Visible Light-Emitting Diode Light-Driven Cu$_{0.9}$Fe$_{0.1}$@RCAC-Catalyzed Highly Selective Aerobic Oxidation of Alcohols and Oxidative Azo-Coupling of Anilines: Tandem One Pot Oxidation–Condensation to Imidazoles and Imines

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Supporting Information

ABSTRACT: Here, we have demonstrated visible light-emitting diode light-driven selective and efficient aerobic oxidation of primary/secondary alcohols to aldehydes/ketones and oxidative azo-coupling of anilines using biomass rice husk-derived chemically activated carbon sheet-supported copper–iron bimetallic hybrid nanomaterials (Cu$_{0.9}$Fe$_{0.1}$@RCAC) under oxidant and additive-free conditions. The catalytic activity of the Cu$_{0.9}$Fe$_{0.1}$@RCAC materials has been investigated for the oxidation of alcohols and anilines, and Cu$_{0.8}$Fe$_{0.2}$@RCAC was established as the best catalyst. Moreover, a tandem one-pot protocol has been developed for the sequential oxidation of alcohols followed by condensation to functionalized imidazole and imine derivatives in high isolated yields. The hybrid materials were highly robust and stable under the reaction conditions and were recovered simply by filtration and recycled up to 12th run without considerable loss in catalytic activity.

1. INTRODUCTION

Recently, visible light-driven chemical transformations have emerged as one of the green pathways in organic synthesis. A photosensitizer and an active catalyst are essential for the generation of active electrons/holes and the chemical transformation of reactant molecules to desired products. Delightfully, oxidations under the photochemical condition are considered as one of the sustainable approaches, where active oxygen species can be generated from the oxidant by the irradiation of light under mild and environmental benign reaction conditions. Further, aerobic oxidations are economic with added advantages of avoiding transport and handling of the flammable oxygen cylinder as well as avoiding use of toxic reagents. Among other oxidation reactions, oxidation of alcohols to carbonyl compounds has emerged as the fascinating area of research in the synthetic organic chemistry because of enormous applications of products, aromatic azos, displayed diverse applications in chemical, pharmaceutical, electronics, and optics. The literature study reveals that several Cu-based catalysts in combination with nitrogen-containing ligands have reported for the synthesis of aromaticazo compounds via oxidative azo-coupling of anilines. However, oxidative azo-coupling of anilines under the photochemical condition have been rarely reported. Moreover, there is a lack of general, efficient, and sustainable catalyst for the oxidation of both alcohols and amines. Thus, sustainable development of an efficient and economic photocatalyst for the aerobic oxidation of both alcohols and aromatic amines is highly desirable.

Hence, it still remains important and interesting to develop a economic and sustainable photocatalyst to address these issues.

On the other hand, development of a sustainable protocol for the oxidative azo-coupling of anilines is essential as the products, aromatic azos, displayed diverse applications in chemical, pharmaceutical, electronics, and optics. The literature study reveals that several Cu-based catalysts in combination with nitrogen-containing ligands have reported for the synthesis of aromaticazo compounds via oxidative azo-coupling of anilines. However, oxidative azo-coupling of anilines under the photochemical condition have been rarely reported. Moreover, there is a lack of general, efficient, and sustainable catalyst for the oxidation of both alcohols and amines. Thus, sustainable development of an efficient and economic photocatalyst for the aerobic oxidation of both alcohols and aromatic amines is highly desirable.

Here, we have speculated that the problems associated with the use of precious noble metals, inactivity of TiO$_2$ under visible light, and use of toxic and expensive oxidants and nitrogen-containing ligands could be overcome by developing a visible light-driven sustainable and general protocol for oxidation reactions using first row transition metal–carbonaceous hybrid material as the catalyst and air as the source of oxygen.

