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Short communication

N-doped graphene as a potential catalyst for the direct catalytic decomposition of NO

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ABSTRACT

For the first time, it was experimentally confirmed that N-doped graphene could efficiently catalytically decompose NO to N_2, which proves that the N-doped graphene can be used in the direct catalytic decomposition reaction and that it is a potential catalytic material for the removal of NO.

1. Introduction

N-doped graphene (NG), with the advantages of opening band gap, activated graphene surface, enhanced electronic properties and stability, has been widely studied as a potential catalyst in many chemical reactions since the discovery of graphene in 2004 [1], such as electrocatalysis [2–4], organic synthesis [5] and oxidation of hydrocarbon [6]. The presence of N atom on the surface of NG can introduce catalytic activity toward special reactions compared to pure graphene. When nitrogen atoms are introduced into the carbon lattice of graphene, the dopants and defects will be formed [7], which generate new active sites. In addition, N atom has a larger electronegativity than that of C atom, which leads to electron transfer from C to N easily [8]. However, the spin density and the charge distribution of carbon atoms will be affected by their neighbouring nitrogen dopants [9], which weakens the conjugation between adjacent carbons and forms the activation region on the NG surface [10,11]. This activated region can be participated by catalytic reactions directly [12]. However, thus far, it has been rarely reported that the NG can be applied in direct catalytic decomposition reaction. Therefore, exploring the feasibility of whether the NG can be used in direct catalytic decomposition reaction is of important scientific research significance.

Nitrogen oxides (NO_x) have become the focus of air pollution control. There are many researches concentrating on how to control the emission of NO_x effectively, among them select catalytic reduction process [13] is the main research direction of industrialized application and development in the world because of its mature technology, high deNO_x efficiency and good stability. However, it requires a large number of additional reductants such as NH_3 and high operation costs. Moreover, NH_3 escapes easily causing secondary pollution. The direct catalytic decomposition of NO_x [14] does not have these problems and is considered as a promising method to remove NO. A density functional theory study about NG used for direct decomposition of NO was carried out [15], however, the study lacks experimental confirmation. Therefore, the present study focusses on experimentally exploring the possibility of NG for NO direct decomposition.

2. Experimental procedure

2.1. Synthesis of graphene oxide

In the present work, graphene oxide (GO) was synthesized by the Hummer's method [16].

2.2. Synthesis of NG

NG was prepared by annealing GO powders with urea at 600 °C in flowing argon at certain mass ratios, GO: urea = 1:15, 1:20 and 1:30, respectively. The ratios were chosen such that the N atoms can be efficiently incorporated in the lattice of graphene. If the ratios are low, the N content may be too less to play a role in the reaction,. However, if the ratios are too high, N—N bonds will form easily, which makes the N atom fail to incorporate in the lattice of graphene. The mixture was put into the tube furnace and heated to 600 °C for 0.5 h at the rate of 5 °C/min. Graphene was also synthesized for comparison.

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2.3. Materials characterization

The catalysts were analysed by X-ray diffraction (XRD, Rigaku DMAX-RB) with a radiation of Cu Kα (λ = 1.5406 Å). The 2θ scans cover the range 5–40° with a step size of 0.02° and a scan rate of 5° min^{-1}. Raman measurement was carried on a HR800 Raman spectrometer instrument from Horiba Company using the Ar ion laser with an excitation wavelength of 514.5 nm. The X-ray photoelectron spectroscopy (XPS, the AXIS ULTRA DLD instrument) was performed by monochromatic Al-Kα radiation to analyse the surface electronic structure of the catalysts. After complete removal of moisture from the catalysts by drying at 100 °C for 24 h, the catalysts were analysed without surface sputtering or etching so that the degree of vacuum in the XPS equipment was maintained at 7–10 Pa.

2.4. Activity evaluation and tests

The performance tests were carried out in a fixed-bed quartz reactor, as shown in Fig. S1 of the Supplementary material, using 0.2 g of catalyst and 400 ppm of NO (in Ar atmosphere) at a flow rate of 333 mL/min, corresponding to the gas hourly space velocity of 10,000 h^{-1}. The reaction temperature was increased from 500 to 850 °C. The concentrations of NO and NO_2 were analysed by a flue gas analyser (VARIO PLUS, MRU, Germany) and that of N_2O was analysed by gas chromatograph (Agilent 7890A Series) with a Poropak Q column and a thermal conductivity detector for the N_2O analysis. The NO conversion (φ) and the N_2 selectivity (S) were calculated using the following formulas:

$$\varphi = \frac{\mathrm{NO\ (inlet)} - \mathrm{NO\ (outlet)}}{\mathrm{NO\ (inlet)}} \times 100\%$$

$$S = \frac{\mathrm{NO\ (inlet)} - \mathrm{NO\ (outlet)} - \mathrm{NO2\ (outlet)} - \mathrm{N2O\ (outlet)}}{\mathrm{NO\ (inlet)} - \mathrm{NO\ (outlet)}} \times 100\%$$

NO (inlet) represents the NO concentration at the inlet, NO (outlet) represents the NO concentration at the outlet, NO_2 (outlet) represents the NO_2 concentration at the outlet, N_2O (outlet) represents the N_2O concentration at the outlet.

