

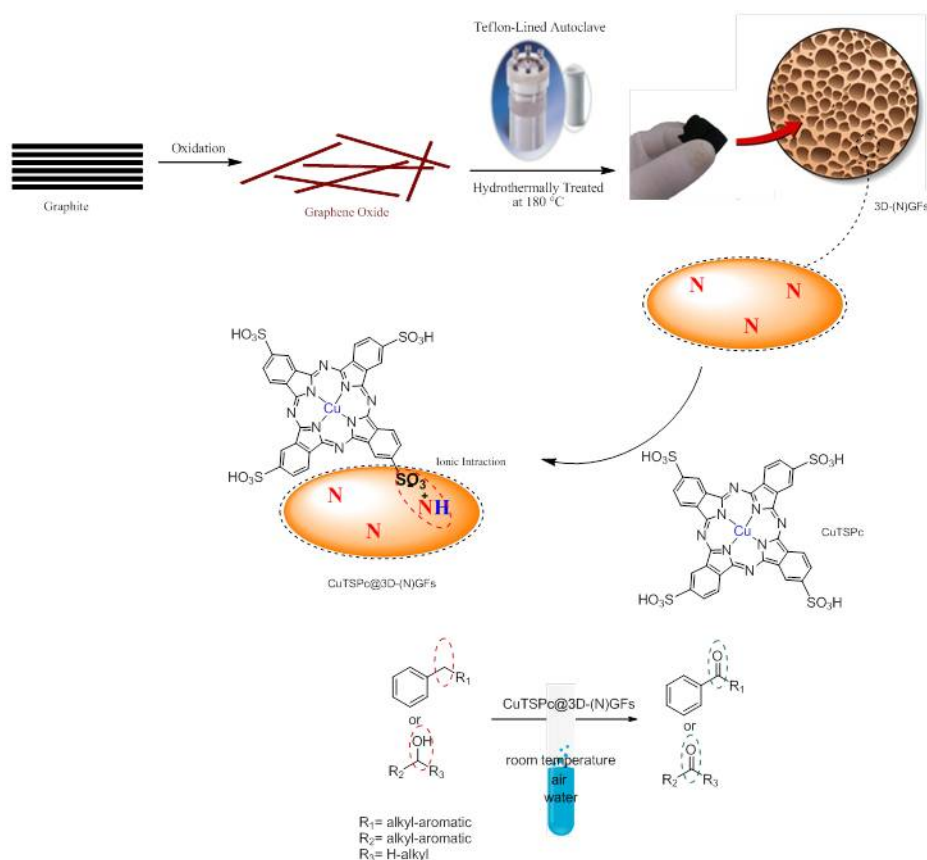
Supplementary information

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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1. Experimental

1.1 Materials and methods

All chemicals were purchased from Aldrich or Merck companies and used without further purification. MCM-41 was purchased from the Aldrich Company. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Transmission electron microscopy (TEM) analyzes were performed by LEO 912AB electron microscope. Hitachi FE-SEM model S-4160 was used for surface imaging. Identification and quantification were carried out on a Varian model 3600 gas chromatograph (Varian Iberica, Madrid, Spain) equipped with a split/splitless capillary injection port and flame ionization detector (FID). A CP-Sil-8 fused silica capillary column (25 m, 0.32 mm i.d. and 0.52 mm film thickness) from Chrompack was employed. The elemental analysis (Carbon/Hydrogen/ Nitrogen/Sulfur (CHNS)) was done by a conventional combustion method based on the burn off of the sample, and the gases are detected by a thermoconductivity detector (TCD). Thermogravimetric analysis (TGA) was carried out using an STA 1500 instrument at a heating rate of 10 C min⁻¹ in air. Ultrasonic bath (EUROSONIC® 4D ultrasound cleaner with a frequency of 50 kHz and an output power of 350 W) was used to disperse materials in solvent. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu K α radiation. Hitachi FE-SEM model S-4160 was used for surface imaging. XPS analysis was performed using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultrahigh vacuum.

