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Additional Information

**Tuning the active sites in reduced graphene oxide by hydroquinone functionalization  
for aerobic oxidation of thiophenol and indane**

Cristina Vallés-García,<sup>a</sup> Eva Montero-Lanzuela,<sup>a</sup> Sergio Navalon,<sup>a,\*</sup> Mercedes Álvaro,<sup>a</sup>

Amarajothi Dhakshinamoorthy,<sup>b,\*</sup> Hermenegildo Garcia<sup>a,c,d,\*</sup>

<sup>a</sup> Departamento de Química, Universitat Politècnica de València, C/ Camino de Vera s/n, 46022, Valencia, Spain

<sup>b</sup>School of Chemistry, Madurai Kamaraj University, Madurai-625 021, Tamil Nadu, India.

<sup>c</sup> Instituto Universitario de Tecnología Química, CSIC-UPV, Universitat Politècnica de València, Av. de los Naranjos, Valencia 46022, Spain

<sup>d</sup>Center of Excellence in Advanced Materials Research, King Abdulaziz University, Saudi Arabia

S.N.: sernaol@doctor.upv.es; A.D.: E-mail: admguru@gmail.com; H.G.: hgarcia@qim.upv.es

H.G. Tel: +34 387 70 00 EXT 73572

**Abstract**

Sustainable reduced graphene oxide (rGO) carbocatalysts for molecular oxygen activation have been developed based on the concept that chemical reduction of graphene oxide to rGO introduces functional groups that can become active sites. Thus, a series of rGOs prepared using hydroquinone, hydrazine and ascorbic acid as reducing agents have been tested as catalysts in the aerobic oxidations of thiophenol and indane. In both oxidation reactions, rGO reduced by hydroquinone (rGO-HQ) exhibited the highest catalytic activity and stability. A high selectivity of ol/one (90%) at around 30 % indane conversion in the absence of transition metals was achieved. Reusability test showed that the activity of rGO-HQ is mostly retained in

three consecutive runs. Quenching experiments indicated that the reaction proceeds with the generation of hydroxyl and carbon centered radicals. The higher activity of rGO-HQ was attributed to the covalent anchoring of some hydroquinone molecules on rGO during the chemical reduction. This knowledge has been used to develop a hydroquinone-functionalized Merrifield resin with enhanced catalytic activity for O<sub>2</sub> activation. The present work illustrates the potential to develop rGO carbocatalysts with an increased density of active sites by selecting the appropriate reducing agent during the chemical reduction of graphene oxide.

**Keywords:** Aerobic oxidation; reduced graphene oxide; hydroquinone; thiophenol; indane; sustainable catalysis;

## 1. Introduction

Reduced graphene oxide (rGO) is among the most widely used carbocatalysts due to its availability and the catalytic activity to promote a large variety of reactions, including oxidations,[1-3] reductions[4-7] and acid catalyzed reactions,[8, 9] among others.[10-13] rGO can be conveniently obtained in multigram scale by exfoliation of graphite oxide and subsequent chemical reduction of single layer graphene oxide (GO).[14, 15]

Due to the mild reaction conditions, hydrazine in aqueous solution has been among the most widely used reducing agents, but other chemicals such as ascorbic acid[16, 17] and hydroquinone have also been used to convert GO into rGO.[18-21] The mechanism of the reduction of GO into rGO has been studied in some detail and it has been shown that the resulting rGO can incorporate in its lattice during its formation some groups from the reducing agent. These functional groups present in rGO would depend on the nature and conditions of the reduction from GO.[22-25]

As consequence of the specific functionalization introduced during its formation, rGO could exhibit distinctive catalytic activity depending on the conditions employed for the reduction of GO.[26, 27] The active sites of rGO are structural defects and adventitious functional groups and, therefore, from the catalytic point of view, the possibility to introduce certain functional groups represents an opportunity to obtain rGO with the optimal catalytic activity for each process. Thus, it has been recently shown that the rGO obtained by hydroquinone reduction (rGO-HQ) of GO is a more efficient catalyst for benzylamine oxidation than other two rGO solids obtained using other reducing agents.[25] This higher activity catalytic activity was justified as derived from the presence of quinone-like units covalently anchored on the rGO sheet during the conversion of GO into rGO.

Continuing with this line of research and considering that hydroquinone/quinone moieties have been proposed as active centres for aerobic oxidations, it would be of interest to extend the above methodology to other process showing that rGO-HQ outperforms twin rGO prepared by other reductive treatments. Accordingly, the present study shows that rGO-HQ is the most active among other four related rGOs to promote the aerobic oxidation of thiols to disulfides and the benzylic oxidation of indane. The role of hydroquinone as active centres in the process has been supported by preparing a Merrifield resin with covalently anchored hydroquinone units and observing that also this resin behaves as a solid catalyst for those processes.

## **2. Experimental Section**

### **2.1 Materials**

The reactants and reagents used in this work were purchased from Sigma-Aldrich and were of analytical or HPLC grade. In particular, the Merrifield resin (100-200 mesh) is a chloromethylpolystyrene-divinylbenzene co-polymer. Substrates used in this study like thiophenol, indane, hydroquinone and other reducing agents were purchased from Sigma Aldrich. These reactants were used without further purification/modification processes.

### **2.2 Catalyst preparation**

The materials employed in this work are from the same batches than those recently published by some of us.[25] The detailed experimental procedures for the preparation and their characterization are described in our recent work.[25] GO was prepared by the Hummers method. In brief, commercial graphite powder was subjected to a chemical oxidation in the presence of  $\text{KMnO}_4$ ,  $\text{KNO}_3$  and  $\text{H}_2\text{SO}_4$  and the resulting solid was subsequently exfoliated to obtain GO by ultrasonication. Later, GO was transformed into reduced graphene oxide (rGO) either by thermal or chemical methods. The thermally reduced GO (rGO-T) was obtained by heating GO (200 mg) in a tubular furnace under argon atmosphere at 200 °C for 4 h.[25]

Further, the as-prepared GO was also reduced with a series of chemical reducing agents like hydroquinone (HQ), hydrazine (HZ) and ascorbic acid (ASC) and the resulting solids were named as rGO-HQ, rGO-HZ and rGO-ASC, respectively. In addition, the rGO-HQ solid was further submitted to a thermal treatment under inert atmosphere at 300 or 700 °C for 4 h and the samples labelled as rGO-HQ-300 and rGO-HQ-700, respectively.

Hydroquinone-functionalized Merrifield resin has been prepared via synthesis of Williamson. Briefly, the resin as fine powder (500 mg) was suspended in dimethylsulfoxide (20 mL) by sonication (450 W, 20 min) using a round-bottom flask (100 mL). Then, hydroquinone (500 mg, 4.55 mmol) and NaOH (4.55 mmol) were added to the resin suspension. The mixture was heated at 140 °C for 16 h and, then, cooled down to room temperature. The solid was recovered by filtration (Nylon membrane, 0.45 µm) and washed under stirring with Milli-Q under neutral pH. The resin was further washed in a Soxhlet system using acetonitrile as solvent for 16 h. Finally, the resin was dried in an oven at 100 °C for 16 h. The same washing procedure has been applied to the as-received Merrifield resin before use.

