La$_2$O$_3$/Reduced Graphene Oxide Nanocomposite: A Highly Efficient, Reusable Heterogeneous Catalyst for the Synthesis of Biologically Important Bis(indolyl)methanes Under Solvent Free Conditions

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Synthesis and characterization of Lanthanum Oxide-reduced graphene oxide (La$_2$O$_3$/RGO) nanocomposite and its application as heterogeneous, reusable catalyst has been reported in this article. Biologically important molecules bis(indolyl)methanes are synthesized in mild reaction condition with excellent yield under solvent free condition. Catalyst was reused for four times without any significant changes in the yields obtained. Reusability, green synthesis and environmentally benign nature makes La$_2$O$_3$/RGO one of the best catalyst for the synthesis of biologically important bis(indolyl)methanes.

Keywords: Bis(indolyl)methanes, Catalysis, Lanthanum Oxide-Reduced Graphene Nanocomposite, Solvent Free Synthesis.

1. INTRODUCTION

Need for the development of new metal oxide catalysts is progressing, albeit at a slower pace, the concurrent and rapid development of high surface area catalyst supports such as graphene and its functionalized derivatives has provided unprecedented promise in the development of multifunctional catalysts.[1] Since its discovery,[2] graphene has been an excellent subject of research, as an attractive material because of its very large theoretical surface area, strong mechanical strength, high thermal conductivity, and excellent electric conductivity.[3,4] These properties of graphene lead to the synthesis of Graphene-based composite materials. Unique properties and structure of these Graphene-based composite materials have shown applications in electrocatalysis[5,6] and sensing.[7] A novel way to develop catalysts is by dispersing metal nanoparticles over the surface of graphene sheets.[8,9] A facile synthesis of graphene/metal NP composites with good control of size and morphology is critical to the practical applications.[10] Some novel catalyst based on the graphene oxide metal nanocomposites has been reported for carrying out different reaction like TiO$_2$ nanorods

immobilized Graphene oxide for enhanced photocatalytic performance.[11] Some more examples include NO$_x$ reduction over TiO$_2$/Graphene oxide nanocomposite,[12] hydrodesulphurization using MoS$_2$/Graphene oxide composite[13] and Palladium/Graphene composite for the asymmetric hydrogenation.[14] A very easy and efficient method for graphene/metal NP composites preparations is where both metal precursor and graphene oxide (GO) sheets were mixed in aqueous solution and then reduced simultaneously.[15,16] Lanthanum oxide is a biocompatible metal oxide[17] and it is being extensively used in sensing, environmental chemistry, and other catalytic reactions.[17–19] Various bioactive metabolites have indole derivatives as their constituents and this is the reason behind the importance of indole derivatives for synthetic as well as biological chemists.[10] Indole and its derivatives possess broad spectrum of biological and pharmaceutical activities[21,22] and have been identified in over 3000 natural isolates. Particularly bis(indolyl)methanes are known to enhance estrogen metabolism in humans and is likely to be drug of choice for breast cancer preventive and antibacterial agent. Because of these interesting biological activities andother uses, development of protocols for the synthesis of bis(indolyl)methanes is of current interest.

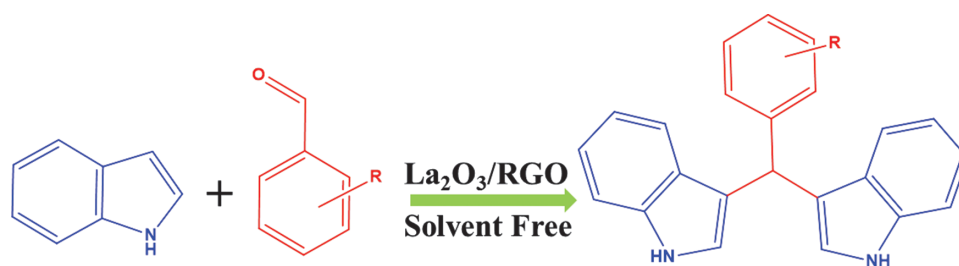*Author to whom correspondence should be addressed.

Figure 1. Schematic representation of the catalytic synthesis of bis(indolyl)methanes.

The electrophilic substitution reaction of indoles with carbonyl compounds to produce bis(indolyl)alkane is an acid catalyzed reaction, and both protic (e.g., HCl, H$_2$SO$_4$)[23, 24] as well as Lewis acids like AlCl$_3$[25] are known to promote this reaction.