Received: September 20, 2019
Accepted: December 4, 2019
Published: December 19, 2019
Iron (Fe) and copper (Cu) are abundant, eco-friendly, first-row transition metals in earth’s crust and constitute an integral part in biological systems and play a vital role in molecular oxygen activation and transportation at ambient temperature. Motivated by the nature’s action, different Fe- and Cu-based catalysts were developed for the aerobic oxidation of alcohols. However, to the best of our knowledge, Fe–Cu-catalyzed photo-oxidation of alcohols and anilines has not been reported, although Fe-based catalysts were reported to be active in photocatalytic water splitting and dye degradation reactions. Similarly, Cu-based materials were also established as excellent candidate for harvesting visible light. Thus, precious noble metals could be replaced by Fe–Cu for the generation of active oxygen species for the oxidation of alcohols which will be beneficial from an industrial and environmental point of view.

On the other hand, over decades, hybrid carbonaceous materials such as graphene oxide (GO)/N-doped graphene, AgBr@TiO2/GO, Au–CNT, and metal-doped g-C3N4 have been established as fascinating excellent visible light-driven photocatalysts for oxidation of alcohols. Interestingly, instead of using commercially available carbonaceous materials, biomass feedstock-derived chemically activated carbonaceous (CAC) materials are attractive. The transformation of biomass to customize carbon is essential as the process results in decrease of the so-called “carbon-footprint” and cost-to-value relationships. In addition to these, biomass feedstock-derived CAC provides several advantages of easy availability at free of cost or at low cost, presence of excellent porosity and electrical conductivity, eco-friendly, and finally and most importantly, the presence of high oxygen-rich surface functional groups which can hold active catalysts securely. Consequently, Zhao and Zhao have prepared graphene sheets from disposable paper cups for fuel cell applications. Ruan and his group have fabricated graphene from cookies, chocolate, grass, plastics, roaches, and dog feces on Cu foil at 1050 °C under H2/Ar flow. Veerakumar and co-workers have reported beetroot-derived activated porous carbon-supported Fe3O4 nanoparticles (NPs) for reduction of nitro-aromatics to amines. Sudhan et al. have developed activated porous carbon from rice straw for a high-energy symmetric super capacitor.

Further, it has been well established that bimetallic NPs showed superior activity compared to monometallic ones. This is due to the synergetic effects, which originates by the change of the electronic structure because of charge transfer or structural strain between metals, interfacial collaboration by two metals, and interfacial stabilization. For example, Au–Pd and Cu–Ag bimetallic catalysts have outperformed the monometallic ones for the oxidation of benzyl alcohols. However, to the best of our knowledge, the catalytic activity of the Cu–Fe bimetallic nanocatalyst has not been investigated in the oxidation of alcohols and oxidative azo-coupling of anilines under visible light irradiation.

As a part of our continuous effort in the development of the synthetic methodology using heterogeneous green nanocatalysts, herein, we have developed biomass rice husk (RH)-derived chemically activated carbon sheet-supported Cu–Fe nanocomposites (CuFe1-x@RCAC) for visible light-driven efficient and selective aerobic oxidation of benzyl alcohols and anilines to carbonyl compounds and azos and a tandem one-pot oxidation–condensation to functionalized imidazole and imine derivatives under oxidant-free reaction conditions (Scheme 1).

Scheme 1. Visible LED Light-Driven Cu0.9Fe0.1@RCAC-Catalyzed Aerial Oxidation and Tandem One-Pot Oxidation—Condensation Reactions

2. RESULTS AND DISCUSSION

Initially, biomass RHs were converted to chemically activated carbon (RCAC). Briefly, RHs were washed with water and digested with few drops of concentrated HCl under boiling conditions for 1 h to remove dust and other impurities, dried under an oven at 80 °C for 24 h. Next, the RHs were carbonized in a muffle furnace at 500 °C for 3 h to obtain black material (RCBA-500 °C) followed by activation with KOH. The KOH–carbon mixture was then calcined at 500, 600, and 700 °C for 3 h. The calcined materials were washed thoroughly with distilled water until the samples became free from alkalis (until pH = 7) and dried at 80 °C for 15 h. The physiochemical properties of the carbonaceous materials before activation and after activation were analyzed by Raman spectroscopy and powder X-ray diffraction (XRD) studies.

