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## Metal Free Carbon as a Catalyst for Oxidative Coupling : Solvent Enhance Poly-Coupling with Regioselectivity

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Melad Shaikh<sup>a</sup>, Aanchal Sahu<sup>a</sup>, A. Kiran Kumar<sup>b</sup> Mahendra Sahu<sup>a</sup>, Sunil. K. Singh<sup>a</sup>, and Kalluri V.S. Ranganath<sup>\*a</sup>

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A heterogeneous, inexpensive and a metal free, environmental friendly graphene oxide (GO), has been developed for the oxidative poly coupling of 2-naphthols in aqueous sodium hydroxide in the presence of air. This study found that GO could function as a heterogeneous catalyst and solvent played a vital role in the coupling. Changing of the solvent from toluene to water leads to the formation of homocoupling to poly-coupling materials.

The catalytic organic transformation is dramatically employed by traditional transition metal-based homogeneous and heterogeneous catalysts which are expensive, widely consumed toxic metal, non-removal and limited availibility.<sup>1</sup> Metal free readily available, non-toxic and inexpensive carbocatalysts like carbon nanotubes, fullerenes, graphene and their functional modifications are recent developments.<sup>2</sup> Because of their remarkable physical, chemical, electronic property, outstanding thermal conductivity, high specific surface area, graphene oxide (GO) shows enormous interest not only for heterogeneous catalytic applications, but also in many important field such as fuel cell, lithium battery, and electric devices.<sup>3-4</sup> The advantage of GO is physicochemical and electronic properties which exhibit  $\pi$ -conjugative structures, which promote the interactions with various reactants and thus activated for catalytic transformation.<sup>5</sup>

Recently, GO has been rapidly using as a readily available catalyst for fine chemical synthesis with sustainable green protocol.<sup>6</sup> Bielawski and co-workers demonstrated the chemoselective oxidation of alcohols and sulfides under mild conditions using GO as a heterogeneous catalyst.<sup>7</sup> Garcia and co-workers were also reported graphenes as a carbocatalyst for hydrogenation of alkenes and the  $H_2$  are activated on the lewis acid-base surface.<sup>8</sup> In addition, Loh et al reported the oxidative homo coupling of amines by base-acid treated graphene oxide (ba-GO) as a catalyst.<sup>9</sup> Szostak and co-workers

reported the seminal study of functionalized graphene for Friedel–Crafts alkylation of arenes with styrenes and alcohols.<sup>10</sup> Moreover, GO has also been used as an oxidating agent and also in oxidative aromatization reactions.<sup>11-13</sup> In addition, the GO, has been employed as a catalyst for reduction reactions, Friedel–Crafts acylation and solvent free multicomponent reaction with high yields.<sup>14-16</sup>

As a part of our seminal interest in developing of new materials as catalysts, we report herein functionalized graphene as a sustainable heterogeneous catalyst for the oxidative coupling of  $\beta$ -napthols in organic medium and poly oxidative coupling in aqueous medium (Scheme 1).



Scheme 1 Graphene oxide catalyzed oxidative coupling in basic medium.

The oxidative coupling of  $\beta$ -napthols to produce axial 2,2'dihydroxy-1,1'-binaphthyl (BINOL), is having its own importance since the resultant compound is widely used in asymmetric reactions, agricultural chemicals, as a catalyst and DNA alkylating reagents.<sup>17</sup> The mostly used homogeneous metal catalyst for synthesis BINOL and BINOL derivatives are Fe, Cu and V at different forms of their complexes.<sup>18-21</sup> In addition, heterogeneous supports have also been realized in the coupling of 2-naphthols in high yields<sup>22-26</sup>.

We initialized our catalytic study for oxidative homocoupling of of  $\beta$ -napthols to BINOLs in the presence of base as an additive. The oxidative coupling of 2-naphthol (a model substrate) in different solvents like methanol, ethanol, toluene, dichloromethane and chloroform in the presence of GO was examined (Table 1). There was no conversion or very less conversion, when GO alone used as a catalyst (in the absence of base) in the oxidative coupling of 2-naphthols at 100 °C (Table 1, entries 1-4) and 20% yield was observed in toluene (Table 1, entry 5).