Here in this article we report the synthesis and characterization of lanthanum oxide-reduced graphene nanocomposite (La$_2$O$_3$/RGO) and use it as reusable catalyst for the synthesis of biologically important heterocyclic molecules i.e., bis(indolyl)methanes under solvent free conditions (Fig. 1).

2. EXPERIMENTAL DETAILS

La(NO$_3$)$_3$ · 6H$_2$O was obtained from Merck Millipore, India; poly(ethylene glycol), MW~35,000, was purchased from Sigma-Aldrich, USA; Indole, carbonyl compounds were purchased from Aldrich and Merck. All the chemicals were of analytical grade and used without further purification. X-ray diffraction pattern of La$_2$O$_3$/RGO nanocomposite was recorded using X-ray diffractometer (model no. D8 DISCOVER). Morphological characterization was carried out using TECNAI 200 Kv TEM (Fei, Electron Optics) with digital imaging and 35 mm photography system. Thin layer chromatography (Merck Kiesel 60 F254, 0.2 mm thickness) was used to monitor the progress of the reactions. The ^{1}H-NMR and ^{13}C-NMR spectrum were recorded on Jeol ECX spectrosp in instrument at 400 and 100 MHz, respectively using TMS as internal standard. The chemical shift values were expressed on δ scale and the coupling constant (J) in Hz. FT-IR of all the synthesized bis(indolyl)methanes were recorded on a spectrometer Perkin Elmer Spectrum BX II from range 4000–400 cm^{-1} by making sample pallets with KBr. The melting points of synthesized compounds were determined on a Thomas Hoover Unimelt capillary melting point apparatus.

2.1. Preparation of Graphene Oxide and Lanthanum Oxide-Reduced Graphene Oxide (La$_2$O$_3$/RGO) Nanocomposite

Graphene oxide was prepared by the Modified Hummers method.[26, 27] Lanthanum oxide-reduced graphene oxide nanocomposite (La$_2$O$_3$/RGO) was synthesized by using 40 mg of La(NO$_3$)$_3$ · 6H$_2$O and 0.2 g of Poly(ethylene glycol), both were ultrasonicated for about one hour in 20 ml double distilled water than 200 mg Graphene oxide is added followed by ultrasonication for 30 min. To the resulting suspension 200 μL 0.1 M NaBH$_4$ was added dropwise under ice cold conditions and left for stirring for two hours. Afterwards solid was recovered by centrifugation after multiple washing with water and ethanol, thus obtained solid was dried in air at 80 °C for 1 h followed by the annealing at 300 °C for 3 h.

2.2. Synthesis of Bis(indolyl)methanes

2 mM Indole and 1 mM benzaldehyde were mixed together followed by addition of 5 wt%La$_2$O$_3$/RGO. Resulting mixture was than stirred at 45 °C for 35 minutes. Completion of the reaction was monitored by thin layer chromatography. After completion reaction mixture was diluted with chloroform (10 mL) and centrifuged to separate the catalyst. Supernatant was reduced under pressure to afford the solid product, which is further purified by recrystallization from petroleum ether.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

Raman spectra of La$_2$O$_3$/RGO and GO can be seen in Figure 2(A), showing the characteristic D (j-point phonons of A$_{1g}$ symmetry of sp^3-bonded carbon atoms of disordered graphene) and G (scattering of E$_{2g}$ phonons of sp^2-bonded carbon atoms) bands of graphene. Raman Spectra of GO shows D and G bands at 1354 cm^{-1} and 1600 cm^{-1} respectively. Similarly for La$_2$O$_3$/RGO Raman spectra showing D band at 1317 cm^{-1} and G band at 1591 cm^{-1}. I_D/I_G ratio for GO and La$_2$O$_3$/RGO found to be 0.86 and 1.47 respectively, this increase in the intensity ration is attributed to the increase in the disorderness of the graphitic structure due to the binding of La^{3+} with the free oxygen moieties on the graphene oxide surface to form La$_2$O$_3$ nanoparticles.