### **2.3 Instrumentation**

X-ray photoelectron (XP) spectra were recorded on a SPECS spectrometer equipped with a MCD-9 detector using a monochromatic Al ( $K\alpha= 1486.6$  eV) X-ray source. Spectra deconvolution has been performed with the CASA software using the C 1s peak at 284.4 eV as binding energy reference. Attenuated total reflectance-Fourier transform infrared (ATR-FT-IR) measurements were carried out with a Bruker Tensor 27 spectrophotometer. Diffuse reflectance UV-visible spectra of previously compressed powders were recorded using a Cary 5000 Varian spectrophotometer having an integrating sphere.

### **2.4 Aerobic oxidation of thiophenol**

In a typical reaction, thiophenol (1 mmol), 20 mg of catalyst and 2 mL of acetonitrile were placed in a 25 mL of round bottom flask. This was connected to oxygen balloon and the reaction was maintained in oxygen atmosphere. This reaction mixture was placed in a preheated oil bath kept at 70 °C. The reaction was monitored by GC and the oxidized product was confirmed by GC-MS.

## **2.5 Aerobic oxidation of indane**

In a 25 mL of round bottom flask, 20 mg of catalyst was placed and indane (20 mmol) was added to this flask. This reaction flask was connected to oxygen atmosphere. This heterogeneous reaction mixture was placed in a preheated oil bath maintained at 130 °C. The reaction progress was monitored by sampling at different time intervals using nitrobenzene as internal standard. The oxidized products were confirmed by co-injection with authentic samples and analyzing by GC-MS.

Quenching experiments with (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and dimethylsulfoxide (DMSO) were performed under identical conditions in the presence of 20 mol % of these quenchers. Further, reusability tests were conducted under identical conditions described above except by the use of recovered catalyst. After the catalytic reaction, the solid was separated by filtration, washed with acetonitrile and dried at 90 °C. This solid was reused in subsequent cycles with the fresh reactants.

The catalytic data presented in this work correspond to the values of at least two independent experiments.

## **3. Results and discussion**

### **3.1. Catalysts under study**

One of the main objectives of this work is to study the influence of different active sites present in rGO on the resulting catalytic activity for the aerobic oxidation of thiophenol and for the solvent-free oxidation of indane. Active site engineering on rGO has been performed by reducing GO to rGO using different reducing agents like thermal treatment (rGO-T), hydroquinone (rGO-HQ), hydrazine hydrate (rGO-HZ) and ascorbic acid (rGO-ASC). The detailed preparation of these catalysts and their characterization data have been recently reported.[25] Figure 1 illustrates the procedures employed to obtain different rGO samples employed in this study having different functional groups. Table S1 in the supplementary material summarizes the experimental procedure employed for the preparation of the graphene-based catalysts employed in this study together with some characterization data obtained from elemental analysis and XPS.[25] These results indicate that both thermal and chemical methods are convenient treatments to promote the reduction of GO as revealed by an increase of the carbon content and concomitant decrease of the oxygen proportion in the rGO samples. Further characterization of the rGO-HQ sample by thermogravimetric analysis, FT-IR, <sup>13</sup>C-NMR and temperature programmed desorption (TPD) coupled to a mass-spectrometer (TPD-MS) analysis confirmed the presence of hydroquinone-like moieties (8 wt %) covalently grafted to the rGO sheet.[25] Furthermore, rGO-HQ thermal treatment under argon atmosphere at 300 or 700 °C results in the removal of oxygen-functional groups including the hydroquinone-like moieties especially at 700 °C. In order to demonstrate the differences in the catalytic activity of rGO solid catalysts depending on its reduction conditions, two model aerobic oxidation reactions of thiophenol and indane were selected and the observed results are discussed below.



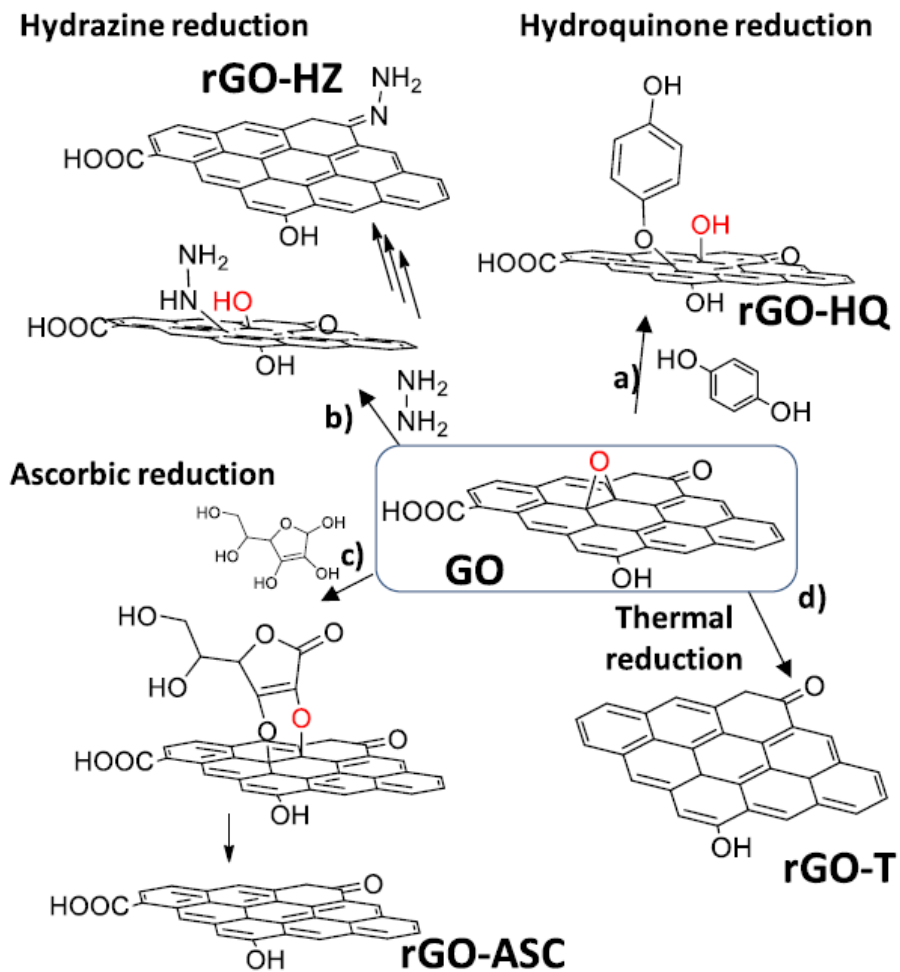


Figure 1.

