuFe\(_2\)O\(_4\) as highly active and efficient nanocatalyst for the synthesis of xanthene derivatives via one-pot two-component reaction of 2-naphthol with various aryl aldehydes under solventless condition. The results demonstrated that the combination of CuFe\(_2\)O\(_4\) with graphene oxide results in a dramatic enhancement of the catalytic activity of CuFe\(_2\)O\(_4\), which can be attributed to the remarkable synergistic effect between the CuFe\(_2\)O\(_4\) and the graphene oxide sheets. The promising points for the presented methodology are efficiency, generality, high yield, cleaner reaction profile and recyclability which make it a useful and attractive process for the synthesis of xanthenes as biologically interesting compounds.

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**Author Contributions**

P.D. designed the study and reviewed the manuscript. A.K. performed experiments, analysed data, and wrote the manuscript. L.R. help in analysing data, L.S.K.A. reviewed the manuscript and R.S.D. performed XPS measurements and analysed data.

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