1.2 Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized by Hummer method.¹ Graphite powder (1.00 g, 325 mesh) and concentrated H₂SO₄ (23 mL) were added to a 250 mL conical flask and the mixture

was stirred. Sodium nitrate (0.50 g) was added and the resulting mixture was cooled to 0 °C. Under vigorous agitation, KMnO_4 (3.00 g) was added slowly and the mixture was stirred for 1h while the temperature was kept below 35 °C. Then, H_2O (45 mL) was added slowly to the reaction mixture and the solution was stirred for 30 min at 90 °C. Next, H_2O_2 (10 mL of a 30% solution) and deionized water (140 mL) were added to the mixture. The resulting precipitate was centrifuged and washed repeatedly with HCl (5%, 3×15 mL) and EtOH and dried under the vacuum at 60 °C. The GO was obtained as a brown powder.

1.3 Synthesis of three-dimensional nitrogen-doped graphene-based frameworks (3D-(N)GFs)

3D-(N)GFs was synthesized with a combined hydrothermal and freeze-drying process.² Typically, the as-prepared GO was firstly dispersed in water with ultrasonication reaching a concentration up to 1.5 mg mL^{-1} . A 10 mL aqueous dispersion of GO (1.5 mg mL^{-1}) and 1.2 mmol dicyandiamide was sonicated for 5 min, and then, the mixture was transferred to a Teflon-lined autoclave and hydrothermally treated at 180 °C for 12 h. Finally, the resulting sample was freeze-dried overnight to obtain 3D-(N)GFs.

1.4 Synthesis of copper(II) tetrasulfophthalocyanine

Copper(II) tetrasulfophthalocyanine was synthesized by a template method.³ The triammonium salt of 4-sulfophthalic acid (1.50 g, 5.0 mmol), urea (2.32 g, 38.6 mmol), copper(II) sulfate pentahydrate (0.32 g, 1.2 mmol), ammonium chloride (0.29 g, 5.5 mmol) and ammonium heptamolybdate (0.02 g, 0.02 mmol) were ground together until homogeneous powder obtained. This powder was placed in a beaker and irradiated in a microwave oven at high power for 5 min.

1.5 Synthesis of copper(II) tetrasulfophthalocyanine supported on three-dimensional nitrogen-doped graphene-based frameworks (CuTSPc@3D-(N)GFs)

3D-(N)GFs (0.5 g) was mixed with 20.0 mL water and was sonicated for 30 min to produce a dispersed mixture. Then copper(II) tetrasulfophthalocyanine (0.1 g) was added under mechanical stirring and the mixture was heated to 100 °C for 24 h. Subsequently, unsupported CuTSPc was removed *via* Soxhlet extraction with water and finally the black concentrated product was obtained.

1.6 General procedure for the catalytic aerobic oxidation of alcohols

A mixture of an organic compound (1.0 mmol) and CuTSPc@3D-(N)GFs (0.4 mol% Cu, 0.005 g) was added in portions to a two-necked vial containing H₂O (4.0 mL) as solvent under bubbling of air at room temperature. The progress of the reaction was followed by gas chromatography (GC). GC conversions and yields were obtained using n-decane as an internal standard based on the amount of organic compound employed relative to authentic standard product. After the reaction, the catalyst was removed *via* centrifuge and extraction twice with CH₂Cl₂ (6.0 mL) to separate the organic compounds. Then the organic phase was combined and extracted twice. Finally the solvent was removed under vacuum to give the pure product.

2. Characterization of CuTSPc@3D-(N)GFs

2.1 CHNS analysis

To confirm the synthesis of copper(II) tetrasulfophthalocyanine supported on 3D-(N)GFs, the atomic percent of nitrogen and sulfur were monitored with elemental analysis (CHNS). The atomic percent of N and S are 3.65% and 0.01% for 3D-(N)GFs, and 11.40% and 8.00% for CuTSPc@3D-(N)GFs, respectively which confirm the successful supporting of copper(II) tetrasulfophthalocyanine on 3D-(N)GFs.