The Raman spectra of carbonized materials before and after KOH activation reveal the presence of peak at ~1500 cm$^{-1}$, corresponding to the G band of sp$^2$-bonded carbon in planar sheets of graphite. Again, a peak at ~1235 cm$^{-1}$ which is assigned to the D band of carbon in the Raman spectra of all materials was observed. The D-band signified the presence of the defect and oxygen functionality in chemically activated carbon (RCAC) (Figure 1a). The $I_D/I_G$ ratios were calculated for all the four samples, and it was observed that the intensity of the D band ($I_D$) is more in KOH-activated samples compared to samples before activation (Figure 1b). Thus, KOH activation leads to formation of defects and generation of oxygen functionality. Again, with increasing temperature of calcination, $I_D$ gradually increases and the RCAC-600 sample was considered for immobilization of NPs as the sample contains balance of sp$^2$-bonded planar carbon sheets and defects/oxygen functionalities. The conversion of biomass RH to amorphous carbon and graphitic carbon via carbonization–activation processes has also been demonstrated by the powder XRD studies. The powder XRD spectra of RCBA-500 (red line) and RCAC-600 (black line) reveal the
existence of two broad peaks at $2\theta \approx 25$ and $44^\circ$ (Figure 1c), corresponding to the reflection plane of $\{002\}$, because of stacking of the layers, and the reflection plane of $\{100\}$, which is attributed to stacking of the layers. These data are in good accordance with those of reported data.\textsuperscript{38,39} The broadening of peaks in powder XRD indicates the formation of disordered amorphous carbon.

Next, different amounts of Fe−Cu NPs were immobilized on the surface RCAC-600 to prepare hybrid nanomaterials. Briefly, an appropriate amount of FeCl$_2$ and CuCl$_2$ were dissolved in methanol under sonication followed by the addition of NaBH$_4$ in methanol (3 equiv) under the similar reaction conditions. The resulting mixture was then sonicated additionally for 2 h. Afterward, the mixture was filtered, washed with distilled water, and dried under oven at 80 °C for 2 h. A series of materials were prepared by the above mentioned procedure by adjusting the amount of metal content. A list of materials along with the composition and Brunauer−Emmett−Teller surface ($S_{BET}$) areas has been given in Table 1.

Table 1. Composition of Biomass Derived Cu$_x$Fe$_{1-x}$@RCAC Materials

| sl. no. | sample | sample name | composition (ICP-AES) | $S_{BET}$ (m$^2$/g) |
|--------|--------|-------------|-----------------------|---------------------|
| 1      | sample-I | RCAC        | pure carbon           | 1035                |
| 2      | sample-II | Cu$_{0.9}$Fe$_{0.1}$@RCAC | 9.93 wt % Fe-0.98 wt % Cu | 981                |
| 3      | sample-III | Cu$_{0.5}$Fe$_{0.5}$@RCAC | 4.97 wt % Fe-4.91 wt % Cu | 968                |
| 4      | sample-IV | Cu$_{0.1}$Fe$_{0.9}$@RCAC | 0.94 wt % Fe-9.07 wt % Cu | 979                |
| 5      | sample-V | Cu@RCAC     | 9.91 wt % Cu@RCAC     | 1035                |
| 6      | sample-VI | Fe@RCAC     | 9.89 wt % Fe@RCAC     | 981                |

The prepared materials were characterized by spectroscopic and analytical techniques. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) study has been performed to determine the metal content in the material and results are given Table 1. The Brunauer−Emmett−Teller surface ($S_{BET}$) area of RCAC was determined to be 1035 m$^2$/g and the $S_{BET}$ for Cu$_{0.9}$Fe$_{0.1}$@RCAC materials were found to be close to the surface area of pure RCAC, indicating that metal loading does not change the surface areas of the biomass-derived chemically activated carbon significantly. EDAX study of Cu$_{0.9}$Fe$_{0.1}$@RCAC demonstrated the presence of C, Cu, Fe, and O element in the sample (Figure 2a). The powder XRD studies have been performed to confirm the crystalline nature of hybrid materials. The powder XRD spectra of Cu$_x$Fe$_{1-x}$@RCAC hybrid materials.
RCAC are presented in Figure 2b, which reveals the immobilization of Cu−Fe on the carbon support. Along with two broad diffraction peaks for carbon at 2θ ≈ 26 and 44° corresponding to {002} and {200} planes. The diffraction peak at 2θ ≈ 43.6, 50.8, and 74.4° corresponds to {111}, {200}, and {220} reflection planes of Cu(0) NPs and peaks at 2θ = 44.9, 65, and 75.2° represents {110}, {200}, and {222} reflection plane of Fe(0) NPs.