3. Results and discussion

3.1. Raman spectroscopy and XRD characterization

Raman spectroscopy is used to determine the structural disorder or defect of NG as shown in Fig. 1. The D band originates from defects and disorders, which represents the level of defects and the dopant contents in graphene. The G band originates from the first-order Raman scattering process, which represents the graphitization degree of graphene. The 2D band is the major mark for confirming graphene, which is induced by the second-order, double-resonance process and related to zone-boundary phonons [17]. All samples have similar concentrations of defects with the I_D/I_G values in a range of 1.0–1.2 (RGO = 1.06, NG15 = 1.14, NG20 = 1.15 and NG30 = 1.19). When N element is doped into graphene, the defect will be increased. As shown in Fig. 1, the I_D/I_G values increase with an increase of N contents, which indicates that the N elements affect the defect levels of graphene. The XRD patterns of all the samples are shown in Fig. S2 of the Supplementary material.

3.2. The performance tests and the N_2 selectivity

Pure graphene has low NO conversion efficiency, and its activation temperature is high as shown in Fig. 2. Notably, when N is doped into graphene, the NO conversion increases markedly and the activation temperature decreases from 700 to 550 °C. The N_2 yield *vs* reaction temperature is shown in Fig. S3 of the Supplementary material. The N_2 yield almost has no change from 600 to 850 °C, which indicates that there is a high N_2 selectivity of about 100% for NG20. NG20 is more excellent than NG15 for catalytic decomposition of NO; however, the conversion does not increase with further addition of N contents such as that for NG30, whose catalytic efficiency is lower than that of NG15. The reason might be the high amount of nitrogen deposited on the graphene surface, which leads to the formation of carbon nitride thereby weakening the NG conductivity.

3.3. X-ray photoelectron spectroscopy of NG-X (X = 20, 30)

X-ray photoelectron spectroscopy (XPS) is the standard technique to study the nitrogen-doping effect in graphene as shown in Fig. 3.

The peaks appear at 284.8, 286.4, 289.3 and 287.2 eV for RGO, which are attributed to the different C—O bonding configurations. The C—O bonding configurations become weak for NGs compared to those of RGO because of the decrease in the oxygen group after thermal annealing of graphene oxide, C1s peak of NGs shifts to high binding energy, which indicates the formation of C—N bonds for NGs [20]. The element contents of NGs and the percentages for the three types of N species in NGs are shown in Table S1 of the Supplementary material. The N/C ratios of NG15, NG20 and NG30 are 0.04, 0.10 and 0.11, respectively. The total percentages of the pyridinic N sites in NG15, NG20 and NG30 are 1.63, 4.12 and 3.38%, respectively, which shows that NG20 is bigger than NG15 because of the higher number of pyridinic N sites. In addition, NG20 obtained better NO conversion than NG30. The XPS data of NG20 after the reaction are shown in Fig. S4 of the Supplementary material.

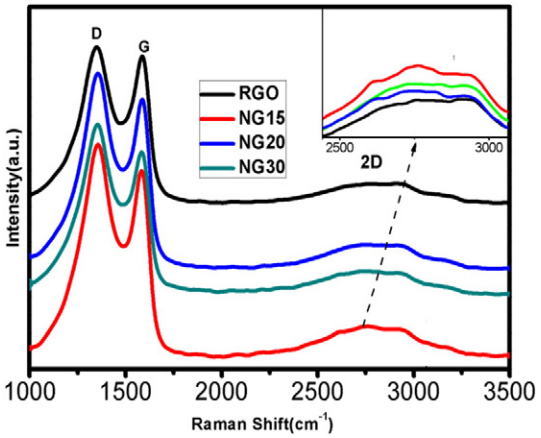

Fig. 1. The Raman spectra of all the samples (NG15, NG20, NG30 and RGO).

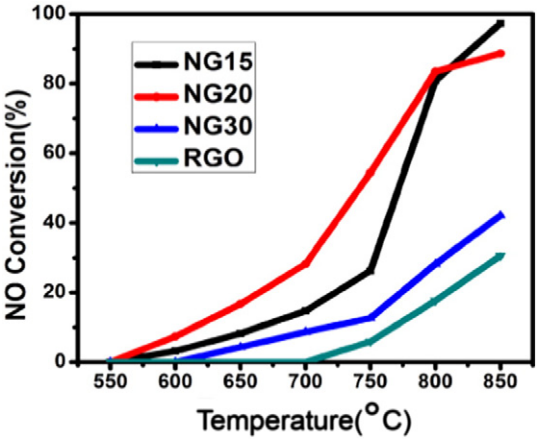

Fig. 2. The NO conversion of all the samples (NG15, NG20, NG30 and RGO).