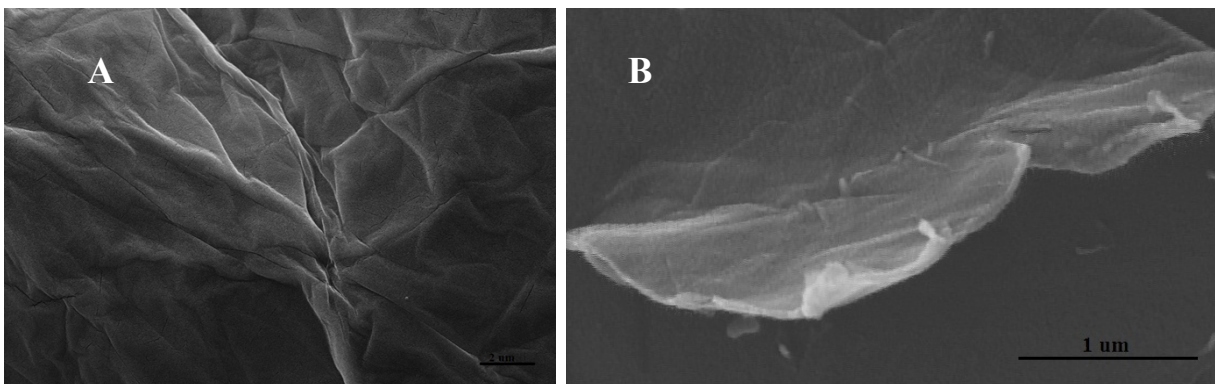


Fig.S1 SEM (A and B) images of GO.

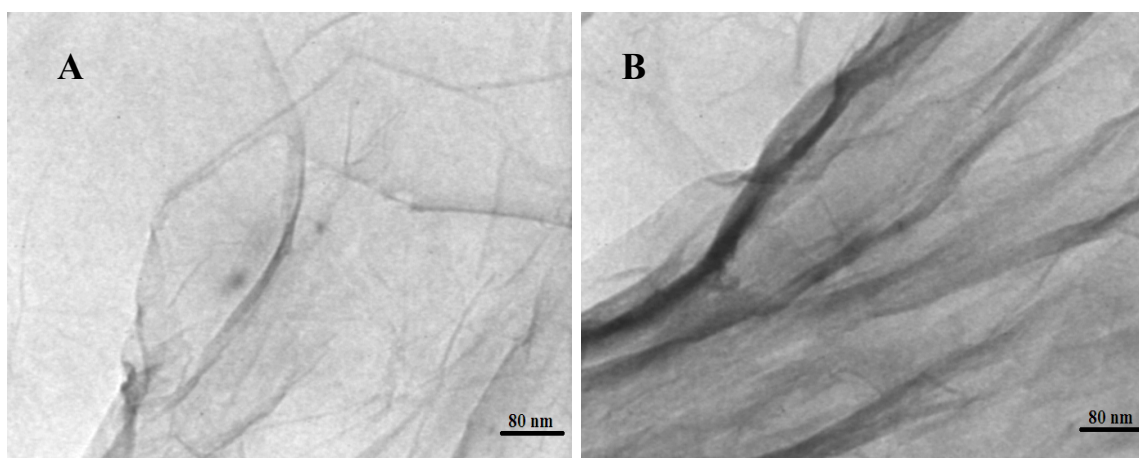


Fig. S2 TEM (A and B) images of the synthesized GO

2.2 FT-IR analysis

FT-IR spectra of GO, 3D-(N)GFs, and CuTSPc@3D-(N)GFs are given in Fig. S3A-C, respectively. The spectrum of GO shows bands around 1060 cm^{-1} (ν C-O), 1210 cm^{-1} (ν phenolic), and 1710 cm^{-1} (ν C=O). The results obtained from Fig. S3B shows that nitrogen doping within 3D-GFs has successfully done. Actually, the bands at to 1580 , 2040 , 2210 , and 3470 cm^{-1} are attributed to $-\text{C}=\text{N}$ and $-\text{C}-\text{N}$ groups, which are possible in a ring-like structure.^{4,5} The absorption bands at 1015 cm^{-1} and 1150 cm^{-1} in Fig. S3C can be ascribed to the symmetric and asymmetric stretching vibrations of $-\text{SO}_3^-$ groups⁶⁻⁸ which confirms the existence of copper(II) tetrasulfophthalocyanine on 3D-(N)GFs.