The morphology of the pristine RCAC and hybrid Cu$_{0.9}$Fe$_{0.1}$@RCAC materials was analyzed by field emission scanning electron microscopic (FESEM) studies. The FESEM images of RCAC reveals that KOH activation generated 2D carbon sheets which are further self-assembled to form porous channels with a length of 580 μm and diameter of 4 μm (Figure 3b). Pore formation by KOH activation has been well demonstrated in the literature. However, the presence of such pores was not observed in the FESEM image of carbon before KOH activation (Figure 3a). Further, FESEM−EDAX indicates that undoped carbon was free from metal impurities. Most importantly, the FESEM image of Cu$_{0.9}$Fe$_{0.1}$@RCAC

Figure 4. TEM images of (a) pristine RCAC and (b,c) Cu$_{0.9}$Fe$_{0.1}$@RCAC materials.

Table 2. Optimization of Reaction Conditions for the Oxidation of Benzyl Alcohol$^a$

| entry | catalyst | oxidant | conditions | time (h) | yield (%) |
|-------|----------|---------|------------|----------|-----------|
| 1     | RCAC     | air$^b$ | PhMe/120 °C/LED | 12       | 35        |
| 2     | RCAC     | air$^b$ | PhMe/120 °C/dark | 12       | 10        |
| 3     | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | PhMe/120 °C/LED | 2        | 98        |
| 4     | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | PhMe/120 °C/LED | 2        | 62        |
| 5     | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | PhMe/120 °C/LED | 2        | 32        |
| 6     | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | PhMe/120 °C/LED | 2        | 25        |
| 7     | Fe$_{0.9}$RCAC | air$^b$ | PhMe/120 °C/LED | 2        | 20        |
| 8     | Cu$_{0.9}$Fe$_{0.1}$@RCAC | H$_2$O$_2$ | PhMe/120 °C/LED | 2        | 96        |
| 9     | Cu$_{0.9}$Fe$_{0.1}$@RCAC | TBHP$^d$ | PhMe/120 °C/LED | 2        | 99        |
| 10    | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | H$_2$O/120 °C/LED | 2        | 2        |
| 11    | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | EtOH/120 °C/LED | 2        | 38        |
| 12    | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | THF/120 °C/LED | 2        | 41        |
| 13    | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | dioxane/120 °C/LED | 2        | 58        |
| 14    | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | DMSO/120 °C/LED | 2        | 67        |
| 15    | Cu$_{0.9}$Fe$_{0.1}$@RCAC | air$^b$ | PhMe/120 °C/dark | 2        | 52        |

$^a$Conditions: benzyl alcohol (0.5 mmol), catalyst (50 mg), total metal loading adjusted to 10 wt %, solvent (2 mL), 10 W LED bulb. $^b$Air flow using air pump. $^c$H$_2$O$_2$ (1.5 mmol). $^d$TBHP (1.5 mmol).

Figure 5. (a) UV−vis studies of comparison of catalytic activity of Cu$_{0.9}$Fe$_{0.1}$@RCAC in benzyl alcohol oxidation, (b) relative yield of formation of benzaldehyde using Cu$_{0.9}$Fe$_{0.1}$@RCAC materials.
The presence of C, Cu, Fe, and O elements (Figure 2a).

**Oxidation of Alcohols**

The pristine RCAC (50 mg) was heated at 120 °C in the presence of visible LED light. When a mixture of benzyl alcohol (0.5 mmol) and benzaldehyde was produced (entry 1, Table 2). Thus, Cu–Fe NP-loaded RCAC hybrid materials were investigated for benzyl alcohol oxidation under LED light. We are delighted to observe a significant increase in the rate of reaction using Cu0.9Fe0.1@RCAC (50 mg) as the catalyst, producing 98% of benzaldehyde within 2 h (entry 3, Table 2).