For comparison, the Merrifield resin has been functionalized with hydroquinone units in basic medium forming an ether bond. The presence of hydroquinone covalently anchored through the ether bond to the Merrifield resin was confirmed by ATR-FT-IR spectroscopy by observing two new FT-IR bands appearing at 3,330 and 1,225  $\text{cm}^{-1}$  attributable to the presence of phenolic and phenyl ether groups, respectively (Figure S1a). In agreement with the FT-IR data, diffuse reflectance UV-Vis spectrum of the hydroquinone-functionalized Merrifield resin exhibits a red shift absorbance respect to the pristine resin due to the presence of hydroquinone molecules anchored through an ether bond (Figure S1b).

### 3.2. Aerobic oxidation of thiophenol

Selective aerobic oxidation of thiophenol to its corresponding 1,2-diphenyldisulfide is an important reaction in organic chemistry (Figure 2). This oxidation reaction has often catalyzed by various transition metals and replacing these transition metals by carbocatalysts would certainly contribute to the green chemistry principles by using renewable catalysts. Further, this reaction is also one of the model reactions to compare various catalysts prepared by different methods.

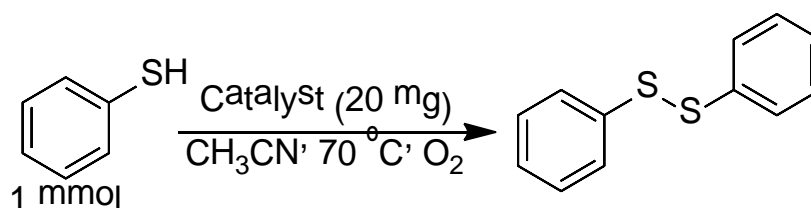


Figure 2.

Hence, this reaction is selected to rank the series of catalysts prepared in this work and the observed catalytic data are given in Table 1. The aerobic oxidation of thiophenol was performed with these solid catalysts in acetonitrile at 70 °C. In the absence of catalyst thiophenol conversion was negligible (Table 1, entry 1). In agreement with previous studies, GO is able to catalyze thiophenol oxidation to its corresponding disulphide (Table 1, entry 2).[28] Interestingly, the catalytic activity for thiophenol conversion strongly depends on the solid employed as catalyst. rGO-HQ solid was the most active catalyst of the series with 78 % conversion after 8 h and full conversion and selectivity after 24 h (Table 1, entry 3). On other hand, the aerobic oxidation of thiophenol in the presence of rGO-HQ-300 and rGO-HQ-700 solid catalysts showed 58 and 14 % conversions under identical conditions (Table 1, entries 4-5). These results indicate that the HQ moieties attached to rGO act as active sites for the aerobic oxidation of thiophenol to 1,2-diphenyldisulfide, while thermally treated rGO-HQ-300 and rGO-HQ-700 resulted in decreased activity due to partial decomposition of the HQ moiety, thus lowering the population of active sites. On the other hand, the activity of rGO-HZ or rGO-

ASC (Table 1, entries 6-7) as catalysts in the conversion of thiophenol to its respective disulfide was 60 and 47 %, respectively, under similar conditions. In addition, the catalytic performance of rGO-T or hydroquinone (Table 1, entries 8-9) as catalysts in the aerobic oxidation of thiophenol was 47 and 12 %, respectively, which is comparatively much lower than the activity observed with rGO-HQ. These results clearly infer that the synergism between rGO and HQ is dominant by generating high density of active sites which are capable of producing the radicals to promote this aerobic oxidation. The most active rGO-HQ catalyst retains most of its initial catalytic activity (Table 1, entry 3) for at least three catalytic cycles (Table 1, entries 10 and 11).

Insert Table 1

In order to rationalize the importance of the presence of HQ-like active sites dispersed in a solid, the HQ molecule was anchored to the so-called Merrifield resin (Figure 3a) and the resulting solid tested as catalyst for the aerobic oxidation of thiophenol. Importantly, the HQ-functionalized Merrifield resin is able to efficiently promote the aerobic oxidation of thiophenol to 1,2-diphenylsulfide (Figure 3b). Control experiments using the as-received Merrifield resin as catalyst results in a negligible thiophenol conversion. These results highlight the role of anchored HQ moieties on a support as active sites to promote molecular O<sub>2</sub> activation.

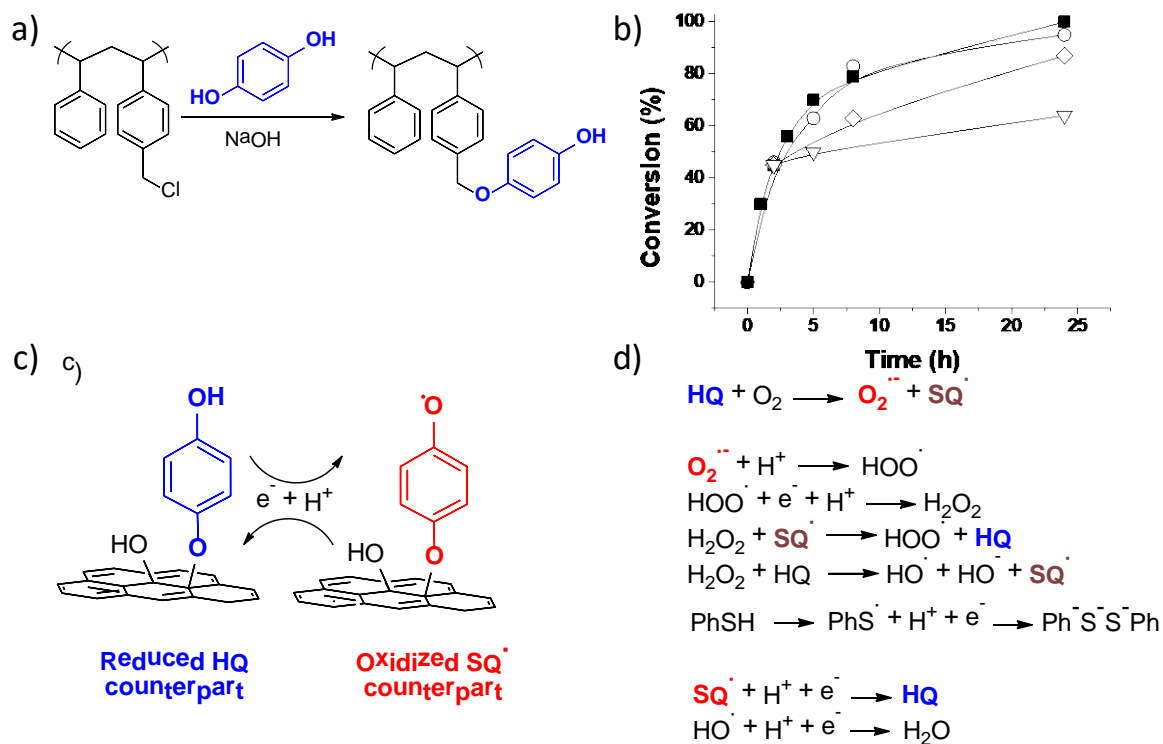


Figure 3.