Figure 2(B) depicting the X-ray diffraction peaks pattern of La$_2$O$_3$/RGO. In the spectrum of GO peak at $2\theta = 10.15°$ and $2\theta = 42.40°$ represents the $\langle 001 \rangle$ plane and $\langle 100 \rangle$ plane respectively. XRD pattern of La$_2$O$_3$/RGO shows peaks at $2\theta = 25.18°$, $2\theta = 42.85$ represents the $\langle 002 \rangle$ and $\langle 100 \rangle$ planes of RGO along with the $2\theta = 30.19$ attributed to $\langle 101 \rangle$ crystal plane of La$_2$O$_3$.
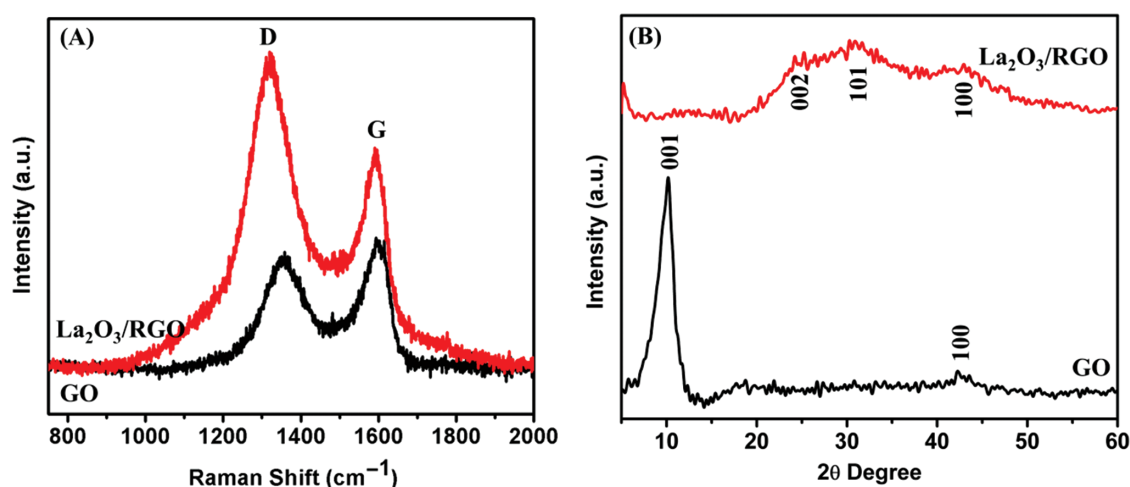
Figure 2. (A) Raman spectra of GO and La$_2$O$_3$/RGO showing D and G bands, (B) XRD pattern of GO and La$_2$O$_3$/RGO with different planes labeled.

TEM images of the GO and La$_2$O$_3$/RGO nanocomposite is shown in Figure 3. Figure 3(A) shows the sheet like morphology of the graphene oxide with wrinkled structures. Nanoclusters of Lanthanum oxide nanoparticles can be seen attached to the wrinkled surface of the RGO sheet in Figure 3(B). Nanoclusters of Lanthanum oxide nanoparticles showing a porous morphology, and this enhance catalytic property of La$_2$O$_3$/RGO nanocomposite in addition to the large surface area of RGO. Inset picture in Figure 3(A) is a HRTEM image of individual La$_2$O$_3$ nanoparticle in nanocluster over RGO surface showing ⟨101⟩ crystal plane of La$_2$O$_3$.

Catalytic activity for the synthesis bis(indolyl) methanes optimized using model reaction between indole and benzaldehyde. First, effect of catalyst amount is investigated, in which different amounts of catalysts are used (Fig. 4(A)), and at 5, 10, and 20 wt.% yield obtained found to be similar in same time but we selected 5 wt.% for our further reactions for its being lesser amount.

Effect of different solvents on the reaction is monitored with chloroform (1), methanol (2), *N*,*N*-dimethyl formamide (3), tetrahydrofuran (4) and water (5) and solvent free (6) as reaction solvents conditions. Results depicted in Figure 4(B), shows that under solvent free conditions excellent yield is obtained in one fourth time as compared to solvated conditions. It established the fact that solvent free condition is best suitable for the synthesis of bis(indolyl)methanes in the presence of La$_2$O$_3$/RGO as catalyst.