It was observed that with decreasing Cu-content in CuFe1−x@RCAC, the conversion of benzyl alcohol to benzaldehyde gradually decreased, and 62 and 32% of benzaldehyde was produced using Cu0.5Fe0.5@RCAC and Cu0.2Fe0.8@RCAC, respectively (entries 4–5, Table 2). Most importantly, Cu–Fe bimetallic NP-immobilized RCAC materials showed better activity corresponding to the individual Cu- or Fe-loaded catalyst (entries 6–7, Table 2). Thus, Cu0.9Fe0.1@RCAC was established as the best catalyst for oxidation of benzyl alcohol under LED light. The photocatalytic oxidation was screened in different solvents and toluene proved to be the best choice of solvent over H2O, EtOH, tetrahydrofuran (THF), dioxane, and dimethyl sulfoxide (DMSO) for the model oxidation reaction (entries 10–14, Table 2). The other oxidant like tert-butyl hydroperoxide (TBHP) and H2O2 produced an almost similar yield of benzaldehyde, and thus, air was used as the eco-friendly oxidant. When the reaction was carried out in dark conditions at 120 °C in toluene in the absence of light, 52% of benzaldehyde was produced (entry 15, Table 2). Thus, Cu0.9Fe0.1@RCAC is also effective to catalyze the oxidation of benzyl alcohol in the absence of light with relatively lower conversion. This can be possibly due to higher activation of molecular oxygen in the presence of light and heat compared to only heat or only light.

The relative catalytic performance of CuFe1−x@RCAC was further demonstrated by UV–vis studies. To do so, we have performed oxidation of benzyl alcohol (0.5 mmol) in toluene (2 mL) at 120 °C in the presence of LED using five different CuFe1−x@RCAC catalysts and stopped the reaction after 1 h. After each reaction, the catalyst was separated, and toluene was evaporated. Next, the crude product was diluted with a fixed amount of n-hexane to perform the UV–vis study. The UV–vis spectra presented in Figure 5a indicate that CuFe1−x@RCAC materials are better than its individual component and a steady increase in absorbance of benzaldehyde (λmax = 239 nm) with increasing Cu-content in bimetallic hybrid materials. The Cu0.9Fe0.1@RCAC catalyst was found to be best among the five catalyst tested here. Figure 5b represents relative conversion of benzyl alcohol to benzaldehyde using CuFe1−x@RCAC.

With the optimized reaction conditions in hand, next, we have explored the scope of catalytic oxidation of alcohols. The results are presented in Table 3. A number of structurally divergent primary and secondary benzyl alcohols were oxidized by Cu0.9Fe0.1@RCAC under aerobic conditions in the presence of visible LED light irradiation, producing excellent yields.

**Table 3. Scope of Cu0.9Fe0.1@RCAC-Catalyzed Aerobic Oxidation of Alcohols**

| Entry | Alcohols | Product | Yield (%) |
|-------|----------|---------|-----------|
| 1     | Benzyl alcohol | Benzaldehyde | 98        |
| 2     | tert-Butyl alcohol | Benzaldehyde | 90        |
| 3     | sec-Butyl alcohol | Benzaldehyde | 95        |
| 4     | tert-Butyl alcohol | Benzaldehyde | 85        |
| 5     | sec-Butyl alcohol | Benzaldehyde | 89        |
| 6     | tert-Butyl alcohol | Benzaldehyde | 92        |
| 7     | sec-Butyl alcohol | Benzaldehyde | 93        |
| 8     | tert-Butyl alcohol | Benzaldehyde | 88        |
| 9     | sec-Butyl alcohol | Benzaldehyde | 86        |
| 10    | tert-Butyl alcohol | Benzaldehyde | 90        |
| 11    | sec-Butyl alcohol | Benzaldehyde | 95        |
| 12    | tert-Butyl alcohol | Benzaldehyde | 85        |
| 13    | sec-Butyl alcohol | Benzaldehyde | 89        |
| 14    | tert-Butyl alcohol | Benzaldehyde | 92        |
| 15    | sec-Butyl alcohol | Benzaldehyde | 93        |