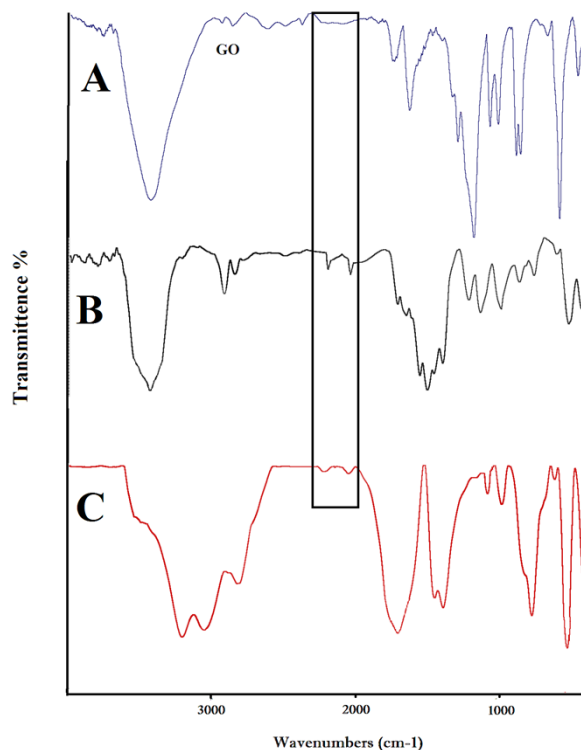


Fig. S3 FT-IR spectra of GO (A), 3D-(N)GFs (B), and CuTSPc@3D-(N)GFs (C)

3.3 XRD analysis

All samples were characterized by powder X-ray diffraction (PXRD). The strong and sharp peak at $2\theta = 10.9^\circ$ corresponds to (0 0 2) of GO indicating that graphite is oxidized completely. Three-dimensional nitrogen-doped graphene-based frameworks were synthesized by dicyandiamide as the nitrogen precursor, *via* the hydrothermal reaction and freeze-drying process (See experimental section). In the XRD pattern of 3D-(N)GFs, the peak of GO at $\sim 10.9^\circ$ completely disappeared and the diffraction line at 26.2° was seen suggesting completely and uniformly exfoliation by the interlayer expansion along the c-axis direction in the 3D-(N)GFs (Fig. S4).⁹ Fig. S4C shows XRD characteristic peaks of copper(II) phthalocyanine and also 3D-(N)GFs which are in consistent with the ICDD Card no. 11-0893 of CuPc.

