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ARTICLE

Nitrogen-doped onion-like carbon: a novel and efficient metal-free catalyst for epoxidation reaction†

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Onion-like carbon (OLC) as a promising carbon material has attracted extensive interest in many fields. In this work, we report for the first time that the nitrogen-doped OLC has been controllably synthesized via a nitric acid pretreatment, followed by the different temperature calcination treatment under ammonia atmosphere. The detailed physicochemical properties of the doped OLC samples are investigated by high resolution transmission electron microscopy (HRTEM), Raman spectra, x-ray photoelectron spectroscopy (XPS), elemental analysis (EA) and electron energy loss spectroscopy (EELS). Moreover, the potential catalytic performance of such doped samples is evidenced by styrene epoxidation reaction, a kind of typical metal-related catalytic reaction. The results indicate that doped OLC samples exhibit more excellent catalytic performance than pristine OLC and some reported metal-related catalysts. The graphitic nitrogen species plays a key role in the catalytic reaction based on some control experiments and a good linear correlation between the content of this species and the activity results. Our work provides the value information on the design and application of modified carbon materials in catalytic reactions.

Introduction

Since the discovery of fullerenes in 1985, the chemistry of non-planar carbon materials has attracted tremendous attention.¹⁻³ A large variety of non-planar-related materials (e.g. nanotubes, nanocones, onion-like carbon (OLC), nanospheres) have been synthesized.⁴⁻⁶ Among them, OLC is a class of quasi-spherical nanoparticle consisting of multiply closed concentric graphitic shells. There are some synthetic methods for OLC-related materials, but the annealing of detonation nanodiamond powders is the only widely used one that allows the synthesis of large amounts of OLC at low cost.⁷ Comparing with other carbon materials, OLC exhibits some unique chemical and physical properties due to its high curvature and surface energy. These advantages suggest extensive potential applications, including supercapacitors, magnetic materials, electrode materials and catalysis.⁸⁻¹¹ The introduction of heteroatoms has been regarded as a facile and effective strategy to adjust surface properties of carbon materials, such as N- or B-doped carbon nanotubes (CNTs) and graphene.¹²⁻¹⁴ In particular, doped carbon materials as metal-free catalysts have been reported to exhibit relatively high efficiency in various catalytic reactions (e.g. the C-H bond activation, oxygen reduction reactions (ORR), the ring opening polymerization and alcohol oxidation).¹⁵⁻¹⁸ Although the fabrication and application of heteroatoms-doped OLC is rarely reported, it could provide interesting catalytic properties as a result of the special doped properties and multilayer curvature graphitic shells.

Catalytic epoxidation reaction of olefins has been widely used in industrial processes. Epoxides are important

intermediates in fine chemicals for the synthesis of perfume, drugs, epoxy resins, sweeteners, etc. Traditionally, two methods for the epoxidation of styrene are employed. One is halogenohydrin, which is simple but causes much pollution. The other method is carried out by using the unsafe, hazardous and expensive stoichiometric peracids as an oxidant.¹⁹ Current researches on the styrene epoxidation has been focused to use metal-related catalysts, such as molecular sieves, heteropolyacid modified complexes and noble metal-related catalysts which are normally prepared by the complicated synthetic approaches.²⁰⁻²² Many attempts have been made to improve the conversion of styrene and the selectivity to styrene oxide (SO). Titanium substituted silicalite (TS-1) has been demonstrated to be very effective for styrene epoxidation using anhydrous urea-hydrogen peroxide as an oxidant, and the usage amount of the catalyst is as high as 20 wt % of substrates.²³⁻²⁴ However, a high selectivity usually goes with low conversion. Therefore, it is desirable to explore a novel metal-free catalytic system with a more effective and minimal environmental footprint.

Herein, we report the preparation of nitrogen-doped OLC based on the chemical substitution of oxygen functional groups and subsequently rearrangement of graphitic layers structure via a two-step method. We highlight that nitrogen-doped OLC (N-OLC) as a novel metal-free catalyst exhibits a stable and excellent catalytic performance for styrene epoxidation. By correlating X-ray photoelectron spectroscopy (XPS) and other control experiments, we identify that graphitic nitrogen is responsible for the epoxidation reaction.

