Titanium Dioxide/Graphene Oxide Nanocomposites as Heterogeneous Catalysts for the Esterification of Benzoic Acid with Dimethyl Carbonate

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Dedicated to Prof. K. Pitchumani on the occasion of his 60th birthday

Graphene oxide (GO) was prepared by modified Hummers' method starting from commercially available graphite. Different amounts of titanium dioxide nanoparticles (TiO₂) were loaded on the sheets of GO to obtain titanium dioxide/graphene oxide (TiO₂/GO) nanocomposites. The as-synthesized 5 wt% TiO₂/GO nanocomposite was characterized by UV/Vis spectroscopy, photoluminescence spectroscopy, FTIR, powder X-ray diffraction, scanning electron microscopy, transmission

electron microscopy, and atomic force microscopy techniques. The catalytic activity of the 5 wt% TiO₂/GO nanocomposite was evaluated in the esterification of benzoic acid using dimethyl carbonate (DMC) as a green methylating agent. Furthermore, the activity of this nanocomposite for the conversion of benzoic acid was higher than that of the parent GO, TiO₂, TiO₂/activated carbon, and TiO₂/graphite.

Introduction

Graphene has received considerable attention for the fabrication of graphene-containing inorganic composites due to its unique electronic properties,^[1] high transparency,^[2] flexible structure, and large specific surface area.^[3] Graphene oxide^[4] (GO) is obtained by an extensive oxidation of graphene thus resulting a graphene nanosheet with carboxylic acid, hydroxy, and epoxy groups attached to the surface. On the other hand, it has been observed that the oxidation of graphene could cause structural distortion of graphene.^[5] Furthermore, it has been reported that decorating inorganic materials with modified graphene could enhance their electronic^[6] and photocatalytic properties.^[7] Recently, GO and related materials have been reported as catalysts for many organic transformations, thus contributing to the development of green and sustainable chemical processes.^[8-12]

 TiO_2 is one of the well-established photocatalysts under UV light.^[13,14] However, it has also been widely explored in the research areas of energy conversion^[15] and degradation^[16] of pollutants due to its cost-effective nature and chemical stability. In recent years much effort has been devoted to developing visible-light-active TiO_2 by heteroatom doping because of its obvious merit in solar energy utilization.^[17] In addition, modify-

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[b] B. Sakthivel, Prof. A. Dhakshinamoorthy School of Chemistry, Madurai Kamaraj University Palkalai Nagar Madurai-21, Tamil Nadu 625021 (India) E-mail: admguru@gmail.com ing TiO_2 with a carbonaceous substance on the surface can also induce visible-light-responsive activity. $^{[18]}$

Methyl halides, dimethyl sulfate, and diazomethane are commonly employed reagents for methylation reactions.^[19] The alkylation of a carboxylic acid to the corresponding methyl ester is a fundamental transformation in organic chemistry.^[20] A number of reports including microwave-mediated processes^[21,22] and zeolite-based catalysts^[23-25] have been developed for the esterification reaction. Dimethyl carbonate^[26] (DMC) is one of the alternative reagents for the replacement of dimethyl sulfate and methyl halides in the development of green chemical processes for the methylation of aromatics.^[27-29]

In recent years, TiO₂/GO composites^[30] have been used as heterogeneous photocatalysts for the degradation of pollutants including Methylene blue,^[31] Methyl orange^[32] and Rhodamine B.^[33] In contrast, TiO₂/GO nanocomposites have not been used as heterogeneous catalysts for organic transformations. Hence, in the present study we wish to report that TiO₂/GO can be used as a heterogeneous catalyst for the esterification of benzoic acid with DMC as a green methylation reagent. Also, we wish to compare the activity of TiO₂/GO with that of bare TiO₂ and GO under identical reaction conditions.

Results and Discussion

The 5 wt% TiO₂/GO nanocomposite was characterized by UV/ Vis spectroscopy, photoluminescence spectroscopy, FTIR spectroscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) techniques. GO provides a plat-

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form to anchor TiO_2 with a uniform distribution through the presence of various oxygen functionalities.