<sup>&</sup>lt;sup>a</sup>Department of Chemistry, Guru Ghasidas University, Bilaspur, India-495009. E-mail: <u>rangakvs1@gmail.com</u>

<sup>&</sup>lt;sup>b</sup>Department of Materials Science and Engineering, RGUKT, Basar, India-50401. Electronic Supplementary Information (ESI) available: [XRD, FTIR of GO and FTIR, TG-DTA, DSC of polymer and <sup>1</sup>NMR of BINOLs]. See DOI: 10.1039/x0xx00000x

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Entry	Catalyst	Solvent	Base	Temperature (°C)	Yield (%) <sup>b</sup>
1	GO	dichlromethane		100	10
2	GO	chloroform		100	10<
3	GO	methanol		100	N.R
4	GO	ethanol		100	N.R
5	GO	toluene		100	20
6	GO	toluene	NaO <sup>t</sup> Bu	100	40
7	GO	toluene	KO <sup>t</sup> Bu	100	35
8	GO	toluene	NaOH	100	90
9	GO	toluene	NaOH	120	92
10		toluene	NaOH	120	N.R
11	CNT	toluene	NaOH	120	N.R
12	CNT- COOH	toluene	NaOH	120	<10
13	activated charcoal	toluene	NaOH	120	N.R
14	GO	toluene	КОН	100	70
15	GO	dichlromethane	NaOH	100	35
16	GO	chloroform	NaOH	100	30
17	Graphite	toluene	NaOH	100	N.R

(2.0 mmol);<sup>b</sup> Isolated yield. N.R stand for no reaction.

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Using of bases like NaO<sup>t</sup>Bu and KO<sup>t</sup>Bu gave moderate yields of binaphthols at 100 °C, in the presence of GO as catalyst (Table 1, entries 6 & 7). Remarkably, in the presence of sodium hydroxide, high yields (upto 90%) of binaphthol were observed (Table 1, entries 8). Increasing of the temperature to 120 °C, leads to formation of little increase in product in the presence of sodium hydroxide (Table 1, entry 9). Notably, the oxidative homocoupling of  $\beta$ -napthol was not observed in the absence of GO under same conditions (Table 1, entry 10). To know the effect of GO, different forms of carbon materials including graphite, carbon nanotubes (CNTs), functionalized CNTs and activated charcoal were used under the reaction conditions and observed with less yields of product in the oxidative coupling of 2-naphthols (< 10%) (Table 1, entries 11-13).

Inorder to test the effectiveness of GO in the oxidative coupling reaction, various substituted naphthols including electron donating and electron withdrawing groups at different positions have been examined. Notably, with all substrates, reaction proceeds well and product was isolated in good to excellent yields (Table 2). The GO catalyst could be able to recycle for three times with little change in activity (Table 2, entry 1).

Surprisingly, when the oxidative coupling reactions were performed in aqueous medium in the presence of sodium hydroxide, no homocoupling product (binaphthol) was observed. However, the maximum conversion of the 2-naphthol took place to polymeric binol (Scheme 1).<sup>27</sup> When the reaction was carried out in polar solvents like DMF and DMSO,

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little conversion of 2-naphthol was observed and no polymeric material was obtained (Table S1, Supporting: Information).2227A

Table 2 Scope of the various  $\beta$ -napthols oxidising coupling using graphene oxide<sup>a</sup>



Entry	Substrates (R)	Yield (%) <sup>b</sup>	
1	н	90, 86 <sup>c</sup> , 80 <sup>d</sup> , 76 <sup>e</sup>	
2	6-MeO	85	
3	6-Br	95	
4	3-NH <sub>2</sub>	83	
5	6-CN	81	
6	7-Br	93	
7	7-MeO	87	
8	Phenanthren-9-ol	91	
All reaction were ca 2.0 mmol); <sup>b</sup> Isolated	nried out using 20 mg of catalys d yield. N.R stand for no reactior	t, solvent (5.0 mL), reacta n. <sup>c</sup> After 1 <sup>st</sup> cycle. <sup>e</sup> 2 <sup>nd</sup> cycl	

Thus obtained naphthol polymer has been characterized by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopt (FTIR) and thermogravemetric analysis (TGA). The SEM image of the polymeric material appers like spherical shape as shown in Fig. 1. The average diameter of the sphere is approximately 1.00 µm and the space between two spheres is approximately 244 nm with various orientations. The crystallinity of polymeric material was also confirmed by PXRD from the Fig. 2 and it shows the high crystalline structure. The strong relections of the peak at  $2\theta = 26^{\circ}$ ,  $32^{\circ}$ ,  $46^{\circ}$  and  $48^{\circ}$ from the PXRD indicates that polymeric materials are highly crystalline and similar reflections were observed for both unsubstituted and bromo substituted naphthols. The regioselectivity of coupling at the ortho position has been confirmed by Raman spectroscopy (Fig. 3).



Fig. 1 SEM image of (A) poly 2-naphthol and (B) poly 6-methoxy-2-naphthol

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Fig. 2 PXRD of (A) poly 2-naphthol and (B) poly 6-methoxy-2-naphthol



Fig. 3 Raman spectroscopy of poly coupling of (a) unsubstituted (b) 6-MeO and (c) 6-Br-2-naphthols (A) Scale of 400 cm<sup>-1</sup> to 1430 cm<sup>-1</sup> and (B) high resolution splitting Raman mode (1350-1410 cm<sup>-1</sup>).