After the model reaction we have tried various substituted aldehydes as summarized in Table I. Different type of substituents i.e., electron withdrawing (entry 2–10) and electron donating (entry 11–12) has shown different trend in reaction time. Electron withdrawing groups tends to stabilize the iminium ion formed during the reaction, hence helping the reaction to complete in lesser time. On the other hand electron donating groups destabilize the iminium ion which causes increment in reaction
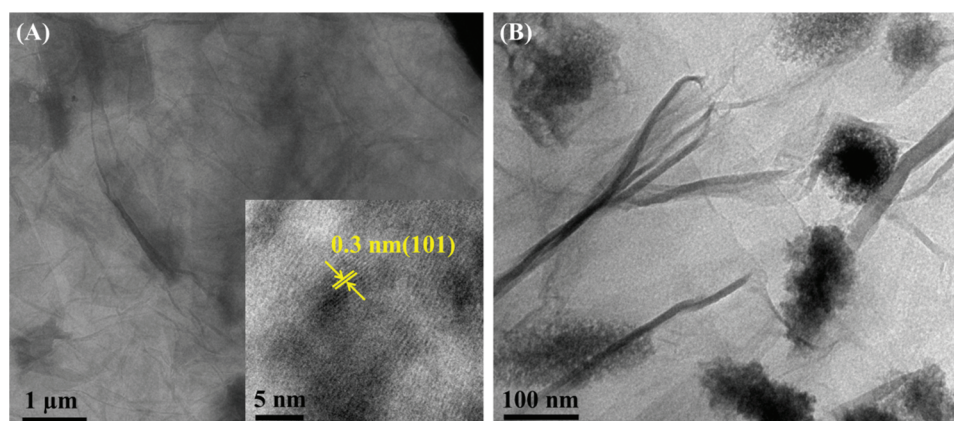

Figure 3. (A) TEM image of GO with sheet like morphology, inset showing HRTEM image of La$_2$O$_3$/RGO showing La$_2$O$_3$ crystal plane of ⟨101⟩, (B) TEM image of La$_2$O$_3$/RGO showing La$_2$O$_3$ nanoclusters over the surface of RGO.
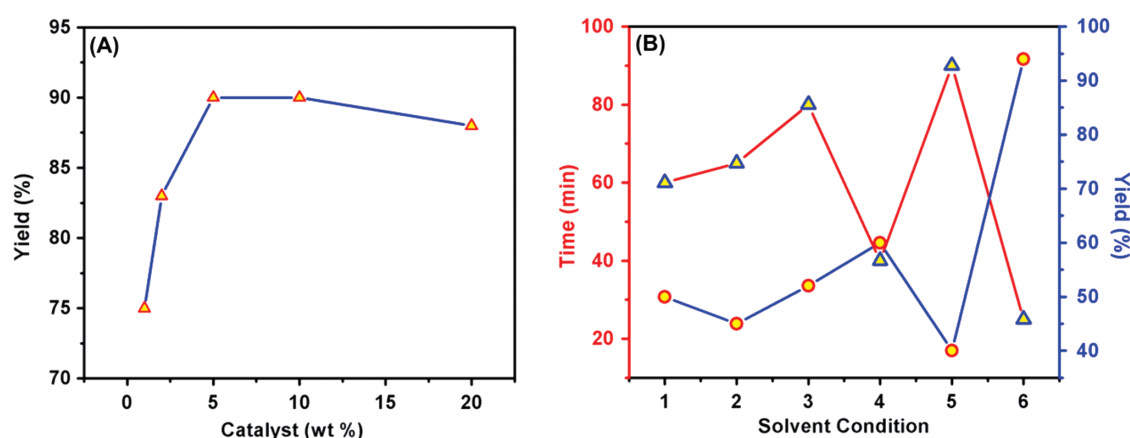
Figure 4. (A) Effect of the amount of catalyst for synthesis of bis(indolyl)methane for 25 minutes, (B) Effect of solvents on the synthesis of bis(indolyl)methanes with different solvents as chloroform (1), methanol (2), *N,N*- dimethyl formamide (3), tetrahydrofuran (4) and water (5) and solvent free (6).

completion time. Substituents with respect to their positions have also shown different behavior in terms of yields and time. *Para* substituted aldehydes has taken less time in reaction completion as compared to *ortho*, and *meta* substituted. This decrease in reaction completion time is due to the greater stability provided by the substituent at *para* position as compared to *ortho* and *meta* position.