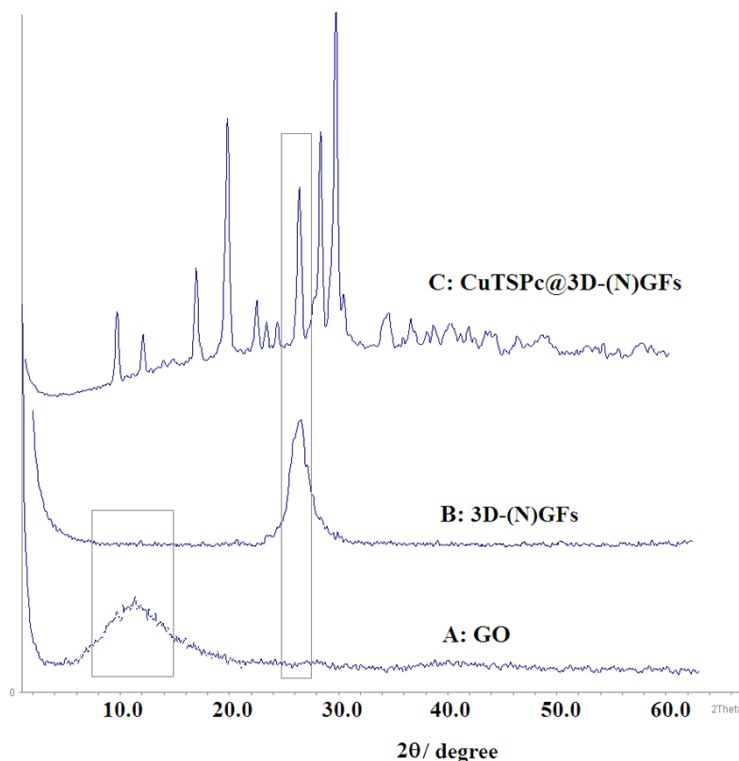


Fig. S4 XRD patterns of GO (A), 3D-(N)GFs (B), and CuTSPc@3D-(N)GFs (C)

4.2 XPS analysis

XPS analysis is often employed for the surface characterization of various materials. So, XPS was prepared to further analyze the as-prepared CuTSPc@3D-(N)GFs and to examine the composition of its surface. As shown in Fig. S5, the labeled peaks C 1s, N 1s, and O 1s present the accurate elemental composition of the as prepared catalyst, which is in good accordance with the designation of the experiment. XPS is also well suited to the task of identifying the oxidation state of metals (Fig. S5).¹⁰ The wide XPS scan of Cu shows prominent absorption band at 935.6 eV which can be readily assigned to Cu(II) 2p_{3/2}(inset of Fig. S5). These binding energy values are consistent with those reported for Cu(II) oxidation states.^{11, 12} The peak at 168.9 eV is related to S 2p_{3/2} in the SO₃⁻ in CuTSPc@3D-(N)GFs (inset of Fig. S5).¹²

