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Graphene / carbon composite nanofibers for NO oxidation at room temperature†

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Novel composite carbon nanofibers (CNFs) were prepared via embedding reduced graphene oxide (rGO) sheets in polyacrylonitrile (PAN) precursor by electrospinning for room temperature oxidation of NO (50 ppm). It is proposed that rGO sheets possess catalytically active sites play an important role in catalytic room temperature oxidation of NO.

CNFs are versatile materials that can be applied to a wide range of applications.[1] Activated CNFs are promising candidates for adsorption and oxidation of nitrous oxides, especially NO,[2] mainly because of their microporous structure that leads to a high specific surface area. Several methods have been proposed to enhance the conversion rate (Rc) of NO to NO_2, However, these methods require a high concentration of NO and a high reaction temperature.[3] CNFs have also been employed in selective catalytic reduction of NO, however, introduction of an additional gas, such as NH_3 is mandatory.[4] Oxidation of NO in low concentrations at room temperature is also very difficult.[5] Graphitized porous CNFs have been reported to considerably improve Rc, resulting in an increase in the graphitization temperature, mostly exceeding 2000°C which consumes large amounts of energy and is thus uneconomical.[6] Furthermore, most of micropores disappear after high temperature treatment, considerably reducing the specific surface area of the CNFs. Thus, for room-temperature catalytic oxidation of NO, it is imperative to fabricate functional CNFs with a large number of micropores leading to a high specific surface area as well as a high degree of graphitization.[7] Graphene, which consists of a single layer of carbon atoms arranged in a hexagonal lattice, has attracted considerably research interest over the past decade.[8] The remarkable properties resulting from the unique two-dimensional structure of graphene include a very high specific surface area and outstanding catalytic ability.[9] These properties could be exploited by incorporation graphene sheets in a desired material, to serves as supports or reactants.

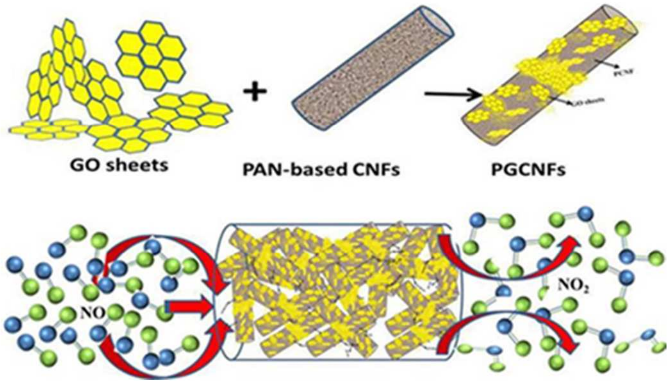


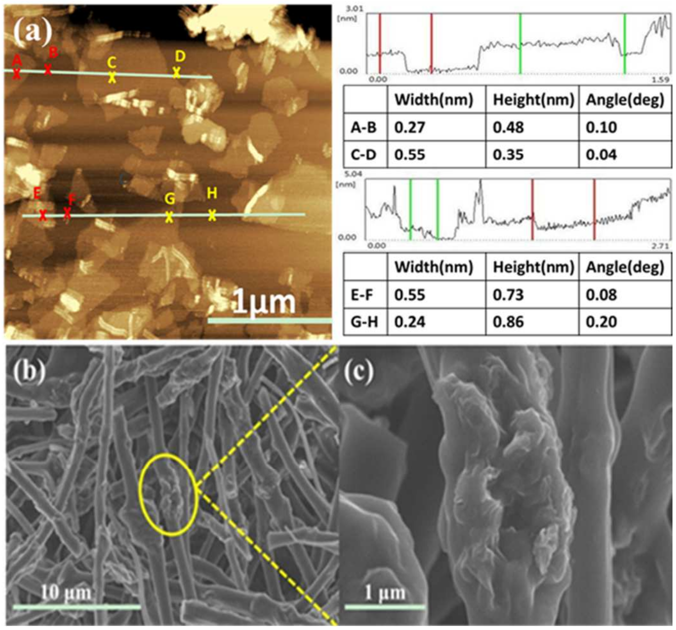
Fig. 1 Schematic diagram of rGO embed in CNFs forming PGCNFs and the process of oxidation for NO to NO_2. (PGCNF denotes nanofibers after NH_3 activation)

In this work, GO sheets were added to a PAN precursor in N, N-dimethylformamide (DMF) forming composite nanofibers by electrospinning. The pristine nanofibers turned into microporous PAN-based CNFs (PCNFs) embedded with the rGO sheets after carbonization in NH_3. The aim of this work is to probe application of these PCNFs embedded with rGO sheets (PGCNFs) for the catalytic oxidation of NO at room temperature (as shown schematically diagram in Fig. 1).