Reusability studies are also performed, where first catalyst is recovered very easily by simple filtration, washed with chloroform, and dried in oven for 2 hours at 80 °C. Afterwards it was reused for next run of reaction with benzaldehyde and indole. This process is repeated for three more times to quantify the reusability of catalyst. A high yield of 82, 80, 76 and 73% is obtained in four repeat reactions for reusability studies.

We also proposed mechanism for the catalytic synthesis of bis(indolyl)methane in the presence of La₂O₃/RGO (Fig. 5), where iminium ion formation takes place from aldehyde and first indole molecules in the presence of active sites O^{2-} and La^{3+} in La₂O₃/RGO, and an intermediate gets stabilized on catalyst. Second indole atom

attacks this intermediate to form another intermediate on the catalyst surface and a final rearrange in intermediate gives desired product.

For the comparison purpose we also used only graphene oxide as catalyst for the same model reaction. Table II summarize the comparision of La₂O₃/RGO with others catalyst reported in literature and La₂O₃/RGO has been found to be the best among these catalysts.

3.2. Spectroscopic Data of the Synthesized Compounds

3,3′-Bis(indolyl)-phenylmethane (1): IR (KBr, cm⁻¹): 3397, 3051, 1457, 1335, 1217, 1092, 1008, 745; 1H NMR (CDCl3, 400 MHz) δ: 5.87 (*s*, 1H), 6.64 (*s*, 2H), 6.96–7.00 (*t*, 2H, *J* = 8.05 Hz), 7.14–7.20 (*m*, 2H,), 7.25–7.27 (*m*, 4H), 7.32–7.38 (*m*, 5H), 7.90 (br, 2H, NH). 13C NMR (CDCl3, 100 MHz): 40.15, 110.97, 119.28, 119.97, 121.85, 123.56, 126.10, 127.19, 128.15, 128.68, 136.22, 144.25.

3,3′-Bis(indolyl)-3-flurophenylmethane (2): IR (KBr, cm⁻¹): 3402, 3051, 1606, 1459, 1338, 1220, 1095, 1011, 745; 1H NMR (CDCl3, 400 MHz) δ: 5.82 (*s*, 1H), 6.61–6.63 (*m*, 2H), 6.97 (*t*, 2H, *J* = 8.05 Hz), 7.03 (*t*, 2H, *J* = 8.05 Hz), 7.14–7.18 (*m*, 3H), 7.26–7.29 (*m*, 2H), 7.31–7.35 (*m*, 4H), 7.82 (br, 2H, NH); 13C NMR (CDCl3, 100 MHz): 39.41, 102.54, 111.15, 114.88, 119.29, 119.81, 122.06, 123.53, 124.82, 129.91, 130.16, 131.45, 135.89, 136.64, 139.56, 143.56.

3,3′-Bis(indolyl)-4-flurophenylmethane (3): IR (KBr, cm⁻¹): 3404, 3053, 1601, 1455, 1335, 1215, 1092, 1009, 741; 1H NMR (CDCl3, 400 MHz) δ: 5.86 (*s*, 1H), 6.61–6.62 (*m*, 2H), 6.92 (*t*, 2H, *J* = 8.05 Hz), 6.99 (*t*, 2H, *J* = 8.05 Hz), 7.14–7.19 (*m*, 2H), 7.26–7.29 (*m*, 2H), 7.33–7.37 (*m*, 4H), 7.80 (br, 2H, NH); 13C NMR (CDCl3 100 MHz): 39.42, 102.59, 111.05, 114.82, 119.27, 119.82, 122.00, 123.51, 129.99, 136.65, 139.64, 143.84.

3,3′-Bis(indolyl)-3-chlorophenylmethane (4): IR (KBr, cm⁻¹): 3406, 3020, 2927, 1687, 1582, 1419, 1215, 1194,

Table I. Effect of different substituents on the rate of the reaction, in the synthesis of bis(indolyl)methanes.