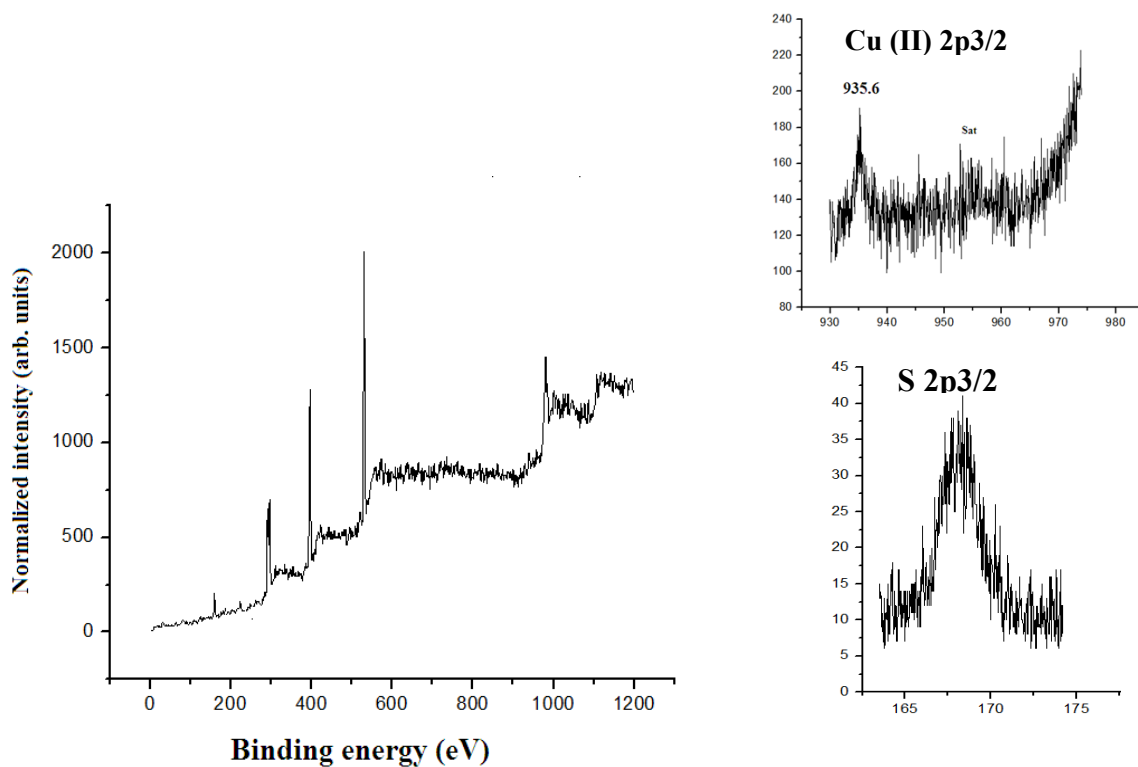


Fig. S5 XPS spectrum of CuTSPc@3D-(N)GFs, wide XPS scan of Cu and S of CuTSPc@3D-(N)GFs (inset).

5.2 TGA analysis

TGA curve of the catalyst shows an initial weight loss (5 wt.%) due to the desorption of water around 100°C. The second weight loss started at ~400 °C related to the loss of the noncovalently bound organic group. Also, from the Fig. 6C can be understood that CuTSPc@3D-(N)GFs has a good thermal stability (until ~400 °C).

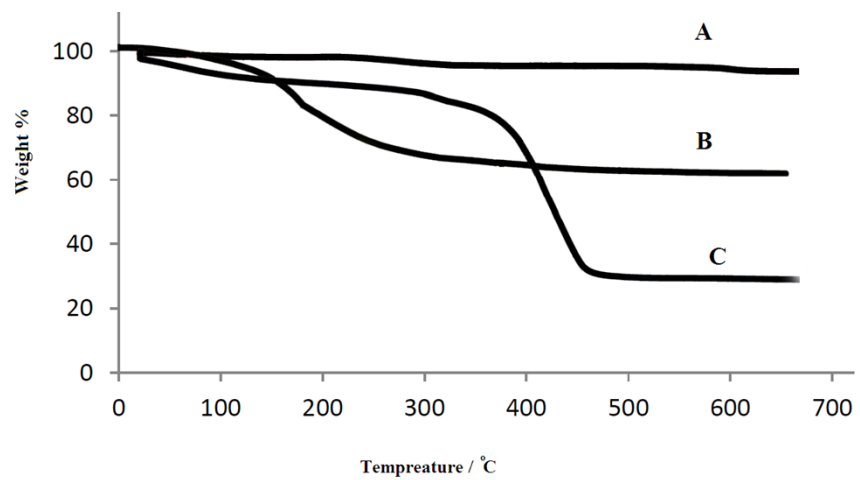
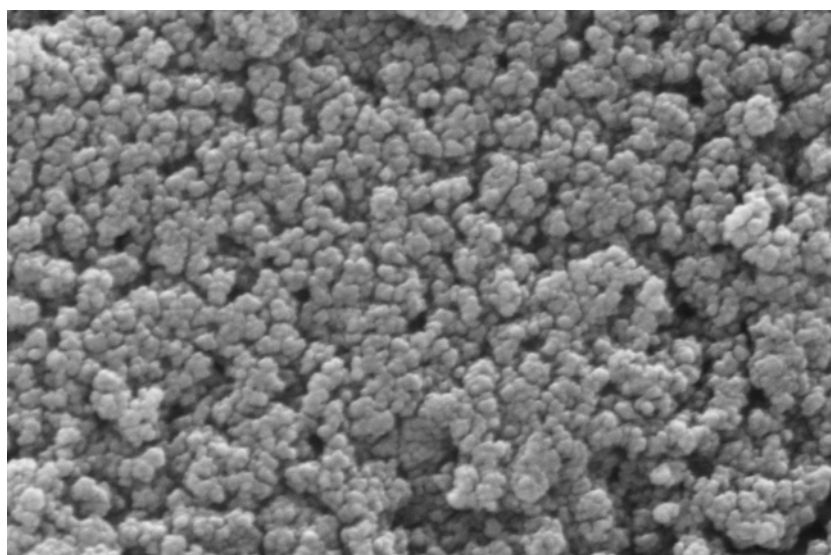