*Reaction conditions: benzyl alcohol (0.5 mmol), Cu0.9Fe0.1@RCAC (50 mg) in 2 mL of toluene at 120 °C for 2.0 h under air in the presence of LED light. The yields refer to isolated pure products.*

The high-resolution transmission electron microscopic (HRTEM) study was performed for both pure and NPs-loaded activated carbon. The HRTEM image of pure RCAC shows sheetlike structure similar to that observed in FESEM (Figure 4a) and TEM images. Figure 4b shows the immobilization of nano-size Fe and Cu on the carbon surface. The average particle size of 5 nm was also confirmed from the TEM image (Figure 4b,c). The well dispersion of NPs on the support was also indicated from the TEM image (Figure 4c).

Next, the catalytic activity of the CuFe1−x@RCAC materials was investigated in the oxidation of primary and secondary alcohol. Initially, we have examined the oxidation of benzyl alcohol as a model reaction under light-emitting diode (LED) light. When a mixture of benzyl alcohol (0.5 mmol) and pristine RCAC (50 mg) was heated at 120 °C in toluene (2 mL) with continuous air flow in the presence of LED light (10 W), a moderate yield of benzaldehyde (30%) was obtained after 12 h (entry 1, Table 2). However, the yield was decreased to 10% when the same reaction was conducted in the dark (entry 2, Table 2). This indicates the photocatalytic activity of biomass-derived chemically activated carbon. The formation of the product was identified by the 1H NMR spectroscopic study. The reaction is highly selective and produced benzaldehyde as the only product. No further oxidation to carboxylic acid was observed. Motivated by this result, subsequently, Cu–Fe NP-loaded RCAC hybrid materials were investigated for benzyl alcohol oxidation under LED light. The yields refer to isolated pure products.
Table 4. Cu_{0.9}Fe_{0.1}@RCAC-Catalyzed Tandem Oxidation−Condensation Leading to Imidazoles^a

| Reaction conditions: benzoin (0.5 mmol), Cu_{0.9}Fe_{0.1}@RCAC (50 mg) in 2 mL of toluene at 120 °C for 2.0 h under air in the presence of LED light followed by addition of aromatic aldehyde (0.5 mmol) and NH$_4$OAc (1.0 mmol) under the same conditions. The yields refer to isolated pure products. |

Scheme 2. Cu_{0.9}Fe_{0.1}@RCAC-Catalyzed One-Pot Tandem Oxidation−Condensation to Imines

Scheme 3. Plausible Mechanism for the Light-Promoted Cu_{0.9}Fe_{0.1}@RCAC-Catalyzed Aerobic Oxidation of Benzyl Alcohol

(85−98%) of aromatic aldehydes (2a−k, Table 3)/ketones (2l−r) within 2 h. Various benzyl alcohols containing electron-donating (e.g., −Me, −OMe, −Br, −Cl, −OH, etc.) groups (entries 2b−g, Table 3) and electron-withdrawing (e.g., −NO$_2$) (entries 2h−i, Table 3) groups at ortho-/meta-/ and para-position of the benzene ring were smoothly converted to corresponding aromatic aldehydes in an excellent yield within 2 h under optimized reaction conditions. Moreover, the protocol is also demonstrated synthesis of hetero-aromatic pyridine-3-aldehyde and thiophene-2-aldehyde (entries 2j−k, Table 3). Secondary benzyl alcohols were also efficiently oxidized by Cu$_{0.9}$Fe$_{0.1}@$RCAC in toluene at 120 °C under air in the presence of LED light to corresponding aromatic ketones of industrial importance such as acetophenone derivatives (entries 2l−p, Table 3), propiophenone (entry 2q, Table 3), and benzophenone (entry 2r, Table 3) in good yields (85−90%).

Further, cinnamyl alcohol was selectively converted to cinnamaldehyde without formation of any by-products in good yield (2v, 86%).