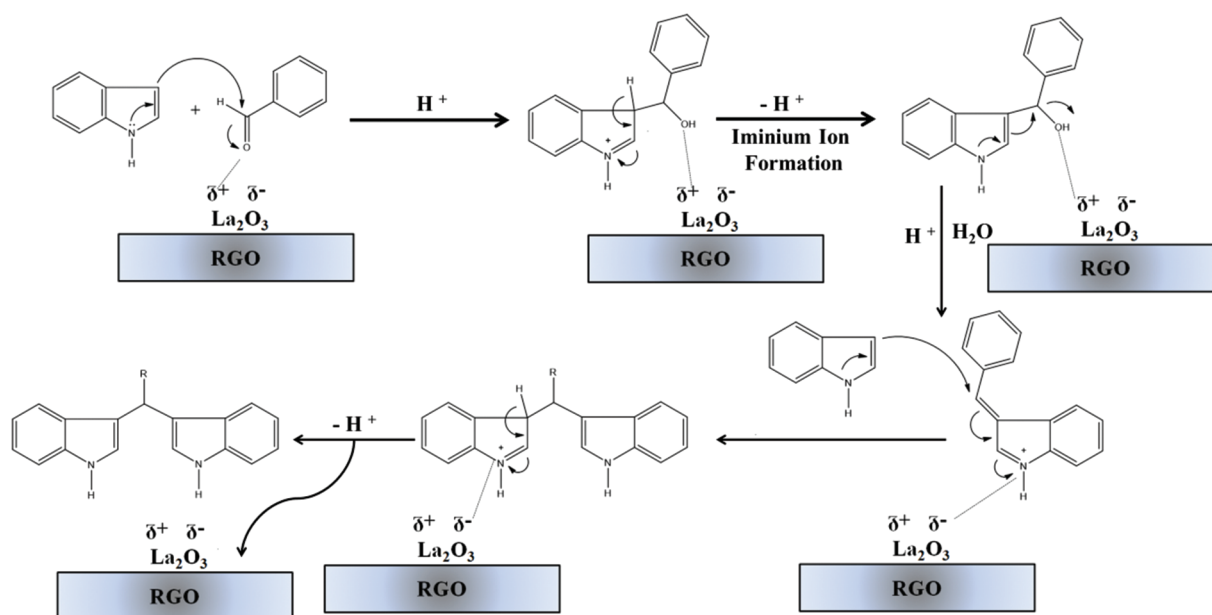|				Mp (°C)	
Entry	R	Time (min)	Yield (%)	Experimental	Lit.
1	H	35	96	122–124	125–126
2	3-F	40	89	81–84	82–83
3	4-F	25	93	78–79	80–82
4	3-Cl	35	94	77–79	78–80
5	4-Cl	25	93	80–82	77–81
6	3-Br	30	92	112–114	115–117
7	4-Br	25	94	107–111	110–112
8	2-NO₂	40	96	137–140	140–141
9	3-NO₂	35	95	217–219	218–220
10	4-NO₂	25	97	210–223	220–221
11	4-CH₃	45	89	94–98	95–97
12	4-C₂H₅	60	88	177–180	179–181

Figure 5. Proposed mechanism of catalytic synthesis of bis(indolyl)methane.

1093, 741; 1H NMR (CDCl3, 400 MHz) δ: 5.86 (s, 1H), 6.65 (s, 2H), 7.01 (t, 2H, $J = 8.05$ Hz), 7.16–7.19 (m, 3H), 7.20–7.22 (m, 2H,) 7.34 (d, 2H, $J = 7.32$ Hz), 7.37 (d, 2H, $J = 7.32$ Hz), 7.92 (br, 2H, NH); 13C NMR (CDCl3, 100 MHz): 39.92, 110.63, 114.49, 118.88, 119.27, 119.87, 120.12, 122.90, 123.71, 124.32, 126.83, 130.57, 131.64, 133.61, 136.61, 146.14.

3,3′-Bis(indolyl)-4-chlorophenylmethane (5): IR (KBr, cm^{-1}): 3404, 3052, 1594, 1455, 1215, 1089, 1011, 742; 1H NMR (CDCl3, 400 MHz) δ: 5.87 (s, 1H), 6.66 (s, 2H), 7.02 (t, 2H, $J = 8.05$ Hz), 7.15 (t, 2H, $J = 8.05$ Hz), 7.22–7.24 (m, 2H), 7.26–7.29 (m, 2H), 7.34 (d, 2H, $J = 7.32$ Hz), 7.36 (d, 2H, $J = 7.32$ Hz), 7.92 (br, 2H, NH); 13C NMR (CDCl3, 100 MHz): 39.58, 102.59, 110.98, 111.08, 119.15, 119.32, 119.79, 122.05, 123.56, 126.84, 128.33, 130.04, 131.75, 136.64, 142.52.