GO sheets were prepared by the method developed by Marcano et al,[10] which proceeded is as follows: H_2SO_4/H_3PO_4

(270 ml/30 ml) was added to a mixture of graphite (2.0 g) and $KMnO_4$ (13.5 g), heated to 50°C and stirred for 12 h. The temperature was reduced to room temperature and then poured onto ice. The yellow solution was centrifuged, and the supernatant was decanted away. The remaining solid material was then washed successively with water, HCl, and ethanol. After repeating the washing until the solution became neutral, the obtained solid was vacuum-dried. The as-prepared GO sheets at 10 wt.% (0.1 g GO and 0.9 g PAN) were added into DMF (9 g) and ultrasonically treated for 2 h, followed by addition of PAN and vigorous stirring at 60°C for 24 h to obtain a homogeneous solution for electrospinning. The as-prepared composite CNFs were treated in N_2 and NH_3 at 850°C for 10 min for NO oxidation.

Dimensional measurements of the GO nanosheets were carried out by AFM. The size of the sheets from 100 to 500 nm and the thicknesses were 0.48, 0.35, 0.73, and 0.86 nm, all below 1 nm (Fig. 2a). While the large inhomogeneous rGO sheets observed mostly on the surface of PGCNFs, appear to be clumped together forming clusters, the small-sized sheets are embedded inside the nanofibers after activation with NH_3 (Fig.2b). The N_2 adsorption-desorption isotherms belong to type I according to the IUPAC classification, representing the adsorption characteristics of the micropores (see supplementary information). The pore size distribution of PGCNF showed that most pores are smaller than 2 nm, revealing a microporous structure (see supplementary information). Catalytic activities for NO oxidation at room temperature were investigated on both CNFs prepared without GO (PCNFs) and PGCNFs. The NO concentration was set as 50 ppm in the presence of N_2 (vol.78%) and O_2 (vol.21%), which simulate atmospheric conditions, and the sample was set in a fixed bed. The conversion of NO to NO_2 and the concentration variation for NO, NO_2, and NOx were measured by a NO-NO_2-NOx analyser. We define Rc as the ratio of the NO_2 concentration in the outlet to NO in the inlet, expressed in percentage.



	Width(nm)	Height(nm)	Angle(deg)
A-B	0.27	0.48	0.10
C-D	0.55	0.35	0.04

	Width(nm)	Height(nm)	Angle(deg)
E-F	0.55	0.73	0.08
G-H	0.24	0.86	0.20

Fig 2. (a) AFM image of GO sheets and their size. (b) SEM image of PGCNFs. (c) the enlarged view of a section of b.

The results of the breakthrough curves for NO, NO_2, and NOx on PCNFs and PGCNFs are depicted in Fig. 3. It can be clearly noted that no NO and NO_2 is detected in the outlet stream at the beginning of the experiment. The breakthrough time of NO can reach 2.5 h because the NO molecules are first adsorbed onto the micropores of the samples during the flow. Similarly, NO_2 was not found within 34 h as the generated NO_2 is also absorbed. After 34 h, the concentration of NO_2 in the gas phase increased sharply and steadied at about 20 ppm for PGNFs, but at only about 5 ppm for PCNFs, which is ascribed to the quick increase in NO_2 desorption and NO oxidation. However, because some NO can be oxidized into a small quantity of other nitric oxide, such as N_2O, N_2O_3, etc, the total concentration of NO_X is not in accord with 50ppm. We can thus calculate that Rc is greater than 40% for PGCNFs, which is much higher than that for the pristine activated CNFs (11%) as seen in Fig. 3. Compared with PCNFs, the PGCNFs exhibit higher crystallinity, evident from the (002) peak in XRD that becomes stronger and sharper (see