To obtain some evidence about the reaction pathway for the aerobic oxidation of thiophenol using rGO-HQ as carbocatalyst some additional experiments including the hot filtration test and the selective quenching of hydroxyl radicals have been performed (Figure 3b). In the hot filtration test, once the reaction is initiated (43 % conversion) the catalyst is removed by filtration and the reaction supernatant allowed to react under the standard reaction. It was observed that the reaction only partially stopped (Figure 3b). This observation is in agreement with the general radical reaction mechanism involving the formation of thyl radicals during the aerobic oxidation of thiophenol to 1,2-diphenylsulfoxide. In order to get some evidences of the presence of oxygen radical species a quenching experiment using DMSO as selective hydroxyl radical scavenger has been carried out. Thus, if once the reaction is initiated, DMSO is added the conversion of thiophenol considerable decreases, a fact that indirectly indicates the presence of  $\text{HO}^{\cdot}$  in the reaction medium. This experimental data together with the known ability of rGO-HQ to activate  $\text{O}_2$  to  $\text{O}_2^{\cdot -}$ [25] allows to propose a

reaction pathway for the oxidation of thiophenol to 1,2-diphenylsulfide (Figure 3c-d). The HQ moieties in rGO-HQ with the presence of O<sub>2</sub> leads to the formation of O<sub>2</sub><sup>-</sup> that subsequently promotes the formation of reactive oxygen species (ROS). These ROS are responsible of the thiophenol oxidation to thiyl radicals that couple forming 1,2-diphenylsulfide. The catalytic cycle is restored by the reduction of the phenoxy-like radical present in rGO to rGO-HQ.

### 3.3. Aerobic oxidation of indane

The preliminary catalytic results on the aerobic oxidation of thiophenol highlight the efficient role of rGO-HQ solid in which HQ units covalently attached to the rGO sheet act as active sites to promote the aerobic oxidation of thiophenol to 1,2-diphenylsulfide. To further demonstrate the ability of rGO-HQ to activate molecular O<sub>2</sub>, the aerobic oxidation of benzylic hydrocarbon, namely, indane was selected and the aerobic oxidation reactions were performed under solvent-free conditions (Figure 4).

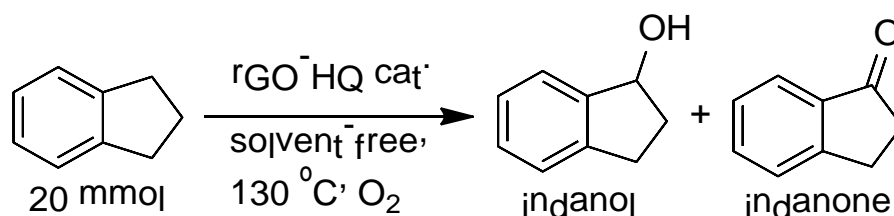


Figure 4.

Aerobic oxidation of benzylic hydrocarbons to their corresponding alcohol/ketone (ol/one) products is one of the challenging industrial processes that often requires transition metal catalysts either in the homogeneous or heterogeneous nature.[29, 30] However, development of sustainable catalytic systems consisting carbocatalysts is one of the appropriate alternatives to the use of transition metal catalysts,[31] without compromising the ol/one selectivity. With these objectives in mind, aerobic oxidation of indane was performed with these solid carbocatalysts under solvent-free conditions. The observed results are summarized in Table 2. In agreement with previous reports, an inefficient indane autoxidation reaction takes

place working at 130 °C under molecular oxygen (1 bar). Importantly, the presence of rGO-HQ in the reaction medium boosted the conversion of indane to 1-indanol and 2-indanone (Figure 5a). As in the case of thiophenol oxidation using rGO-HQ, a thermal treatment of rGO-HQ specially at 700 °C decreases the activity due to the removal of oxygen-functional groups including hydroquinone-like units. These experiments indirectly show that hydroquinone-like groups present in rGO are active sites for O<sub>2</sub> activation and indane oxidation. The use of rGO solids prepared using ASC or HZ as reducing agents or by hydrothermal GO reduction (rGO-T) results in a lower catalytic activity. These data highlights the importance of an adequate GO reduction to obtain a rGO solid with specific functional groups as active sites for the O<sub>2</sub> activation.

Insert Table 2

Importantly, the use of the HQ-functionalized Merrifield resin resulted an active solid for the aerobic oxidation of indane (Figure 5a). Control experiments using the non-functionalized Merrifield resin show an inefficient indane conversion attributed to the autooxidation process using O<sub>2</sub>. These experiments reinforce the possibility to anchor HQ molecules in a solid for its use as heterogeneous catalyst for the molecular oxygen activation.

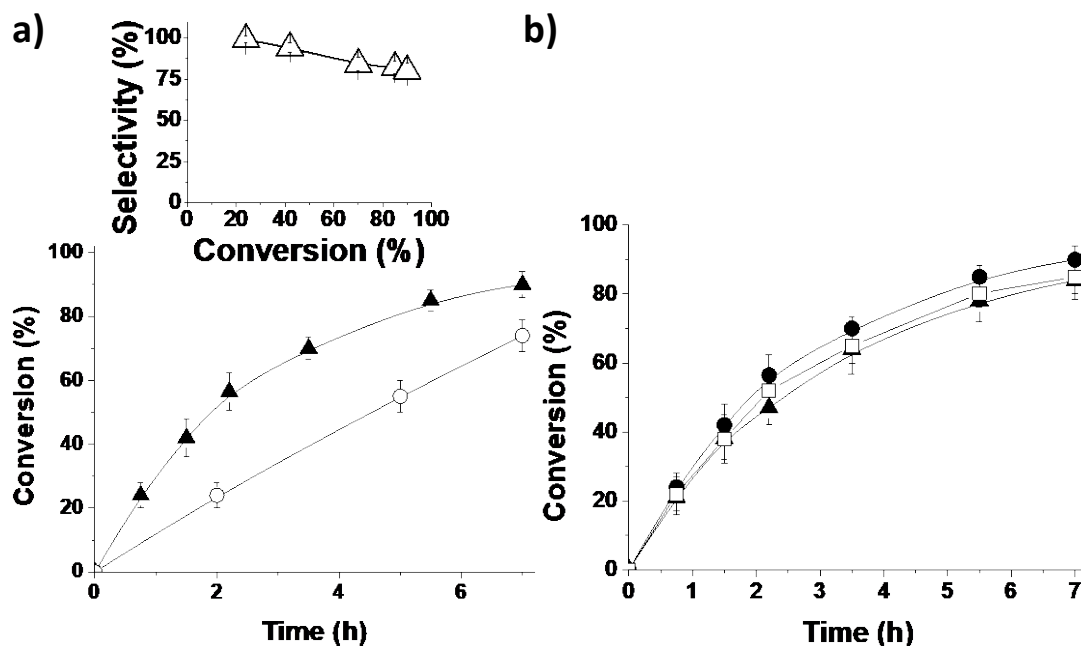


Figure 5.

