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Three-dimensional graphene oxide: A promising green and sustainable catalyst for oxidation reactions at room temperature

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Three-dimensional graphene oxide foam (3DGO) was found to be a highly efficient and recyclable catalyst for the oxidation of thioanisole. We found that 3DGO is more efficient than 2DGO, and that the efficiency increases with the number of cycles for 3DGO, in opposition to the 2D counterpart.

Nowadays, the negative impact induced by the presence of organosulfur compounds in petroleum products is well established, both from industrial and environmental reasons.[1] Firstly, they are responsible for the poisoning of the catalysts and for the corrosion of parts of the internal combustion engines in petrochemical industries. Secondly, the SOx emissions from organosulfur combustion are responsible by air, water, and soil pollution, being harmful to health, besides promoting acid rains.[2] Therefore, the deep desulfurization of liquid fuels has become a worldwide challenge.[1,3] In recent years, oxidative desulfurization (ODS) has become a promising and emerging alternative to conventional hydrodesulfurization (HDS) technology used by most of the oil refineries all over the world.[2-5] Many oxidants have been tested in several ODS methodologies such as peroxyacids, $NaIO_4$, MnO_2, CrO_3, SeO_2, *tert*-butyl or cumene hydroperoxides, PhIO, O_3 and O_2, being H_2O_2 the most commonly used, due to its efficiency and to obvious environmental reasons.[1]

Graphene oxide (GO) has sparked huge interest among researchers in several areas of chemistry, namely those interested in the development of new sustainable metal-free heterogeneous catalysts.[6-8] GO is an intermediate product to achieve mass production of graphene by solution chemistry, and holds carboxylic acid groups at the edges and hydroxyl as well as epoxide groups at the basal planes, which makes it a promising 2D nanoplatform for further chemical functionalization giving rise to new materials. The use of GO as a catalyst is attractive from a practical perspective owing to the abundance of natural carbon sources, as well as the catalyst low density, extensive chemical functionalization, hydrophilicity, low cost, and simplicity of preparation.

The potential catalytic properties of GO have been explored in some reactions,[9-11] namely hydration of alkynes,[12] oxidation,[6,12,13] oxidative coupling,[10] Friedel-Crafts addition,[14] Aza-Michael addition,[15,16] polymerization,[17] and photo-oxidation.[18]

Recently, the focus of scientists' attention has moved towards more elaborated systems such as chemically modified graphene taking profit of the oxygen functionalities present at its surface,[19] giving rise to chemically modified GO, and therefore expanding the range of reactions that can be catalysed by this carbocatalyst.[20,21] On the other hand, the preparation of a three-dimensional (3D) graphene nanostructure is believed to be one step closer to more extensive applications.[22-26] The large surface areas of these foams arouse our interest, and we decided to study its ability to catalyse the oxidation of an organosulfur compound, namely thioanisole, in comparison to its 2D counterpart.

First, GO sheets were prepared by the oxidation of graphite powder under harsh oxidizing conditions.[19] The GO sheets were then thoroughly washed and purified by dialysis. A 3DGO foam structure was obtained after the hydrothermal treatment of an aqueous suspension of GO sealed in a Teflon-lined autoclave at 180 °C for 12 h (Fig. 1a).
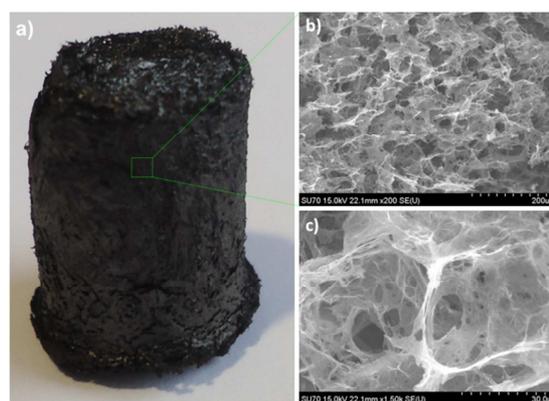

Fig. 1 (a) Photograph of the 3DGO foam; (b) and (c) SEM images of 3DGO internal microstructure with different magnifications.

This material is an open-cell foam with a 3D porous network as imaged by scanning electron microscopy of the freeze-dried samples (Fig. 1b and 1c). The characteristic N_2 adsorption–desorption

isotherm for 3DGO has an H3 hysteresis loop, which is typical for plate–like particles (Fig. S1, S.I.). Moreover, the curve reveals the existence of both micro and mesoporosity, while the distinct upward turn at p/p^0 close to 1 implies additional macroporosity.[27] This is in accordance with the pore size distribution obtained (Fig. S2, S.I.). The determined BET surface area (SA) for 3DGO was of 210 m^2 g^{-1}. No reproducible SA values for 2DGO were obtained. It is known that upon drying, GO sheets form dense aggregates with complex structure and porosity,[28] thus hindering the nitrogen molecules to penetrate into the interlayer space of dried GO.

