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COMMUNICATION

Aqueous aerobic oxidation of alkyl arene and alcohols catalyzed by copper(II) phthalocyanine supported on three-dimensional nitrogen-doped graphene at room temperature

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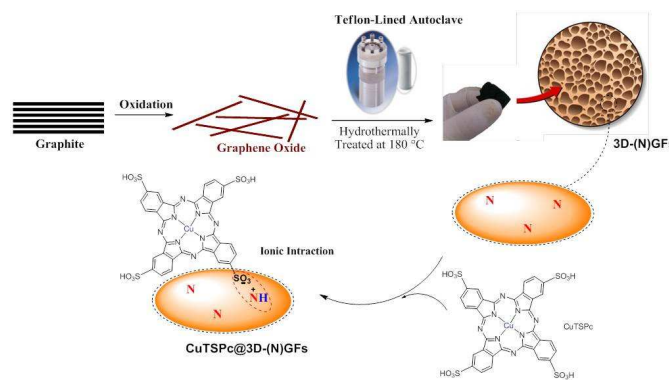
Copper(II) tetrasulfophthalocyanine supported on three-dimensional nitrogen-doped graphene-based frameworks was synthesized and introduced as a bifunctional catalyst for selective aerobic oxidation of alkyl arene and alcohols to the corresponding carbonyl compounds. The ease of catalyst separation, high turnover, low catalyst loading and recyclability could potentially render it applicable in industrial setting.

The selective oxidation of organic compounds as a pivotal transformation in the organic synthesis is one of the most challenging reactions both on laboratory and industry scale.^{1,2} Removing the need for the activators such as inorganic bases and accomplishing the reaction without any activation at ambient temperature and in a green solvent such as water are three important aspects which should be considered in the aerobic oxidation reactions.³⁻⁷ The combination of these aspects is highly challenging and will provide the more benefits for these chemical transformations in industry.⁸⁻¹⁰ As the key for this challenge is catalyst, studies are still ongoing to obtain the proper catalysts, which have the above mentioned aspects.¹¹⁻¹⁴

In recent years, the designs of catalysts focus on the development of new catalytic materials based on biomimetic and green principles.^{2,15-21} Due to this fact, metal porphyrins and metal phthalocyanines as biomimetic catalysts have been widely employed in several oxidation reactions.^{19,21} Compared to porphyrins, phthalocyanines have improved thermal and chemical stability, low cost and more availability.

Three-dimensional graphene-based frameworks (3D-GFs) like graphene aerogels and foams are important types of new generation porous carbon materials, which can be employed as robust matrices for accommodating metals, metal oxides, and active polymers for different applications, especially catalytic systems.²²⁻²⁴ On the other hand, to increase the performance and interaction of oxygen with the support and the substrate in the catalytic oxidation reaction, the chemical modification of the surface with nitrogen doping and transition metals are promising methods. The solvent-free aerobic oxidation of alkyl arene and alcohols with Pd@N-doped carbon was presented by Zhang et al,²⁵ which the reactions were carried out at 120 °C, with low yields. Also using Pd, an expensive metal, as active sites in the catalyst limited its application.

Because of the above mentioned reasons and also our interest in the synthesis of phthalocyanines and new catalysts,^{5,26-31} herein we report the successful preparation and excellent catalytic activity of copper(II) tetrasulfophthalocyanine supported on three-dimensional nitrogen-doped graphene-based frameworks (CuTSPc@3D-(N)GFs). It should be notable that the presented catalyst is the first example of synthesis and using 3D-(N)GFs-supported phthalocyanine as a novel bifunctional (nitrogen acts as a base and copper(II) as active site) catalyst with unique properties for the selective aerobic oxidation of alkyl arene and alcohols to the corresponding carbonyl groups. The selective aerobic oxidation reactions were carried out under environmentally-friendly conditions with excellent yields in short reaction time at room temperature. Moreover, the effect of nitrogen doping on the catalytic activity of CuTSPc decorated on 3D-(N)GFs was investigated. The synthesis of CuTSPc@3D-(N)GFs was schematically shown in Scheme 1.



Scheme 1. Synthesis of CuTSPc@3D-(N)GFs.

The morphologies, and sample surfaces of the suspended single layers of GO have been shown in Fig. S1A and B and Fig. S2A and B by SEM and TEM images, respectively. The 3D morphology and size of as-prepared 3D-(N)GFs were confirmed by SEM images. Fig. 1A and B show an interconnected framework of ultrathin graphene nanosheets with porous structure. As can be seen, the pore size is ranging from a few hundred nanometers to several micrometers. The surface area in porous materials is an important factor affecting the loading of catalytic sites. So,

Brunauer-Emmett-Teller (BET) method was used to estimate the surface area of the as-prepared 3D-(N)GFs. Nitrogen adsorption-desorption analysis reveals a typical BET surface area of up to $266.0 \text{ m}^2 \text{ g}^{-1}$ for 3D-(N)GFs. Therefore, the synthesized support has high surface area to embed CuTSPc as active catalytic sites.