UV/Vis spectroscopy

The normalized UV/Vis spectrum of GO (Figure 1 a) shows absorption bands at 230 and 298 nm. The absorption peak at 230 nm is attributed to the π - π * transition of C=C bonds while the band at 298 nm corresponds to the n- π * transition of C=O bonds, which further confirms the presence of carbonyl groups. Further, the normalized UV/Vis spectrum of the 5 wt% TiO₂/GO nanocomposite (Figure 1 b) clearly shows the presence of the same bands with no possible shift implying that the loading of TiO₂ is very low in the 5 wt% TiO₂/GO nanocomposite sample.



Figure 1. Normalized UV/Vis spectra of a) GO and b) 5 wt % TiO_2/GO nanocomposite.

Photoluminescence spectroscopy

The photoluminescence (PL) spectra of GO and the 5 wt% TiO₂/GO nanocomposite are shown in Figure 2. The PL spectrum of GO shows an emission peak centered at 365 nm corresponding to the crystalline graphitic C(sp²) network in GO. In contrast, the PL spectrum of the 5 wt% TiO₂/GO nanocomposite exhibits a similar emission pattern with a slight decrease in its intensity, which is attributed to the interaction between GO and TiO₂.^[34]



Figure 2. PL spectra of a) GO and b) 5 wt % TiO₂/GO nanocomposite.

FTIR spectroscopy

FTIR measurements were carried out to explore the functional groups present in the as-synthesized GO and 5 wt% TiO₂/GO nanocomposite samples. Figure 3 shows the FTIR spectrum of GO with stretching frequencies at 1229 and 1061 cm⁻¹ corresponding to epoxide (C–O) functional groups and the stretching frequency for carboxyl (C=O) groups is observed at 1728 cm⁻¹. The FTIR spectrum of 5 wt% TiO₂/GO nanocomposite typically shows no difference except lower intensities. These studies clearly indicate that various oxygen groups such as hydroxyl, carboxyl, epoxy, alkoxy, and carbonyl groups are observed in the FTIR spectra of both GO and 5 wt% TiO₂/GO nanocomposite samples.



Figure 3. FTIR spectra of a) GO and b) 5 wt % TiO₂/GO nanocomposite.

Powder XRD analysis

Powder XRD measurements were carried out to explore the structural integrity of the as-prepared GO and 5 wt% TiO₂/GO nanocomposite samples (Figure 4). The powder XRD pattern of GO exhibits a peak at 10.44° corresponding to the basal spacing of 0.846 nm, which is a characteristic peak supporting the existence of GO. Furthermore, the obtained diffraction peak corresponds to the 002 plane, suggesting the formation of GO. On the other hand, the 5 wt% TiO₂/GO nanocomposite shows peaks at 10.44, 25, and 45° representing the 002, 101, and 200 planes , respectively. The new peaks appearing at 25 and 45° correspond to the anatase phase of TiO₂ loaded onto GO nanosheets. Also, it is interesting to note that the intensity of the peak at 10.44° is higher for GO than for 5 wt% TiO₂/GO, thus suggesting that the oxygen-containing functional groups are involved in the stabilization of TiO₂.

Morphological studies

The morphological and layered features of the as-prepared samples were examined through TEM, SEM, and AFM microscopic techniques. The fact that the TiO_2 nanoparticles are on





Figure 4. Powder XRD analysis of a) GO and b) 5 wt % TiO_2/GO nanocomposite.

the surface of GO indicates a strong interaction between GO and TiO_2 via chemisorption. Also, the particle size and some of the characteristic features of GO sheets will also be explored.

SEM analysis

SEM measurements were carried out to navigate the surface features of the as-prepared GO and 5 wt% TiO₂/GO samples (Figure 5). The GO nanosheets show characteristic foldings/ wrinkles which can feasibly accommodate guest molecules. On the other hand, the SEM image of 5 wt% TiO₂/GO sample shows that TiO₂ nanoparticles are arranged on GO uniformly without much agglomeration.



Figure 5. SEM images of a,b) GO and c,d) 5 wt % TiO_2/GO nanocomposite.