The Raman mode at 650-880  $\text{cm}^{-1}$  and 1000-1100  $\text{cm}^{-1}$  indicate the presence the biphenyl C-C linkage.<sup>28</sup> Importantly, the Raman mode at 1320-1410 cm<sup>-1</sup> reveals that an axial (1,1'position) and dynamic (3,3'-position) rotational vibration mode of polymer and clear splitting pattern is shown in Fig. 3B. Remarkably, the band at 635 cm<sup>-1</sup> explained the presence of the bromo group. Further, from FTIR analysis, (Fig S1) the stretching frequency at 797.23 cm<sup>-1</sup> indicates the aromatic C-H out-of-plane bending vibration. Moreover, the broad stretching peak at 3447.68 cm<sup>-1</sup> confirms the presence of hydroxyl groups along with 2955 cm<sup>-1</sup> for aromatic and 1088.48cm<sup>-1</sup> for C-O stretching frequency of C-O-H group.<sup>27a</sup>

The fresh and recovered heterogeneous catalyst, GO was characterized by FTIR as shown in the Fig S3. The FTIR spectroscopy revealed the existence of O-H stretching frequency at 3420 cm<sup>-1</sup> and CO<sub>2</sub> stretching frequency at 2920 cm<sup>-1</sup>. The carbonyl stretching frequency at 1630 cm<sup>-1</sup> suggesting that carboxyl groups are retained on the GO and bending vibrations at 1460 cm<sup>-1</sup> attributed to R-COO-H group. Further, it also revealed that the signal at 1570  $\text{cm}^{-1}$ , attributed to the presence of sp<sup>2</sup> C=C bonds corresponding to aromatic carbon of GO surface. Furthermore, the stretching frequency at 1110 cm<sup>-1</sup> is due to the C–O (epoxy) groups present on graphene surface.



Fig. 4 Raman spectra of (a) freshly prepared GO and (b) Recycled GO.

Further, the GO has been characterized by Raman spectroscopy for identification of carbon materials and their surface functionality (Fig. 4a and 4b). The D band at 1335 cm<sup>-1</sup> and a G band at 1582 cm<sup>-1</sup> were observed for fresh GO and reused GO respectively. Further, the "G" band arises due to the bond stretching of sp<sup>2</sup>-bonded C=C and C=O in graphite sheets and the D band is due to the sp<sup>3</sup> C-C bond defect sites of GO. Notably, the intensity ratio of the  $I_D/I_G$  ratio, is an indication of the number of structural sp<sup>3</sup> C-C bond defects and a quantitative measurement of the number of layers in a graphene sheets and its overall  $\pi$ - $\pi$  stacking behaviour in layer to layer. The  $I_D/I_G$  ratios further indicated that a high degree of sp<sup>3</sup> disorder was retained after recycle as shown in Fig. 4.

To explore the crystalline structures of the grapheme, GO were analyzed by powder X-ray diffraction patterns (XRD) (Fig. S4). The sharp diffraction peak at  $2\theta = 11.7^{\circ}$  corresponding to (002) reflection with a C-axis linear interlayer spacing 7.6 Å, which is larger than graphite 3.3 Å, indicating that functional defects or groups were introduced onto graphite surface to form GO with a stacking pattern and completely oxidized.

In addition, X-ray photoelectron spectroscopy of C-1s peak analysis also confirms that the signature of oxygen containing hydroxyl, carboxylic acid and epoxide functional groups on GO surface. In Fig. 5 the C 1s spectra resolved into four different spin-orbital, which are sp<sup>2</sup> C=C (284.8 eV), C–OH (285.6 eV), O-C-O (286.4 eV) and HO-C=O (288.3 eV). The binding energy of O 1s attributed at 530.1 eV, 531.4 eV and 533.8 eV for different oxygen functional groups of GO (Fig. S5 & Fig. S6).



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#### Fig. 6. The TEM image of GO (left) and its SERD pattern (right)

The morphology of multilayer GO was confirmed from transmission electron microscopy (TEM) image (Fig. 6). The GO surface with relatively thick, randomly stacked aggregates and crumped sheets loosely stack together was observed. However, the SAED from the GO shows ring pattern with a closed bright spots, unlike the symmetric hexagonal lattice with an average d-spacing of about 0.71 nm. The plausible mechanism for the oxidative coupling of 2-naphthol to BINOL is shown in the Scheme S2 (supporting information).<sup>25,29</sup>

In conclusion, in this communication demotrated the metal free GO as an efficient catalyst for the oxidative polymerization of 2-naphthols in aqueous basic medium and homocoupling of 2-naphthols in organic medium in high yields.

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