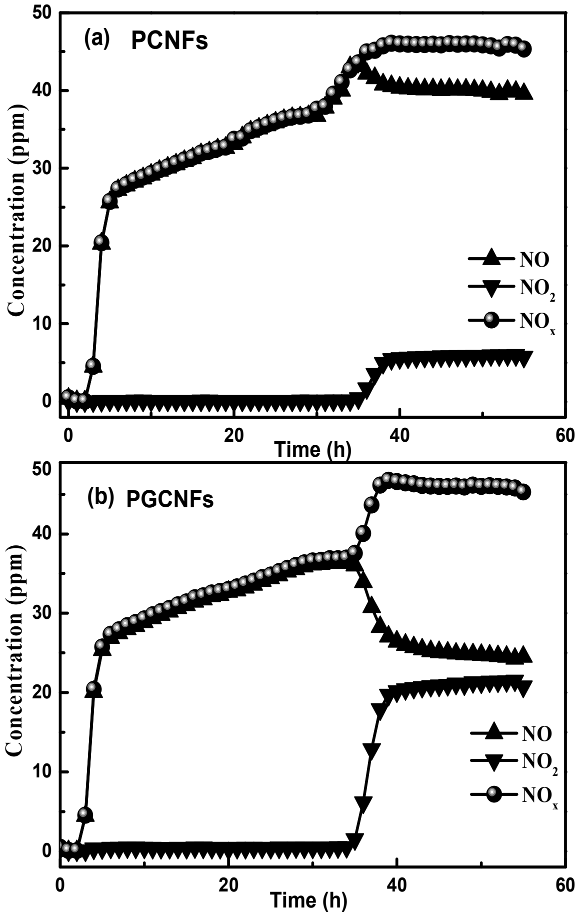


Fig 3. Result of catalytic oxidation of NO (50 ppm) by (a)pure PAN-based CNFs and (b)PGCNFs at room temperature.

supplementary information). From the value of I_D/I_G and the FWHM of the D peak and the G peak in the Raman spectra, it can also be found that PGCNFs also have an improved degree of graphitization (see supplementary information).

The rGO sheets play an important role in the catalytic oxidation of NO. The PGCNFs can generate catalytically active sites which enhance Rc. After activation, PCNFs become affluent in micropores, which have the adsorption capacity for both NO and NO_2, which suggests that any amount of NO_2 formed by the initial oxidation of NO is also absorbed into micropores. In PCNFs, the number of catalytically active sites is severely limited either on the surface or in the micropores, and accordingly, the effectiveness of catalytic oxidation of NO is also limited. While our work sheds light on the correlation between the emergence of catalytically active sites due to incorporation of rGO and the efficiency of NO oxidation, elucidation of precise mechanisms of the catalytic activity provided by rGO need further detailed studies.

Conclusions

The embedding of rGO sheets in CNFs generates a large number of active catalytic sites both on the surface and in the micropores exposed to NO gas molecules, which considerably enhancing the value of Rc. The enhancement of catalytic activity for NO oxidation of PGCNFs can thus be ascribed to the following aspects. Firstly, the catalytic sites appear to be evoked by the generation of N-H after being activated by NH_3, which is confirmed by the FT-IR spectra (See supplementary information). Second, unidentified sites and more unsaturated carbon appear to be introduced on the surface, both acting in the favor of the NO catalytic oxidation. Finally, it is also possible that more topological defects in PGCNFs, as compared to the pristine structures, are beneficial in terms of improving the contact with NO molecules.

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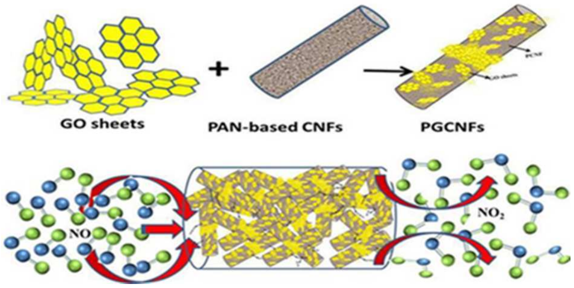
Table of contents entry



Novel structure of composite CNF was prepared via embedding reduced graphene oxide sheets for oxidation of NO at room temperature.