One of the effective strategies to study the catalyst stability in heterogeneous catalysis is to perform reusability tests under the optimized reaction conditions. In this context, the reusability test of rGO-HQ was performed in the oxidation of indane under oxygen atmosphere in solvent free conditions at 130 °C. The time conversion plot for the aerobic oxidation indane in the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> runs are shown in Figure 5b. It can be seen here that the conversion in these three runs slightly decreases during these three runs. In order to assess this decrease of activity the three times used catalyst was characterized by XPS. Figure 6, shows the XPS C1s and O1s for the fresh and used rGO-HQ catalyst. The XPS C1s and O1s of the three-times used rGO-HQ catalyst shows a decrease of the C=C component, accompanied by an increase of the bands related with the C-OH, C=O and -COO respect to the fresh catalyst. Considering the presence of the hydroquinone-like moieties in the fresh rGO-HQ of about 20.2 % (Figure 6b), it is reasonable to propose their partial oxidation to quinone-like moieties (Figure 6d) and, therefore, decrease of activity.

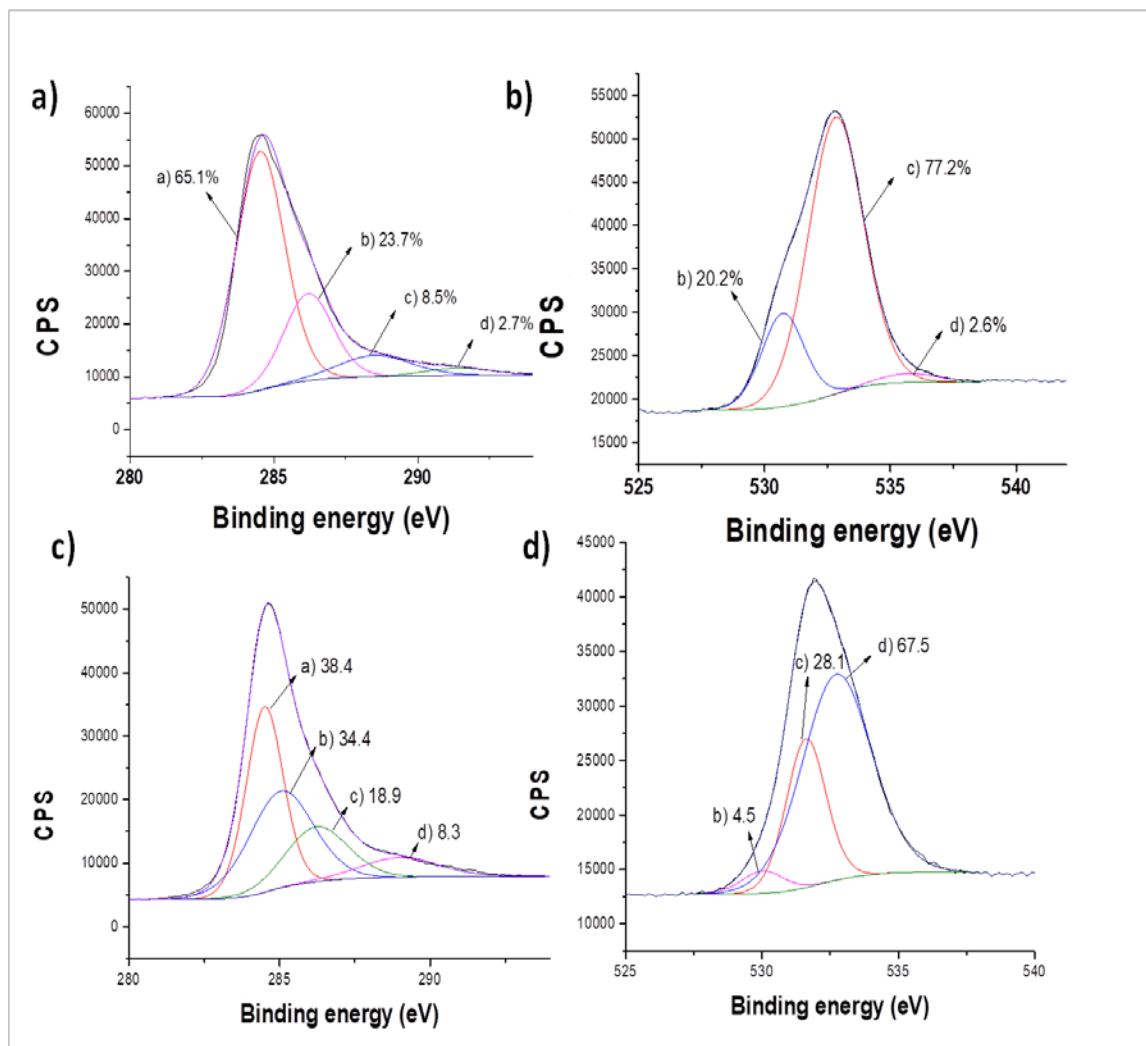


Figure 6.

A series of control experiments were also performed to gain some insights on the reaction pathway for the aerobic oxidation of indane using rGO-HQ as carbocatalyst (Figure 7). A hot filtration test shows that once the reaction has been initiated reaching 23 % conversion, oxidation does not completely stop if the catalyst is removed and the clear supernatant is allowed to react under the same reaction conditions. In addition, if TEMPO is added to the filtered reaction and the mixture is allowed to react further under the same reaction conditions, the reaction completely stops. These experiments indirectly indicate that the reaction proceeds via carbon centred radicals that can be quenched by TEMPO.