3,3′-Bis(indolyl)-3-bromophenylmethane (6): IR (KBr, cm^{-1}): 3407, 3052, 1585, 1455, 1336, 1214, 1091, 1009, 741; 1H NMR (CDCl3, 400 MHz) δ: 5.84 (s, 1H), 6.61–6.62 (br, 2H), 7.01 (t, 2H, $J = 8.05$ Hz), 7.12 (t, 2H, $J = 8.05$ Hz), 7.17 (d, 2H, $J = 7.32$ Hz), 7.26 (d, 1H, $J =$

7.32 Hz), 7.32–7.37 (m, 4H), 7.48–7.49 (m, 1H), 7.89 (br, 2H, NH); 13C NMR (CDCl3, 100 MHz): 39.90, 111.08, 118.89, 119.35, 119.71, 119.92, 122.36, 123.63, 124.34, 126.81, 127.34, 129.33, 129.80, 131.66, 136.62, 146.44.

3,3′-Bis(indolyl)-4-bromophenylmethane (7): IR (KBr, cm^{-1}): 3408, 3055, 1490, 1455, 1335, 1216, 1092, 1009, 743; 1H NMR (CDCl3, 400 MHz) δ: 5.87 (s, 1H), 6.63–6.64 (br, 2H), 6.98 (t, 2H, $J = 8.05$ Hz), 7.15 (t, 2H, $J = 8.05$ Hz), 7.19 (d, 1H, $J = 7.32$ Hz), 7.27 (d, 1H, $J = 7.32$ Hz), 7.33 (d, 4H, $J = 7.32$ Hz), 7.37 (d, 2H, $J = 7.32$ Hz), 7.88 (br, 2H, NH); 13C NMR (CDCl3, 100 MHz): 40.01, 110.99, 119.19, 119.67, 119.90, 121.88, 123.57, 126.10, 127.03, 128.18, 128.68, 136.63, 143.95.

3,3′-Bis(indolyl)-2-nitrophenylmethane (8): IR (KBr, cm^{-1}): 3403, 3058, 1620, 1531, 1457, 1420, 1222, 1082, 1001, 746, 690. 1H NMR (CDCl3, 400 MHz) δ: 5.94 (s, 1H), 6.61 (s, 2H), 7.02 (t, 2H, $J = 8.05$ Hz), 7.22 (t, 2H, $J = 8.05$ Hz), 7.41 (t, 4H, $J = 8.05$ Hz), 7.43 (t, 1H, $J = 8.05$ Hz), 7.68 (d, 1H, $J = 7.32$ Hz), 7.99 (br, 2H, NH), 8.04 (d, 1H, $J = 7.32$ Hz), 8.23 (s, 1H); 13C NMR (CDCl3 100 MHz): 39.17, 110.23, 111.25, 118.29,

Table II. Comparison of bis(indolyl)methane preparation with different catalysts at various reaction conditions.

Entry	Catalyst (amount)	Conditions	Time (h)	Yield (%)	Reusable catalyst (Yes/No)	Ref.
1	Polyindole salt (20 wt%)	Methanol/r.t.	3	98	Yes	[28]
2	[Et$_3$NH][H$_2$PO$_4$] (0.4 g)	[Et$_3$NH][H$_2$PO$_4$]/100 °C	10 min	97	No	[29]
3	Al(HSO$_4$)$_3$ (0.636 g)	Ethanol/r.t.	2.5	92	No	[30]
4	Ferric dodecyl sulfonate (1 mol%)	H$_2$O/r.t.	6	90	No	[31]
5	CuBr$_2$ (10 mol%)	MeCN/r.t.	30 min	94	No	[32]
6	FeCl$_3 \cdot$6H$_2$O (5 mol%)	[omim][PF$_6$]/r.t.	1.5	98	Yes	[33]
7	SBA-15/SO$_3$H (70%)	CCl4/70 °C	24	52	Yes	[34]
8.	Graphene oxide	Solvent free	35 min	36	Yes	Present work
9	La$_2$O$_3$/RGO	Solvent free	35 min	96	Yes	

119.67, 119.78, 121.49, 122.18, 123.67, 123.89, 124.14, 126.89, 129.18, 134.57, 136.78, 137.98, 146.79.