XPS analysis was used to evaluate the degree of unsaturation and oxyfunctionalization of the two materials. The 3DGO presents a sp^2/sp^{3}C ratio of 1.32 against 0.28 for the 2DGO, which is indicative of a reduction process during the hydrothermal treatment. Although some carbonyl and carboxylic groups are still present in the 3DGO structure, the C-O/C-OH groups initially present at 2DGO (54.89 at%) are predominantly removed during the foam formation (Fig. S3 and Table S1, S.I.).

For the catalytic experiments, both 2DGO and 3DGO nanostructures were compared. For a typical oxidation experiment the substrate (thioanisole, 0.3 mmol), the catalyst (2DGO or 3DGO, 4.0 mg), and the internal standard (chlorobenzene, 0.3 mmol) were placed in CH$_3$CN, for a total reaction volume of 2.0 mL. Three 31 μl aliquots (0.3 mmol each) of the oxidant, a H$_2$O$_2$ 30 % (w/w) aqueous solution, were added at the beginning, after 24 h, and after 48 h of reaction. The course of the oxidation reactions was followed by GC-FID using chlorobenzene as the internal standard. Both 2DGO and 3DGO materials were recovered by centrifugation, carefully washed with different solvents (CH$_3$CN, CH$_2$Cl$_2$, and acetone, in this order) and dried at open air for two days, before its reutilization under similar conditions.

The results of the oxidation reactions with the two heterogeneous catalysts (2DGO and 3DGO) are summarized in Table 1. The 3DGO foam proved to be a more efficient catalyst in the oxidation of thioanisole affording the corresponding sulfoxide and sulfone at very high conversion. In fact, the results clearly show that on the first cycle of the oxidation reaction the conversion is ~65% for 2DGO and ~87% for 3DGO. More interestingly, the conversion using 3DGO increases after recycling the material (97.2% of conversion for the 2nd cycle, 97.0% for the 3rd cycle and 99.7% for the 4th cycle), in opposition to the 2DGO (34.6% of conversion for the 2nd cycle, 28.2% for the 3rd cycle and 29.5% for the 4th cycle).

FTIR analysis of the 3DGO catalyst before and after the catalysis reactions (Fig. 2) shows an increment of oxygen functional groups on its surface, especially carboxylic groups, and a decrease on C=C bonds during the catalytic process. XPS analysis after the 4th cycle shows effectively an increase on the carbonyl/carboxylic groups, concomitantly to a decrease on the C=C sp^2, and a reciprocal increment on the sp^3 carbons after the catalysis reactions (Table 2). In fact, the sp^{2}C/sp^{3}C and the C/O ratios both decrease, suggesting an increase of oxygen contents on carbon structure after catalysis reactions. This increase can be due to the availability of oxygen species in the reaction medium, and seems to have an important contribution in the oxidation of organosulfur compounds. Although 2DGO has a higher percentage of oxygen on its structure than the 3DGO foam (Fig. S2 and Table S1, S.I.), the conversion of thioanisole into the corresponding oxidation products is less efficient for 2DGO. This suggests that the thioanisole oxidation reaction is promoted by the carbon double bonds that react with H$_2$O$_2$ by forming oxygen functional groups on the 3DGO surface and oxygen free radicals able to oxidise the organosulfur compound, which is in accordance with the literature.[9] Still, we have tested the presence of radicals by adding known radical scavengers (KI and 1,4-benzoquinone) to the reaction medium, specific to scavenge the •OH

and •O$_2^-$ radicals, respectively.[29] The results show that no conversion of thioanisole occurs by adding KI and only 23% of conversion is observed by adding 1,4-benzoquinone. This point out to two very important conclusions: 1) the oxidation of thioanisole with H$_2$O$_2$ as oxidant, using 3DGO as a heterogeneous catalyst, seems to be a radicalar reaction, and 2) the radicals responsible for the oxidation reaction process seem to be essentially the •OH. Moreover, in the blank experiments performed in the presence of 3DGO, but without the addition of H$_2$O$_2$ or alternatively, just in the presence of the oxidant, no products from the oxidation of thioanisole were detected.

We propose that the formation of •OH may occur by the homolytic cleavage of H$_2$O$_2$ mediated by 3DGO with the formation of oxygen functional groups on its surface (C-OH on Fig. 2). This is in accordance with some H$_2$O$_2$ non-productive degradation by 3DGO, evidenced by the increase on the oxygen content of the 3DGO material after 4 cycles (Table 2) concomitantly to the decrease of sp^{2}C (Table 2). This was confirmed by the titration of H$_2$O$_2$ during the catalytic reactions (Fig. S4, S.I.).
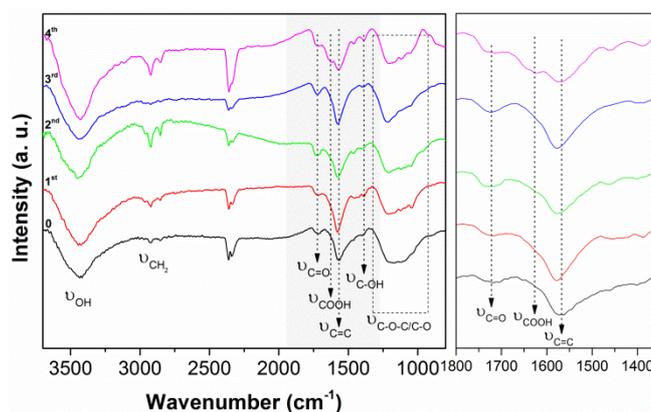