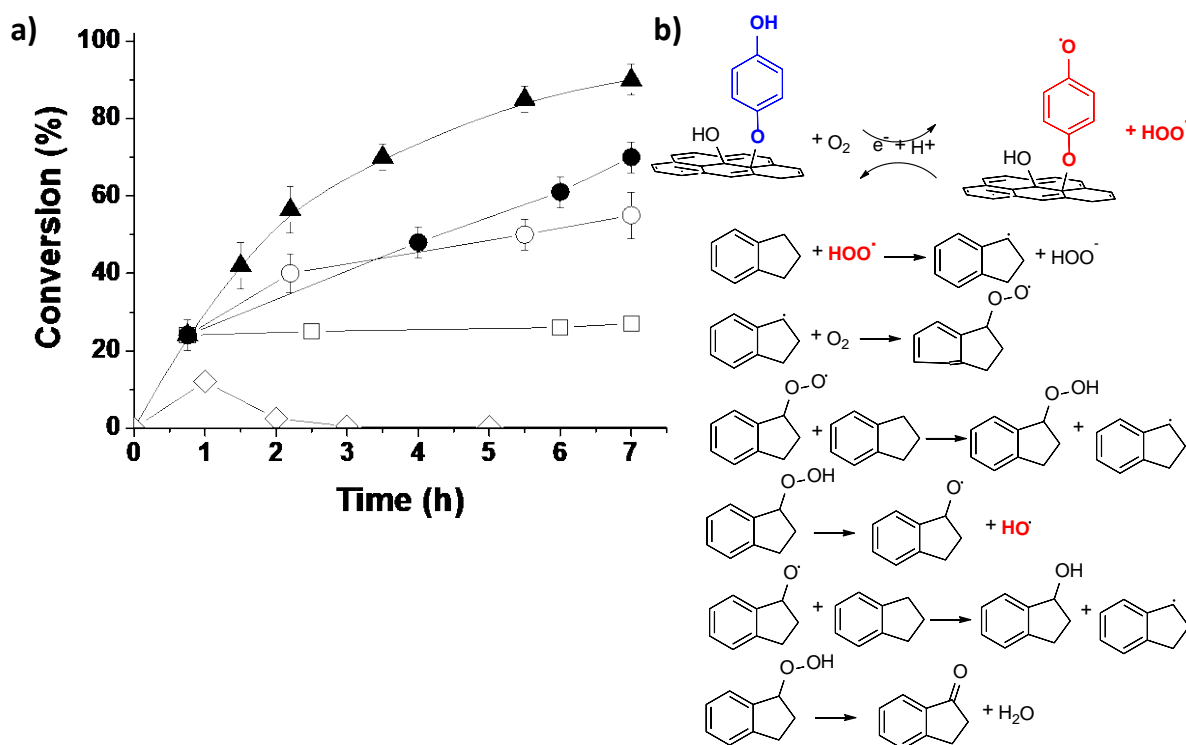


Figure 7.

In order to get further evidence about the reaction mechanism of indane oxidation by rGO-HQ, the possible presence of indanyl hydroperoxide was analyzed. As previously reported, indanyl hydroperoxide can be indirectly determined by monitoring the formation of triphenylphosphine oxide upon addition of triphenylphosphine to the reaction aliquots sampled at different reaction times. It should be noted that indanyl hydroperoxide cannot be directly determined by gas chromatography due to its decomposition to indanol and/or indanone. Using the triphenylphosphine reagent, formation of indanyl hydroperoxide with a selectivity of 12 % at about 32 % conversion was estimated in the presence of rGO-HQ as catalyst. Furthermore, the addition of DMSO to the reaction medium at 30 % conversion results in partial decrease of indane conversion. These catalytic data are attributed to the presence of hydroxyl radicals in the reaction system. Similarly, the initiated reaction (24 % conversion) was completely quenched upon addition of TEMPO to the reaction medium, thus indicating the presence of carbon center radicals in the reaction system.

Based on these observations, Figure 7 shows a plausible reaction pathway for the oxidation of indane with molecular O<sub>2</sub> using rGO-HQ as catalyst. According to a recent report, the formation of free hydroperoxides and semiquinone-like radicals on the rGO-HQ catalyst is proposed to occur in the initial reaction steps. Then, these radicals can react with the benzylic position of indane leading to the formation of indanyl hydroperoxide, indanol and indanone. In addition, indanyl hydroperoxide can decompose leading to the formation of hydroxyl radicals that can be quantified using DMSO as selective radical scavenger. It should be noted that once the reaction is initiated hydroxyl radicals as well as semiquinone-like radicals can promote the benzylic oxidation of indane.

#### **4. Conclusions**

The present study has shown that the catalytic activity of rGO samples prepared by different procedures differs depending on the GO reduction conditions. Considering that among the most active sites for aerobic oxidations on rGO are unsaturated ketones with quinone-like structure, the possibility exists to introduce extra density of these centres by performing the GO reduction to rGO with hydroquinone. Hence, rGO-HQ is the most active catalyst for the two aerobic oxidation reactions like thiophenol and indane. Furthermore, the catalytic activity of thermally treated rGO-HQ is decreased due to the lower density of HQ sites than rGO-HQ catalyst. Rationalization of the nature of the active sites has served not only to engineer the most active rGO, but also to prepare a Merrifield resin with remarkable catalytic activity to promote aerobic oxidations by grafting hydroquinone units in the aryl rings. Overall, this study shows the ability to design metal-free catalysts based on the understanding of the structure of the active sites.