3,3′-Bis(indolyl)-3-nitrophenylmethane (9): IR (KBr, cm⁻¹): 3404, 3052, 1616, 1521, 1453, 1415, 1218, 1092, 1006, 741, 692. 1H NMR (CDCl3, 400 MHz) δ: 5.93 (*s*, 1H), 6.61 (*s*, 2H), 7.05 (*t*, 2H, *J* = 8.05 Hz), 7.14 (*t*, 2H, *J* = 8.05 Hz), 7.31 (*t*, 4H, *J* = 8.05 Hz), 7.40 (*t*, 1H, *J* = 8.05 Hz), 7.60 (*d*, 1H, *J* = 7.32 Hz), 7.91 (br, 2H, NH), 8.04 (*d*, 1H, *J* = 7.32 Hz), 8.15 (*s*, 1H); 13C NMR (CDCl3 100 MHz): 39.47, 111.11, 118.21, 119.56, 119.89, 121.22, 122.59, 123.60, 123.68, 124.71, 126.84, 129.34, 130.98, 134.93, 136.71, 146.33.

3,3′-Bis(indolyl)-4-nitrophenylmethane (10): IR (KBr, cm⁻¹): 3404, 3052, 1521, 1346, 1212, 1093, 742; 1H NMR (CDCl3, 400 MHz) δ: 5.97 (*s*, 1H), 6.66–6.68 (*m*, 2H), 6.98–7.02 (*t*, 2H, *J* = 8.05 Hz), 7.16–7.20 (*m*, 2H), 7.30–7.38 (*m*, 4H), 7.42–7.49 (*m*, 2H), 7.99 (br, 2H, NH), 8.10–8.13 (*m*, 2H); 13C NMR (CDCl3, 100 MHz): 39.88, 111.25, 117.44, 119.58, 119.68, 122.35, 123.64, 126.66, 129.57, 136.55, 146.44.

3,3′-Bis(indolyl)-4-methylphenylmethane (11): IR (KBr, cm⁻¹): 3413, 3044, 1457, 1339, 1213, 1092, 1008, 738; 1H NMR (CDCl3, 400 MHz) δ: 2.32 (*s*, 3H), 5.84 (*s*, 1H), 6.62–6.63 (*s*, 2H), 6.98 (*t*, 2H, *J* = 8.05 Hz), 7.08 (*d*, 2H, *J* = 7.32 Hz), 7.16 (*t*, 2H, *J* = 8.05 Hz), 7.22 (*d*, 2H, *J* = 7.32 Hz), 7.33 (*d*, 2H, *J* = 7.32 Hz), 7.40 (*d*, 2H, *J* = 7.32 Hz), 7.84 (br, 2H, NH); 13C NMR (CDCl3, 100 MHz): 21.05, 39.71, 110.98, 119.13, 119.81, 119.91, 121.82, 123.51, 127.04, 128.52, 128.87, 135.45, 136.61, 140.93.

3,3′-Bis(indolyl)-4-ethylphenylmethane (12): IR (KBr, cm⁻¹): 3404, 3051, 1480, 1453, 1211, 1095, 1010, 740; 1H NMR (CDCl3, 400 MHz) δ: 1.30 (*t*, 3H), 2.39 (*q*, 2H), 5.82 (*s*, 1H), 6.61 (*s*, 2H), 7.01 (*t*, 2H, *J* = 8.05 Hz), 7.09 (*d*, 2H, *J* = 7.32 Hz), 7.17 (*t*, 2H, *J* = 8.05 Hz), 7.24 (*d*, 2H, *J* = 7.32 Hz), 7.36 (*d*, 2H, *J* = 7.32 Hz), 7.40 (*d*, 2H, *J* = 7.32 Hz), 7.81 (br, 2H, NH); 13C NMR (CDCl3, 100 MHz): 16.11, 26.05, 39.70, 110.92, 119.15, 119.84, 119.95, 121.86, 123.54, 127.08, 128.54, 128.88, 135.46, 136.66, 140.97.

4. CONCLUSION

A novel La₂O₃/RGO catalyst for the synthesis of bis(indolyl)methanes under solvent free conditions at room temperature has been reported. This procedure offersseveral advantages such as easy catalyst separation from the reaction medium, a simple workup procedure, catalyst reusability, short reaction time, and good to excellent product yields. In addition, the use of environmentally benign catalysts and avoidance of hazardous organic solvents are important features of this method.

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