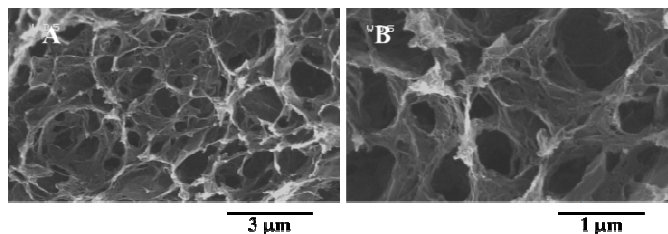


Fig. 1 SEM images of 3D-(N)GFs.

The chemical composition of 3D-(N)GFs and CuTSPc supported on the 3D-(N)GFs was confirmed by elemental analysis (CHNS), FT-IR, Thermogravimetric analysis (TGA), and X-ray powder diffraction (XRD). Moreover, X-ray photoelectron spectroscopy (XPS) was employed for the surface characterization of CuTSPc@3D-(N)GFs (see ESI, Fig. S3-S6).

To optimize the required amount of catalyst and solvent, the oxidation of 2,3-dihydro-1H-indene was performed as model reactions which the results were summarized in Table S1. The optimum conditions were 0.4 mol% Cu and H_2O as solvent at room temperature for both reactions.

The advantages of the support were clearly presented in the revised version of manuscript as following: Some important advantages of the 3D-(N)GFs as support are: (i) Having macroporous structures, low mass density, excellent chemical and physical stability and high surface area to embed the active sites; (ii) Easy synthesis; (iii) Having a bifunctional heterogeneous catalyst (copper(II) as active site and N as base) and therefore removing the need for the activators such as inorganic bases and carrying out the reaction without any activation at ambient temperature; (iv) Increasing the performance and interaction of oxygen with the support and the substrate in the catalytic oxidation reaction via the chemical modification of the surface with nitrogen doping; and (v) Being hydrophilic to have good dispersion in water as the reaction solvent.

To show the role and performance of the support, the catalytic oxidation reactions of 2,3-dihydro-1H-indene and benzaldehyde were accomplished using GO, 3D-(N)GFs, and CuTSPc under the same reaction conditions which the results are shown in Table 1 (Entries 2-4). It should be notable that to have a correct comparison, the metal contents of CuTSPc@3D-(N)GFs, CuTSPc, and CuTSPc@MCM-41 were the same for model reactions. We examined GO (0.005 g) as the catalyst for oxidation reaction, which showed low yields under our mild reaction conditions (Table 1, entry 2). It has been proposed that the use of 3D-(N)GFs as support can promote the adsorption of aromatic reactants due to the formation of π - π interaction between benzene skeleton of the reactants and graphene. Moreover, 3D-(N)GFs enhance oxygen adsorption on the bridge sites of graphene with migration energy of over 1.0 eV and lead to activation of the oxygen molecules due to their interaction with the nitrogen-doped support. The existence of mobile oxygen on graphene can promote the elimination of hydrogen and thus promote the aerobic oxidation of organic compounds.³² Actually the improvement of the results, in comparison with the homogeneous catalyst (Table 1, entries 1, 4), is due to a couple of factors, on the one hand the presence of basic

cites on the solid and, in the second, π - π interactions of the aromatic groups with the support favoring the close proximity of the reagents to the catalytic sites, and the active role of this support in aerobic oxidations, as shown by the results described in Table 1. Given that the better behavior of the supported catalyst may be due to other factors, for instance site isolation has been shown to be advantageous in some other oxidation reactions, this catalyst was compared with the same Cu(II)-complex immobilized, using the same strategy, in a different support, silica, to be sure of the advantages related to the use of this particular solid. At first, MCM-41- NH_2 was synthesized according to the literatures,³³ then copper(II) tetrasulfophthalocyanine was introduced to the support with the same process of CuTSPc@3D-(N)GFs (See experimental section). SEM image of the synthesized CuTSPc@MCM-41 was presented in Fig S7. The as prepared catalyst was used for the catalytic aerobic oxidation of benzyl alcohol and 2,3-dihydro-1H-indene as model reactions, which gave the lower yields compared to CuTSPc@3D-(N)GFs (Table 1, entries 5). So, we concluded that using 3D-(N)GFs as support plays an important role in the catalytic activity. Moreover, increasing the stability of the catalyst and facilitating the recovery process are the other advantages of using 3D-(N)GFs as the support.