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## References

- [1] M. Masteri-Farahani, S. Mirshekar, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 538 (2018) 387-392.
- [2] S. Sakthinathan, H.F. Lee, S.-M. Chen, P. Tamizhdurai, *J. Colloid Interface Sci.* 468 (2016) 120-127.
- [3] X. Gao, Y. Ji, S. He, S. Li, J.-M. Lee, *Catal. Sci. Technol.* 6 (2016) 3143-3148.
- [4] A. Kumar, J.M. Gonçalves, A.R. Lima, T.A. Matias, M. Nakamura, J.S. Bernardes, K. Araki, M. Bertotti, *Electrochimica Acta*. 326 (2019) 134984.
- [5] N. Garino, A. Sacco, M. Castellino, J.A. Muñoz-Tabares, A. Chiodoni, V. Agostino, V. Margaria, M. Gerosa, G. Massaglia, M. Quaglio, *ACS Appl. Mater. Interfaces*. 8 (2016) 4633-4643.
- [6] N. Garino, A. Sacco, M. Castellino, J.A. Muñoz-Tabares, M. Armandi, A. Chiodoni, C.F. Pirri, *ChemistrySelect*. 1 (2016) 3640-3646.
- [7] C.K. Chua, M. Pumera, *ACS Nano*. 9 (2015) 4193-4199.
- [8] J. Porwal, N. Karanwal, S. Kaul, S.L. Jain, *New J. Chem.* 40 (2016) 1547-1553.
- [9] M. Karthik, P. Suresh, *New J. Chem.* 42 (2018) 17931-17938.
- [10] M. Azloul, M. Durmaz, E. Zor, H. Bingol, *Mater. Chem. Phys.* 239 (2020) 122298.
- [11] S. Gupta, R. Banu, C. Ameta, R. Ameta, P.B. Punjabi, *Top. Curr. Chem.* 377 (2019) 13.
- [12] A. Dandia, A. Sharma, V. Parewa, B. Kumawat, K.S. Rathore, *RSC Adv.* 5 (2015) 91888-91902.
- [13] A. Dhakshinamoorthy, M. Alvaro, M. Puche, V. Fornes, H. Garcia, *ChemCatChem*. 4 (2012) 2026-2030.
- [14] Y. Qiu, F. Guo, R. Hurt, I. Kulaots, *Carbon*. 72 (2014) 215-223.
- [15] A. Yar, J.O. Dennis, M.S.M. Saheed, N.M. Mohamed, M.I. Irshad, A. Mumtaz, R. Jose, *J. Alloys Comp.* 822 (2020) 153636.
- [16] A.B. Bourlinos, D. Gournis, D. Petridis, T. Szabó, A. Szeri, I. Dékány, *Langmuir*. 19 (2003) 6050-6055.
- [17] J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang, S. Guo, *Chem. Commun.* 46 (2010) 1112-1114.
- [18] L.G. Guex, B. Sacchi, K.F. Peuvot, R.L. Andersson, A.M. Pourrahimi, V. Ström, S. Farris, R.T. Olsson, *Nanoscale*. 9 (2017) 9562-9571.
- [19] S. Eigler, S. Grimm, M. Enzelberger-Heim, P. Müller, A. Hirsch, *Chem. Commun.* 49 (2013) 7391-7393.
- [20] L. Bellucci, V. Tozzini, *Molecules* 25 (2020) 339.
- [21] X. Zhang, L. Hou, F. Richard, P. Samorì, *Chem. Eur. J.* 24 (2018) 18518-18528.
- [22] S. Navalon, A. Dhakshinamoorthy, M. Alvaro, M. Antonietti, H. García, *Chem. Soc. Rev.* 46 (2017) 4501-4529.
- [23] D. Majumdar, *Carbon Nanostructures* (2019) 63-103.
- [24] C.K. Chua, M. Pumera, *ACS Nano* 9(2015) 4193-4199.
- [25] J.C. Espinosa, M. Álvaro, A. Dhakshinamoorthy, S. Navalón, H. García, *ACS Sustainable Chem. Eng.* 7 (2019) 15948-15956.
- [26] K. Muthoosamy, S. Manickam, *Ultrasonics Sonochemistry*. 39 (2017) 478-493.
- [27] D. Wang, H. Duan, J. Lü, C. Lü, *J. Mater. Chem. A*. 5 (2017) 5088-5097.
- [28] D.R. Dreyer, H.-P. Jia, A.D. Todd, J. Geng, C.W. Bielawski, *Org. Biomol. Chem.* 9 (2011) 7292-7295.
- [29] R. Burch, D.J. Crittle, M.J. Hayes, *Catal. Today*. 47 (1999) 229-234.
- [30] G. Bilisa, K.C. Christoforidis, Y. Deligiannakis, M. Louloudi, *Catal. Today*. 157 (2010) 101-106.
- [31] S. Biswas, M. Maes, A. Dhakshinamoorthy, M. Feyand, D.E. De Vos, H. Garcia, N. Stock, *J. Mater. Chem.* 22 (2012) 10200-10209.

## Figure captions

**Figure 1.** Procedures used to obtain the rGO samples under study and plausible functional groups present on their structure: (a) hydroquinone; (b) hydrazine; (c) ascorbic acid as reducing agents, or (d) by thermal treatment. Reprinted with permission from ref.[25]

**Figure 2.** Aerobic oxidation of thiophenol to 1,2-phenyldisulfide using different rGO catalysts.

**Figure 3.** a) Merrifield resin functionalization using hydroquinone units; b) Time-conversion plot for the aerobic oxidation of thiophenol under different conditions: rGO-HQ as catalyst in the absence ( $\circ$ ) or in the presence of DMSO after 2 h ( $\nabla$ ); hot filtration test using rGO-HQ as catalyst at 43 % conversion ( $\diamond$ ); hydroquinone-functionalized Merrifield resin ( $\blacksquare$ ) as catalyst. c) Simplified illustration of redox catalytic cycle for hydroquinone/phenoxy-like radical anchored on rGO-HQ catalyst during the aerobic oxidation of thiophenol to 1,2-diphenylsulfide (d).

**Figure 4.** Aerobic oxidation of indane to indanol and indanone.

**Figure 5.** a) Time profile for the conversion of indane using different rGO-HQ ( $\blacktriangle$ ) or HQ-functionalized Merrifield resin ( $\circ$ ) as catalyst. The inset shows the selectivity-conversion plot using the rGO-HQ catalyst. b) Time profile for the conversion of indane during three consecutive cycles using rGO-HQ as catalyst. Reaction conditions: Catalyst (10 mg), indane (20 mmol), oxygen (1 bar), 130 °C. The bars indicate the standard deviation of two independent experiments.

**Figure 6.** XPS C1s (a, c) and O1s (b, d) for the fresh (a, b) and three-times used (c, d) rGO-HQ catalyst. The best deconvolution for fresh and three-times used rGO-HQ sample is shown.

Legend: (a) C sp<sup>2</sup>, (b) alcohol/ether, (c) carbonyl, (d) carboxyl. Panels a-b are reprinted with permission from ref.[25]

**Figure 7.** a) Time-conversion plot for the aerobic oxidation of indane using rGO-HQ as catalyst ( $\blacktriangle$ ), after catalyst removal at 23 % conversion ( $\bullet$ ), in the presence of catalyst and DMSO ( $\circ$ ), in the presence or in the absence of catalyst and TEMPO ( $\square$ ). The indanyl hydroperoxide yield evolution in the reaction in the presence of catalyst is also shown in the graph ( $\diamond$ ). Reaction conditions: indane (20 mmol), catalyst (20 mg), reaction temperature (130 °C); b) Proposed reaction mechanism for the aerobic oxidation of indane using rGO-HQ catalyst.

## Tables

<b>Table 1.</b> Selective aerobic oxidation of thiophenol to 1,2-diphenyldisulfide by several carbocatalysts. <sup>a</sup>		
S. No	Catalyst	Conversion (%) <sup>b</sup>
1	-	< 2 %
2	GO	70 (43)
3	rGO-HQ	100 (78)
4	rGO-HQ-300	58
5	rGO-HQ-700	14
6	rGO-HZ	60 (35)
7	rGO-ASC	10 (5)
8	rGO-T	47 (15)
9	HQ	12 (9)
10	rGO-HQ <sup>c</sup>	100 (76)
11	rGO-HQ <sup>d</sup>	100 (75)

<sup>a</sup>Reaction conditions: thiophenol (1mmol), catalyst (20 mg), CH<sub>3</sub>CN (2 mL), oxygen purged, 70 °C, 24 h.

<sup>b</sup> Determined by GC. Values in parentheses indicate conversion after 8 h. The numbers are the average values of two independent experiments.

<sup>c</sup> Reused two times.

<sup>d</sup> Reused three times.

**Table 2.** Aerobic oxidation of indane to indanol and indanone by several carbocatalysts.<sup>a</sup>

S. No	Catalyst	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>
1	-	16 %	-
2	GO	31	88
2	rGO-HQ	90	80
3	rGO-HQ-300	70	83
4	rGO-HQ-700	56	88
6	rGO-HZ	60	88
7	rGO-ASC	52	87
8	rGO-T	68	81
9	rGO-HQ <sup>c</sup>	85	81
10	rGO-HQ <sup>d</sup>	84	82

<sup>a</sup> Reaction conditions: indane (20 mmol), catalyst (20 mg), oxygen purged, 130 °C, 7 h.