TEM analysis

TEM measurements were performed to explore the structural features of the as-synthesised GO and 5 wt % TiO_2/GO nano-

composite to unravel their atomic structure and lattice atoms. Figure 6a shows the presence of nanosheets with wrinkles and edges spreading over a few microns in length indicating a high aspect ratio, and Figure 6b shows the SAED pattern for GO. The TEM image of the 5 wt% TiO₂/GO nanocomposite (Figure 6 c) reveals that TiO₂ nanoparticles are uniformly distributed on the surface of GO. In contrast, Figure 6e provides the TEM image of the 5 wt % TiO₂/GO nanocomposite after the catalytic reaction with a slight applomeration of TiO₂ nanoparticles as well as stacking of GO. The incorporation of TiO₂ onto the GO lattice prevents heavy agglomeration or restacking of GO nanosheets. Furthermore, TiO₂ nanoparticles are found to be distributed uniformly on the surface of GO. The nanoparticles deposited onto the sheets are found to be in the range of 5-10 nm. The SAED patterns of the 5 wt % TiO₂/GO nanocomposite (Figure 6 d,f) correspond to a diffused ring pattern indicating the polycrystalline nature of the sample.



Figure 6. TEM images of a) GO, c) 5 wt % TiO₂/GO nanocomposite, e) 5 wt % TiO₂/GO nanocomposite after the catalytic reaction; the respective SAED patterns are given in (b,d,f).

AFM analysis

AFM measurements were carried out to explore the quality of exfoliation of GO nanosheets, to authenticate the presence of TiO₂ nanoparticles on the sheets, and to determine the thickness of the as-prepared nanosheets. AFM topograph and line profiles of GO and 5 wt % TiO_2/GO nanocomposite are given in Figure 7 a,b and Figure 8 a,c, respectively. All these AFM images confirm the sheet-like morphology. The line profiles of GO and $5 \mbox{ wt \% TiO}_2/GO$ suggest that the thickness of GO is 1 nm and the thickness of 5 wt% TiO2/GO nanosheets corresponds to one monolayer with TiO₂ nanoparticles and ranges between 5 and 10 nm. Figure 8 a shows the AFM image of 5 wt % TiO₂/GO which clearly reveals the existence of TiO₂ nanoparticles, which appear as discrete bright dots homogenously distributed on the surface of the GO. Further, the root mean square (rms) values of roughness of GO and 5 wt % TiO₂/GO are found to be 0.25 and 0.94 nm, respectively. An increase in the rms value of roughness for the latter material compared to GO suggests the interaction of TiO₂ nanoparticles with GO. Also the surface of





Figure 7. AFM images of GO (a,b); c) base plane corresponding to the line in (b).



Figure 8. AFM images of 5 wt % TiO₂/GO nanocomposite (a,c); b,d) base planes corresponding to the lines in (a,c).

the GO nanosheets is found to be very smooth with base plane and edges. These basal plane and edges are very effective for high performance in many applications. In particular, edges are highly significant sites for the anchoring of guest molecules. Among the various edge states of graphene-based systems such as hexagonal, rectangular, and triangular edges, it is observed that monolayer GO nanosheets with a highly distorted rectangular lattice exhibit large area.