Table 1 Comparison of the results obtained from CuTSPc@3D-(N)GFs with GO, CuTSPc, and 3D-(N)GFs for the oxidation reactions^a

Entry	Catalyst	Product	Yield ^b (%)	Selectivity ^b (%)
1	CuTSPc@3D-(N)GFs	2,3-dihydro-1H-indene	98	>99
		benzaldehyde	98	>99
2	GO	2,3-dihydro-1H-indene	24	>99
		benzaldehyde	30	>99
3	3D-(N)GFs	2,3-dihydro-1H-indene	33	>99
		benzaldehyde	35	>99
		2,3-dihydro-1H-indene	86	97
4	CuTSPc	benzaldehyde	88	98
5	CuTSPc@MCM-41	2,3-dihydro-1H-indene	75	98
		benzaldehyde	81	99

^a Reaction conditions: 2,3-dihydro-1H-indene or benzyl alcohol (1.0 mmol), catalyst, H_2O (4.0 mL), air (1 atm), r.t., 3 h. ^b Yield and selectivity determined by GC analysis

The presence of nitrogen is necessary to make ionic interaction between complex and support and also easy functionalization of support with CuTSPc. The contact between the active copper(II) tetrasulfophthalocyanine sites and supporting material plays a vital role in activity of the catalyst. Copper(II) tetrasulfophthalocyanine was introduced to the 3D-(N)GFs by ionic interaction which also increases the hydrophilic properties of the catalyst and consequently improves the dispersity and stability of the catalyst in aqueous solution (Fig. S8). The good dispersity of CuTSPc@3D-(N)GFs in the aqueous solution seems to be an important factor that affects the efficiency.^{28,34,35} The interaction between support and complex also has a critical effect on the true heterogeneity of the catalyst, and the possible contribution by leached, homogeneous species. To examine the leaching, in a separate experiment the catalyst was removed by filtration after ~50% conversion. Then, the residue mixture was permitted to further treat under similar reaction conditions and the conversion yield was gained by GC which indicated

the reaction did not proceed. In addition, atomic absorption spectroscopy shows that the copper content in the solution of the residue mixture is below the 0.1 ppm. With respect to these results, we conclude that leaching in the catalyst is negligible and excellent heterogeneity is displayed by CuTSPc@3D-(N)GFs. Exchange of anionic phthalocyanines guarantees complex retention on positively charged 3D-(N)GFs.

To show the applicability of the prepared catalyst for the oxidation reactions, a large variety of alkyl arene, primary and secondary aliphatic, allylic, and aromatic alcohols were subjected to the optimized conditions. As given in Table S2, all products were obtained in high yields. To evaluate the efficiency of catalyst in the presence of oxygen, some derivatives were examined and good yields were obtained which are comparable with those obtained in presence of air but in relatively shorter reaction time.

Since catalysis is a totally kinetic phenomenon, measurement of initial rates obtained from kinetic plots is a good approach to investigate the recyclability and deactivation of the catalyst. So, we investigated the oxidation reaction of 2,3-dihydro-1H-indene as a model reaction after 1 h (the reaction proceed was monitored by GC). After 1 h, the reaction mixture was filtered off and CuTSPc@3D-(N)GFs separated as a black solid, washed with EtOH (2 × 5 mL) and reused. The conversion yields and selectivity for each run are shown in Fig. S9A. CuTSPc@3D-(N)GFs showed good stability and recyclability as the conversion yields for six runs didn't decrease significantly. Also, to investigate the productivity of prepared catalyst, we examined the oxidation reaction of 2,3-dihydro-1H-indene up to six cycles after completion of the reaction. The results shown in Fig. S9B demonstrates that after every run, the yield of product does not change considerably indicating the high productivity of the catalyst.

The approach of this research is introducing copper(II) tetrasulfophthalocyanine (CuTSPc) supported on three-dimensional nitrogen-doped graphene-based frameworks (using an anionic CuTSPc complex anchored electrostatically on 3D-(N)GFs) as an efficient catalyst with easy preparation, reusability, high catalytic activity, and low cost for the aerobic oxidation of alkyl arene and alcohols. These advantages make it promising candidate to be employed as catalyst for developing highly efficient oxidation reaction. The catalyst was easily recovered and reused several times without loss of activity. Further investigations of the application of this catalyst for other oxidation processes and also other organic transformations are currently in progress.

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