<sup>b</sup> Determined by GC. The numbers are the average values of two independent experiments.

<sup>c</sup> Reused two times.

<sup>d</sup> Reused three times.



## Supplementary Information

### **Tuning the active sites in reduced graphene oxide by hydroquinone functionalization for aerobic oxidation of thiophenol and indane**

Cristina Vallés-García,<sup>a</sup> Eva Montero-Lanzuela,<sup>a</sup> Sergio Navalon,<sup>a,\*</sup> Mercedes Álvaro,<sup>a</sup>

Amarajothi Dhakshinamoorthy,<sup>b,\*</sup> Hermenegildo Garcia<sup>a,c,d,\*</sup>

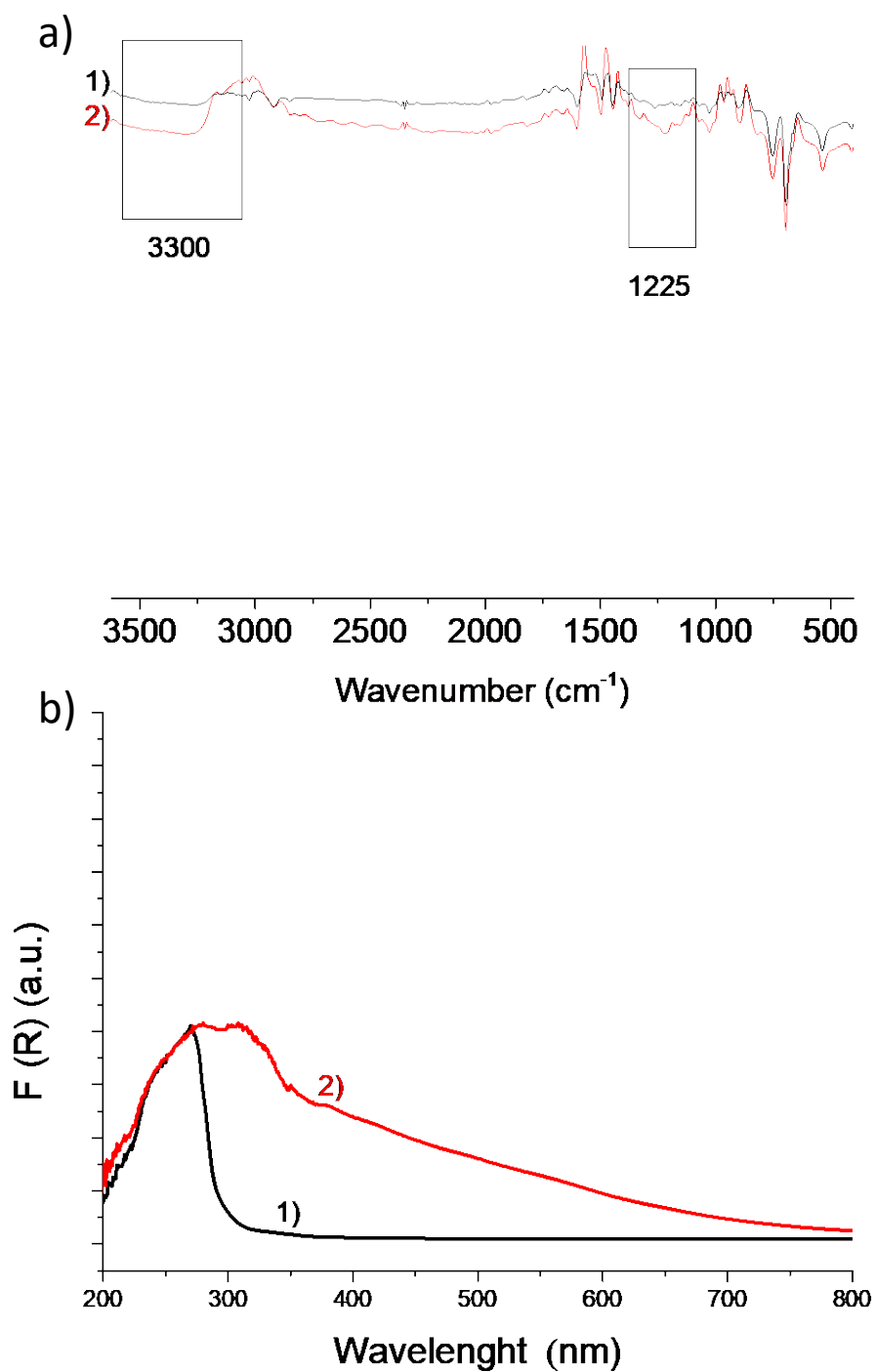


Figure S1. ATR-FT-IR (a) and diffuse reflectance UV-Vis (b) spectra of pristine (1, black color) and hydroquinone-functionalized (2, red color) Merrifield resin.

Table 1. Summary of the Catalysts Employed and their characterization data with permission from ref. (J.C. Espinosa, M. Álvaro, A. Dhakshinamoorthy, S. Navalón, H. García, ACS Sustainable Chem. Eng. 7 (2019) 15948-15956) (I think we should apply for permission of Table 1 from the publication)

	Preparation method	Elemental analysis		
		C (wt %)	H (wt %)	O (wt %)
GO	Graphite oxidation by Hummers method	50.0 (46) <sup>b</sup>	2.3	47.7 (54) <sup>b</sup>
rGO-HQ	GO chemical reduction using HQ (32 mmol) at 100 °C in water for 24 h	80.9 (79.5) <sup>b</sup>	1.0	18.1 (20.5) <sup>b</sup>
rGO-HQ-300	rGO-HQ1pyrolysis at 300 °C for 2 h	83.0 (75.6) <sup>b</sup>	1.1	15.9 (24.4) <sup>b</sup>
rGO-HQ-700	rGO-HQ pyrolysis at 700 °C for 2 h	92.9 (86.6) <sup>b</sup>	1.1	6.0 (13.4) <sup>b</sup>
rGO-HZ <sup>a</sup>	GO chemical reduction using hydrazine hydrate (32 mmol) at 100 °C in water for 24 h	81.4 (82) <sup>b</sup>	0.9	14.8 (15.8) <sup>b</sup>
rGO-ASC	GO chemical reduction using ascorbic acid (32 mmol) at 100 °C in water for 24 h	78.7 (75.2) <sup>b</sup>	1.4	19.9 (24.8) <sup>b</sup>
rGO-T	GO thermal reduction at 200 °C under argon atmosphere	81.1 (74.2) <sup>b</sup>	0.95	17.95 (25.8) <sup>b</sup>
<sup>a</sup> 2.9 wt % of nitrogen has been found in this sample				
<sup>b</sup> Values in parentheses indicate C/O wt % from XPS analysis				