Catalytic performance

The catalytic activity of TiO₂/GO was evaluated for the esterification of benzoic acid using DMC as a green methylating agent. A control experiment in the absence of catalyst afforded no product, while in the presence of catalyst, product formation is observed. Furthermore, no and low conversions of benzoic acid were observed at 90 and 140°C, respectively. The reaction between benzoic acid and DMC using GO and TiO₂ (7-9 nm) as catalysts resulted in conversions of 27 and 34% after 8 h, respectively. On the other hand, commercially available TiO₂ (Degussa) was also examined as a catalyst and 29% conversion of benzoic acid was observed after 8 h at 180°C. Furthermore, the conversion of benzoic acid gradually increased with the amount of TiO₂ and reaches an optimum level. For instance, 2 wt % TiO₂/GO afforded 29% conversion of benzoic acid after 8 h. In contrast, the 5 wt % TiO₂/GO catalyst drastically enhanced the conversion of benzoic acid to 78% conversion after 8 h. Under identical reaction conditions, the activities of $3 \text{ wt}\% \text{ TiO}_2/\text{GO}$ and $6 \text{ wt}\% \text{ TiO}_2/\text{GO}$ were examined and their activities were similar to those of $2 \text{ wt} \% \text{ TiO}_2/\text{GO}$ and 5 wt %TiO₂/GO, respectively. On the other hand, a noticeable conversion to 70% of benzoic acid was achieved using 10 wt % TiO₂/ GO as catalyst under the optimized reaction conditions. Further increasing the loading of TiO_2 on GO to 20 wt % TiO_2/GO did not enhance the reaction further (74% conversion) after 8 h. On the other hand, the conversion of benzoic acid was decreased to 48% when the DMC volume reduced from 1 to 0.5 mL using 5 wt% TiO₂/GO as catalyst. In contrast, the conversion of benzoic acid using 5 wt% TiO₂/GO was not further enhanced when the volume of DMC was increased to 1.5 and 2 mL. Also, 0.5 mL of DMC was considered to be an optimal volume for a uniform dispersion of substrate and catalyst.

Under identical reaction conditions, the catalytic activity of 5 wt% TiO₂/GO was compared with that of other carbon materials such as graphite and activated carbon containing same the weight percentage of TiO₂ and the observed results are summarized in Table 1. Conversions of 39 and 23% of benzoic

Table 1. Catalytic data for the esterification of benzoic acid using DMC and various catalysts. ^[a]						
Entry	Catalyst	TiO ₂ loading [mol%]	DMC [mL]	t [h]	<i>Т</i> [°С]	Conv. [%] ^[b]
1	GO ^[c]	-	1.0	8	180	27
2	TiO ₂	2.5	1.0	8	180	34
3	TiO ₂ (Degussa)	2.5	1.0	8	180	29
4	2 wt % TiO ₂ /GO	0.25	1.0	8	180	29
5	5 wt% TiO ₂ /GO	0.62	1.0	8	180	78
6	10 wt% TiO ₂ /GO	0.62	1.0	8	180	70
7	5 wt % TiO ₂ /GO	0.62	0.5	8	180	48
8	5 wt% TiO ₂ /GO	0.62	1.0	8	140	2
9	20 wt % TiO ₂ /GO	2.5	1.0	8	180	74
10	5 wt % TiO ₂ /AC	0.62	1.0	8	180	39
11	5 wt% TiO ₂ /graphite	0.62	1.0	8	180	23
12	$TiO_2 + GO$	-	1.0	8	180	51
[a] Reaction conditions: benzoic acid (100 mg), catalyst, DMC, required time, and temperature. [b] Determined by GC. [c] 10 mg was used.						

acid were achieved with 5 wt% TiO₂/AC and 5 wt% TiO₂/ graphite, respectively. In contrast, the physical mixture of GO (9 mg) and TiO₂ (1 mg) showed 51% conversion under identical reaction conditions; this conversion is lower than that with 5 wt% TiO₂/GO but higher than with 5 wt% TiO₂/AC and 5 wt% TiO₂/graphite as catalysts. These experiments clearly indicate the superior activity of 5 wt % TiO₂/GO due to the synergism between GO and TiO₂ as well as optimal loading of TiO₂ to achieve maximum conversion.

One of the advantages of using heterogeneous catalysts is the reusability after their recovery from the reaction mixture. In this context, the catalyst reusability was also checked under



the optimized reaction conditions (Table 1, entry 5). After the required time, the autoclave was removed from the muffle furnace and cooled to room temperature. The required volume of acetonitrile (3 mL) was added to the reaction slurry and stirred for 3 h. The analysis of the reaction mixture recovered from the first reuse of the 5 wt % TiO₂/GO catalyst showed 32% conversion, which is lower than with fresh catalyst. It is very clear that the activity of this catalyst is limited and further investigations are required to improve the stability of this catalytic system. This decrease in catalytic activity was hypothesized to be due to the agglomeration of TiO₂ or partial stacking of GO nanosheets during the catalytic reaction. This was further confirmed by subjecting 5 wt% TiO₂/GO to TEM analysis and the observed results are given in Figure 6. It can be seen clearly that the particle size increased (13-18 nm) considerably after the reaction (Figure 6e). Furthermore, powder XRD analyses of fresh and used 5 wt % TiO₂/GO catalysts reveal the broadening of peaks corresponding to TiO₂ (Figure 9). These results clearly suggest that preserving the particle size of TiO₂ as well as GO in a single monolayer surface is highly essential to achieve high conversion. A leaching experiment under the optimized reaction conditions would provide evidence of the catalyst stability, but it is not performed here as one of the reactants (DMC) is in the gas phase. Further work is in progress to explore this synergetic behavior in other organic transformations.