Afterward, Cu$_{0.9}$Fe$_{0.1}@$RCAC was employed for oxidation of benzoin to benzil, an important diketone found several applications as photosensitizers, ligands, and starting material for drugs, agro-chemicals, and perfumes. We are delighted to observe 100% conversion of benzoin to benzil under the optimized reaction conditions (2s, Table 3). 4,4′-dichlorobenzoin and 4,4′-dimethyl benzoin also oxidized to corresponding benzil derivatives (2t−u, Table 3). All the reactions listed in Table 3 are very clean and highly selective in nature. No further oxidation of aldehydes took place. The method is free from using a toxic and expensive oxidant as the air was used as the sole oxidant. After the reaction, the catalyst was separated simply by filtration, washed with ethyl acetate, dried in oven, and reused for subsequent reactions. The combine organic extract was evaporated to yield the crude products, which was purified by short column chromatography over silica gel (mesh size 60−120) using 5% ethyl acetate in petroleum ether. All the products listed in Table 3 are known from the literature and were identified by $^1$H NMR spectroscopy study. The NMR spectra are provided in the Supporting Information.

Further, we have extended the scope of this methodology in one-pot oxidation of benzoin followed by condensation with aromatic aldehyde and ammonium acetate (NH$_4$OAc) for the synthesis of imidazole derivatives. Initially, benzoin (1 mmol)
and Cu$_{0.9}$Fe$_{0.1}$@RCAC were irradiated with LED under an air flow condition for 2 h; then, benzaldehyde (1 mmol) and NH$_4$OAc (2.5 mmol) were added to the reaction mixture and continued to run the reaction under the same conditions for 1 h (TLC monitored) with appearance of a solid product. The solid product was dissolved in ethanol (3 mL), and the catalyst was separated by simple filtration with filter paper washed with few drops of ethanol. Pure 2,4,5-triphenyl imidazole recrystallized from ethanol solution. The pure product was initially identified by melting point determination (observed mp 267−269 °C; reported mp 270−274 °C) and further confirmed by $^1$H NMR study. The scope of Cu$_{0.9}$Fe$_{0.1}$@RCAC-catalyzed one-pot tandem oxidation−condensation was explored by using different aromatic aldehydes. The results of tandem oxidation−condensation reactions are presented in Table 4.

Series of tri-substituted imidazole derivatives (3a−e, Table 4) were synthesized. All the reactions were very clean and high yielding (92−98%). The products were purified by recrystallization from ethanol, and no column chromatography was required.

Further, we have also demonstrated Cu$_{0.9}$Fe$_{0.1}$@RCAC-catalyzed one-pot oxidation of benzyl alcohol and sequential condensation with amines to produce imines using the hybrid nanocatalyst. Air was passed through benzyl alcohol (1 mmol) in the presence of 50 mg of catalyst under LED light, and benzyl amine (1 mmol) was added after 2 h, the reaction was continued for additional 1 h under normal conditions in the absence of LED, and an excellent yield of imines (4a, 92%) was produced. The results are summarized in Scheme 2.

Finally, we have presented a plausible mechanism for visible light-promoted Cu$_{0.9}$Fe$_{0.1}$@RCAC-catalyzed aerial oxidation of alcohol in Scheme 3.

The catalytic system also was effective for the oxidation of benzyl alcohol under LED-free conditions, and an alternative pathway for the oxidation of benzyl alcohol has been proposed when the reaction was carried under the heating condition in the absence of LED (see Figures S18 and S25).

Motivated by the catalytic activity of Cu$_{0.9}$Fe$_{0.1}$@RCAC in selective and efficient oxidation of primary and secondary alcohols and tandem oxidation−condensation reaction, next, we have investigated its catalytic performance in the oxidative azo-coupling of anilines, leading to synthesis of aromatic azos.

When a mixture of 4-methoxyaniline (1 mmol), Cu$_{0.9}$Fe$_{0.1}$@RCAC (50 mg) is heated at 120 °C in toluene (2 mL) under continuous air flow in the presence of LED light, a good yield of (E)-1,2-bis(4-methoxyphenyl)diazene (5c, 88%) was obtained. The yield was increased to 98% when the reaction was performed in CH$_3$CN at 80 °C under LED light. A decrease in yield (72%) was observed when the same reaction was performed in the absence of LED under dark conditions. A comparative UV−vis study was accomplished to compare the catalytic activity of various Cu$_{x}$Fe$_{1−x}$@RCAC materials. The results were depicted in Figure 6. The comparative UV−vis studies clearly indicate that bimetallic...
nanocomposites have shown better activity compared to its mono-metallic one, and Cu$_{0.9}$Fe$_{0.1}$@RCAC is the best and Fe@RCAC showed least reactivity among other all five catalysts tested here.