Fig. S6 TGA curves of pristine graphite (A), GO (B), and CuTSPc@3D-(N)GFs (C), obtained under air atmosphere



300 nm

Fig. S7 SEM image of CuTSPc@MCM-41

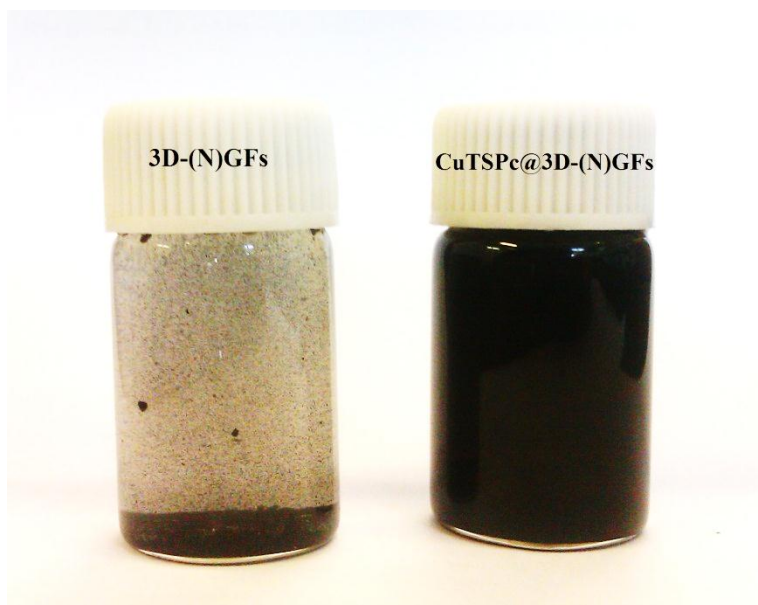


Fig. S8 Dispersity of 3D-(N)GFs and CuTSPc@3D-(N)GFs

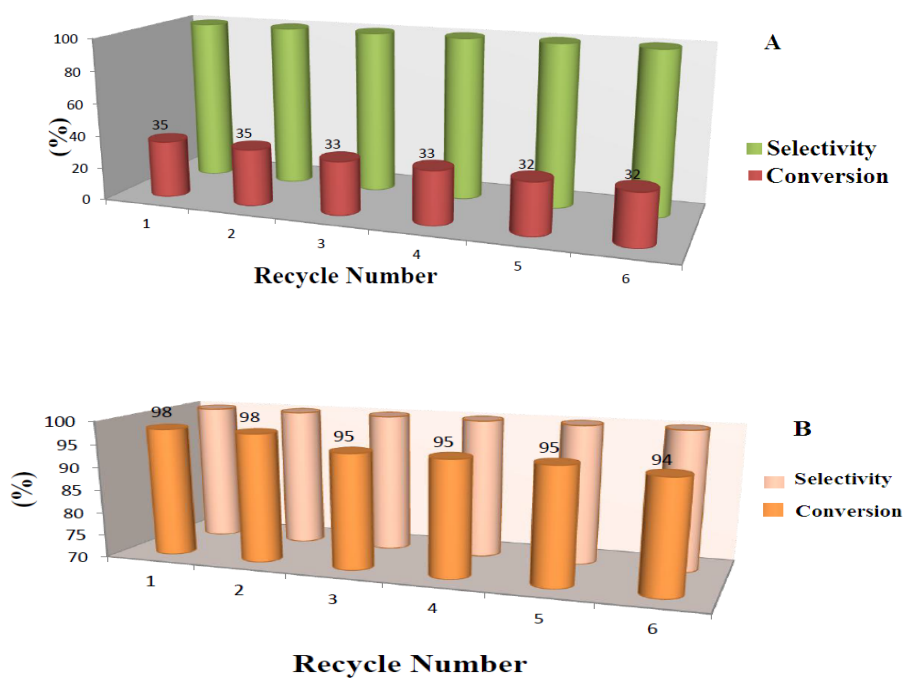
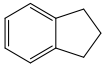
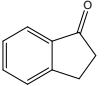