Figure 9. Powder XRD analysis of a) fresh 5 wt % TiO_2/GO and b) the used 5 wt % TiO_2/GO catalyst.

Conclusion

In summary, GO/TiO₂ nanocomposites were prepared and characterized by UV/Vis spectroscopy, photoluminescence spectroscopy, FTIR spectroscopy, powder XRD, SEM, TEM, and AFM techniques. The catalytic activity of the 5 wt% TiO₂/GO nanocomposite was compared with that of GO and bare TiO₂ and performance of the former is superior to that of its parents in the esterification of benzoic acid using DMC as a green methylating agent. Furthermore, 5 wt% TiO₂/GO exhibited higher activity than 5 wt % TiO₂/AC and 5 wt % TiO₂/graphite as catalysts. Among the various nanocomposites of TiO₂/GO examined for catalytic activity, 5 wt % TiO₂/GO exhibits the highest activity under the present experimental conditions. The catalyst could not be reused and suitable evidence was given for the catalyst deactivation.

Experimental Section

Materials

Graphite powder and DMC were purchased from Sigma Aldrich. Potassium permanganate (KMnO₄, 99%), sulfuric acid (H₂SO₄ 98%), hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), benzoic acid, and DMC were purchased from Alfa Aesar. Titanium dioxide nanoparticles (7–9 nm) were purchased from SRL. All these materials were of analytical grade and used as received without further purification.

Synthesis of TiO₂/GO nanocomposite catalyst

GO was synthesized via modified Hummers' procedure.^[35] In a typical synthesis, 0.1 g of GO was suspended in 200 mL of deionized water. After this mixture was stirred for about 10 min, it was sonicated for 2 h to exfoliate GO into nanosheets. Further 0.005 g of TiO₂ (5 wt%) was suspended in 200 mL of deionized water through sonication for 10 min. This suspension was then mixed with the dispersed GO and stirred for 24 h to obtain a homogenous distribution of TiO₂ on GO nanosheets. This mixture was then washed with deionized water and centrifuged at 5000 rpm for 15 min to remove unwanted residues and the resulting material was dried at 100 °C. A similar procedure was also adopted for the synthesis of 5 wt% TiO₂/AC and 5 wt% TiO₂/graphite using activated carbon (AC) and graphite instead of GO as the support.

Instrumentation details

The morphological studies were carried out using HR-TEM (Tecnai, operated at 200 KV accelerating voltage), SEM [JEOL (JSM-5610LV)] and AFM (noncontact mode, A100 SGS, APE Research). Powder XRD was measured using a Brucker D8 Advance X-Ray diffractometer with 2θ ranging from 10 to 80°, CuK_{α} (1.540 Å). FTIR measurements were performed using a Bruker instrument in the range of 400–4000 cm⁻¹. Further, the absorbance and emission spectra were carried out with a Shimadzu-UV 2450 double-beam spectrophotometer at room temperature in the wavelength range of 190–900 nm and with a RF-5301 spectrofluorometer in the range of 300–800 nm, respectively.

Catalytic studies

In general, benzoic acid (0.1 g), TiO₂/GO, and DMC were added into a Teflon container and stirred manually for uniform distribution. This suspension was kept in an autoclave at 180 °C for the required time as shown in Table 1. The heterogeneous slurry was extracted with acetonitrile by stirring for 3 h and filtered. The filtrate was washed with water and the organic layer was dried over anhydrous sodium sulfate. Product was characterized by GC-MS and ¹H NMR spectroscopy.



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