Fig. 2 FTIR spectra of 3DGO (0), and after the 1st, 2nd, 3rd and 4th catalytic cycles in the oxidation of thioanisole with aqueous H$_2$O$_2$.

The •OH radicals are then able to oxidize the organosulfur compound at room temperature. The products' selectivity is similar for both catalysts, always with higher selectivity for sulfoxide over sulfone (Table 1). In general, 3DGO is more selective for the sulfoxide than 2DGO along the 4 cycles. The higher selectivity for sulfone in the case of 2DGO can also be related to the higher amount of oxygen functional groups on the GO surface, namely hydroxyl groups, potentially available to form •OR radicals and the subsequent over-oxidation of the sulfoxide to the sulfone.

The 3DGO catalyst was also tested under similar conditions for the oxidation of diphenyl sulfide, an organosulfur compound typically present in fuels. The conversion of diphenyl sulfide is ~45%, which is lower than for thioanisole (87%), probably due to higher steric hindrance.

The 3DGO catalysts stands out from other metal-free catalysts not only for its high catalytic activity (>90%) for the oxidation of thioanisole, but also by presenting the particularity to increase the catalytic activity with the number of cycles (Table 1). In fact, similar catalytic studies using fullerenes,[30,31] periodic mesoporous silicas,[32] and cyclodextrins[33] showed lower conversion values.
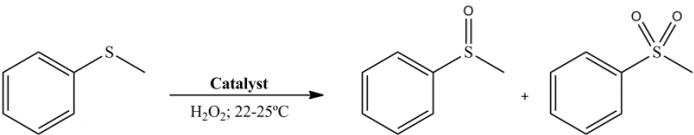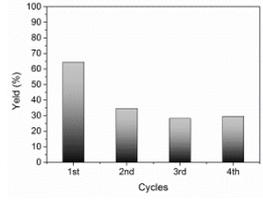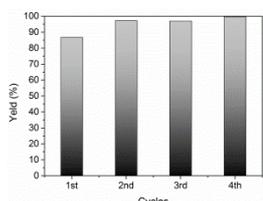
In conclusion, some advantages can be pointed out in the reactions using this 3DGO foam, since it is a simple, metal-free, and inexpensive catalyst, additionally to its facile recovery from the reaction media and subsequent reutilization. Contrarily to the results usually found in the literature, requiring high ratios (60-400 wt%) of GO for typical oxidative reactions,[9,10] the ratio of 3DGO used in the present reactions is very low, around 11 wt% relative to the

substrate, and the reactions are run at room temperature, two major gains of the present system.

Table 1. Oxidation of thioanisole with aqueous H_2O_2 catalysed by 2DGO and a 3DGO foam[*]

Reaction scheme	Catalyst	Conversion (%)[#]	Cycle[□]	Selectivity[#]	
				S=O	SO₂

Catalyst	Cycle	S=O	SO₂
2DGO	1st	60.5	39.5
	2nd	79.7	20.3
	3rd	80.6	19.4
	4th	74.6	25.4
3DGO	1st	91.2	8.8
	2nd	89.8	10.2
	3rd	74.8	25.2
	4th	93.1	6.9

[*]Reaction conditions: thioanisole (0.3 mmol), catalyst (2DGO or 3DGO, 4.0 mg), internal standard (chlorobenzene, 0.3 mmol); CH_3CN, for a total reaction volume of 2.0 mL; three 31 μL aliquots (0.3 mmol each) of H_2O_2 30 % (w/w) aqueous solution were added at the beginning, after 24 h, and after 48 h of reaction; room temperature.
[□]Each cycle have the duration of 72 h.
[#]Detemined by GC with chlorobenzene as the IS.

Table 2. XPS analysis of 3DGO before catalysis and after the 4th cycle

Chemical Bonds	3DGO		3DGO (after 4th cycle)	
	BE (eV)	AC (at.%)	BE (eV)	AC (at.%)
sp²C	284.4	46.1	284.4	43.1
sp³C	285.3	35.0	285.3	38.5
C-O/C-OH	-	< 0.1	-	< 0.1
C=O/COOH	288.1	4.23	288.2	11.9
π-π*	289.7	14.68	290.9	6.6
Ratio sp²C/sp³C	1.32		1.12	
Ratio C/O	2.10		1.92	

Notes and references

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