A series of anilines underwent oxidative azo-coupling in the presence of Cu$_{0.9}$Fe$_{0.1}$@RCAC under LED light in air to afford good to excellent yields (85 – 92%) of products within 6 – 8 h. We have also observed a cleared electronic effect on this reaction. The electron-rich mono-substituted aryl amines demonstrated admirable reactivity with higher isolated yields of azos compared to aryl amine with electron-withdrawing groups. The results are summarized in Table 5.

Finally, we have investigated the stability and recyclability of the Cu$_{0.9}$Fe$_{0.1}$@RCAC catalyst by considering the oxidation of benzyl alcohol (2a, Table 2) as a model reaction under optimized conditions. The catalyst was separated from the reaction mixture simply by filtration, washed with ethanol (2 × 2 mL), dried in an oven at 80 °C for 4 h, and reused the catalyst for successive reactions. The recyclability study reveals that the RCAC provided sufficient stability to NPs and the catalyst remained stable and active under the reaction conditions and recycled up to 12 times without significant loss in yields of the reaction (Figure 7a). Further, heterogeneity of the oxidation reaction was recognized by performing the leaching study by the hot filtration test. Cu$_{0.9}$Fe$_{0.1}$@RCAC was separated from the reaction mixture by filtration under hot conditions just after 15 min which was allied with 15% conversion and the remaining filtrate was continued to run up to 2 h further under the standard conditions. However, no significant development of the reaction was observed after filtration, which indicates that no leaching of Cu and Fe NPs had taken place from the chemically activated carbon sheets (see Figure 7b). The fate of the reused catalyst was analyzed by powder XRD and FESEM studies (Figure 7c, d). The powder XRD spectrum (Figure 7c) of the recycled catalyst indicates partial oxidation of copper to cuprous oxide, and substantial loss of the porous channel structure was also evident from the FESEM image (Figure 7d).

3. CONCLUSIONS

In conclusion, we have synthesized Cu$_x$Fe$_{1-x}$@RCAC hybrid photoactive materials by immobilization of different amounts of Cu- and Fe-NPs on the surface of biomass RH-derived activated porous carbon sheets. The formation of graphitic carbon sheetlike hybrid materials was identified by Raman spectroscopy, powder XRD, FESEM, EDAX N$_2$ absorption–desorption, and HRTEM studies. The photocatalytic activity of hybrid materials were tested the oxidation of benzyl alcohols as well as oxidative azo-coupling of aniline to aromatic azos under visible LED light in air as oxidant. It was observed that bimetallic catalysts were better compared to its mono metallic counterpart, and Cu$_{0.9}$Fe$_{0.1}$@RCAC yielded best results among others. The present catalytic protocol offered following advantages such as clean reaction condition as air used as source of oxygen, use of visible LED light active and reusable catalyst, broad substrate scope, excellent isolated yields (85–100%) and biomass feedstock was used as source of carbon. We have also reported a one-pot tandem oxidation of benzoic acid followed by condensation with aldehyde and NH$_4$OAc, leading to synthesis of tri-substituted imidazole derivatives and one-pot oxidation–condensation to imines in excellent yields. Most importantly, the present research demonstrated biomass management and utilization in commercially important organic transformation, and we believe that the hybrid materials will find numerous applications.
Detailed procedures for the preparation of hybrid materials and N2 absorption–desorption isotherm; detailed procedure for the oxidation of alcohols; oxidative azo-coupling of anilines and one-pot synthesis of imidazoles and imines; representative NMR copies and the proposed mechanism for the Cu0.9Fe0.1@RCAC-catalyzed oxidation of benzyl alcohol under heating conditions in the absence of LED light (PDF).

We are pleased to acknowledge funding agency CCOST, Raipur (ENDT no. 2096/CCOST/MRP/2017).

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