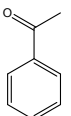
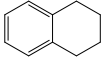
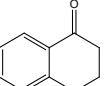
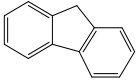
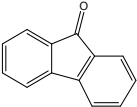
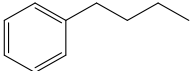
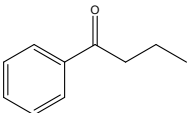


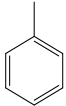
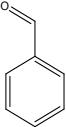
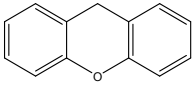
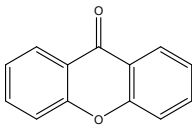
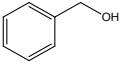
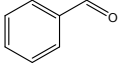
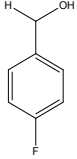
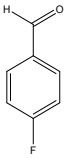
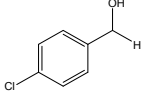
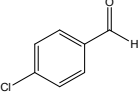
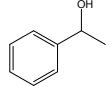
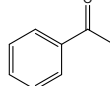
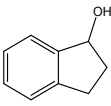
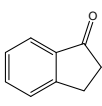
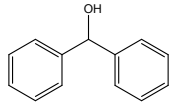
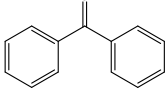
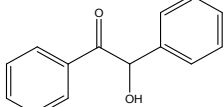
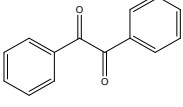
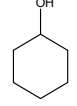
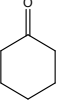
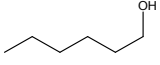
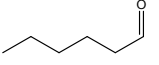
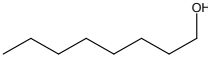
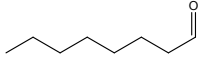
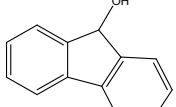
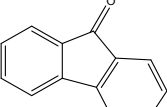
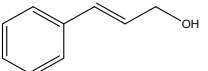
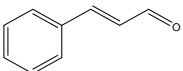
Fig. S9 Recyclability of CuTSPc@3D-(N)GFs

Table S1 Effect of amount of catalyst and solvent on oxidation reaction^a

Entry	Amount of catalyst (Cu content/mmol %)	Solvent	Conversion ^b (%)	Selectivity (%) ^b
1	None	H ₂ O	5	>99
2	0.1	H ₂ O	25	>99
3	0.2	H ₂ O	43	>99
4	0.3	H ₂ O	81	>99
5	0.4	H ₂ O	99	>99
6	0.4	Solvent free	77	>99
7	0.4	CH ₃ CN	69	>99
8	0.4	DMF	86	>99
9	0.4	THF	74	>99

^a Reaction conditions: 2,3-dihydro-1H-indene (1.0 mmol), solvent (4.0 mL), r.t, air (1 atm), 3 h.^b Conversion and selectivity determined by GC analysis**Table S2** Aerobic oxidation of alkyl arene and alcohols with CuTSPc@3D-(N)GFs as catalyst^a

Entry	Reagent	Product	Time (h)	Yield (%) ^b	Selectivity (%) ^b
1			12	98	>99
2			12	97	>99
3			12	98	>99
4			12	96	>99
5			12	98	>99

6			12	97	>99
7			12	98	>99
8			8	98	>99
9			8	97	>99
10			8	95	>99
11			8	99	>99
12			8	99	>99
13			8	97	>99
14			8	98	>99
15			8	98	>99
16			8	95	>99
17			8	97	>99
18			8	98	>99
19			8	95	>99

^a Reaction conditions: organic compound (1.0 mmol), CuTSPc@3D-(N)GFs (0.4 mol% Cu, 0.005 g), H₂O (4.0 mL), air (1 atm), r.t. ^b Conversion and selectivity determined by GC analysis.

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