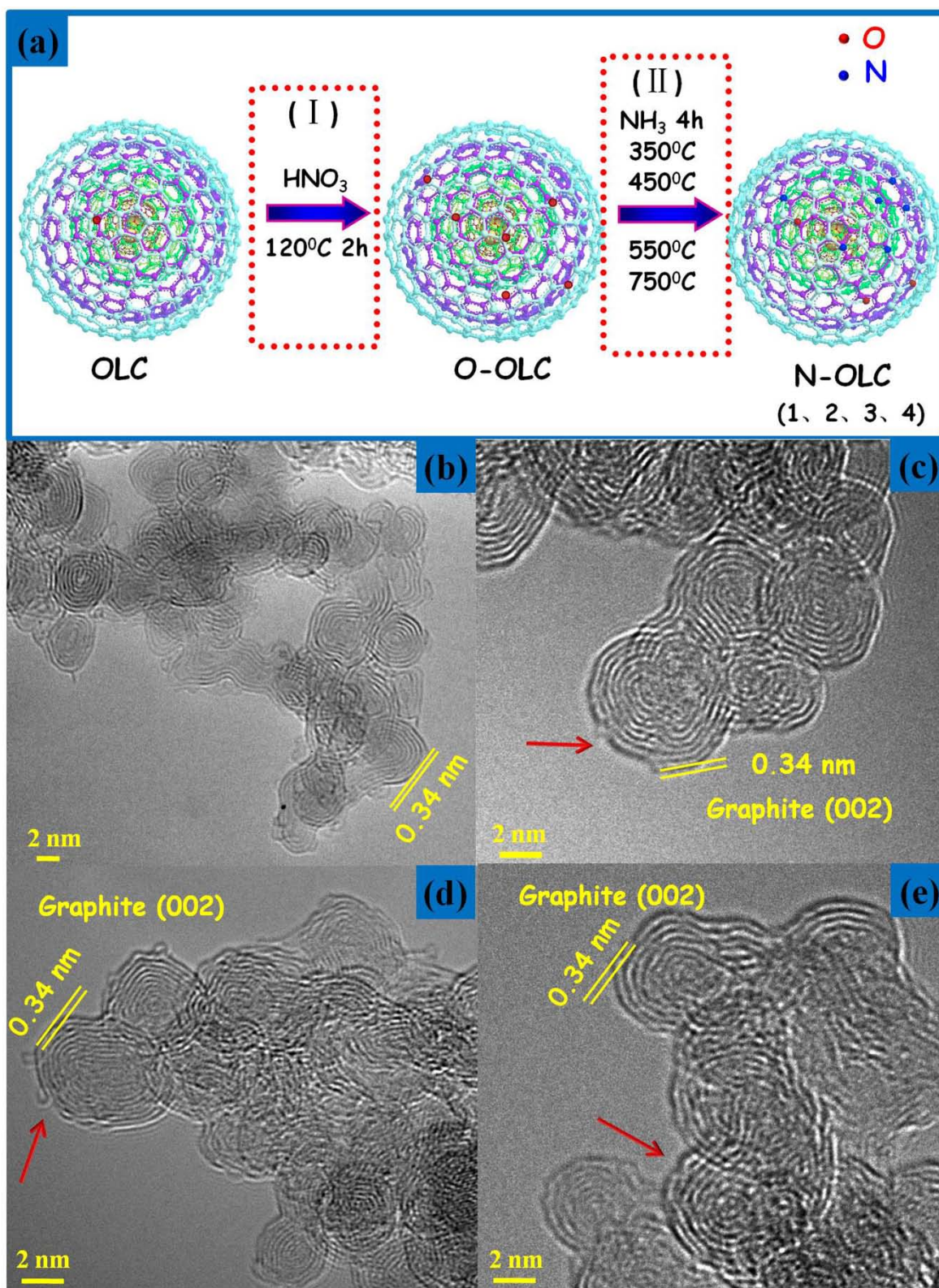


Fig. 1. (a) Schematic illustration for fabrication and HRTEM images of various N-OLC samples (b) OLC, (c) N-OLC-1, (d) N-OLC-3 and (e) N-OLC-4.

Experimental section

Materials Purified ultra-dispersed nanodiamond (UDD) was bought from Beijing Grish Hitech Co. (China), produced by detonation and followed by acid washing. The average particle

size was about 5 nm. Styrene, styrene oxide (SO), ethylbenzene, trifluorotoluene (TFT), acetonitrile (ATN), dimethyl formamide (DMF), dioxane (DX), tributyl phosphate (TP), dichloromethane (DCM), toluene (TU) and tert-butyl hydroperoxide (TBHP) were supplied by Alfa-reagent. All chemicals were analytical grade without further purification.

Sample preparation and activity test A schema for sample preparation is shown in Fig. 1a. Shortly, undoped OLC was produced by thermal annealing of ultra-disperse nanodiamond (UDD) powder (Beijing Grish Hitech Co.) at 1300 °C for 4 h under argon atmosphere. As-prepared OLC sample was added to 100 mL concentrated nitric acid with continuous stirring at 120 °C for 4 h. The product was filtered and washed with deionized water and ethanol, and then dried at 60 °C for several hours. The product was denoted as O-OLC. Doped OLC samples were synthesized by thermal annealing of O-OLC sample at different temperature (350 °C, 450 °C, 550 °C and 750 °C) under ammonia atmosphere for 4 h. These products were labeled as N-OLC-1, N-OLC-2, N-OLC-3 and N-OLC-4, respectively. The epoxidation reactions of styrene were carried out in a 25-mL two-necked flask containing 0.01 g catalyst, 10 mL trifluorotoluene, 1 mmol styrene, and 3 mmol TBHP (65 wt%) at 90 °C for 4 h. A certain amount of ethylbenzene as an internal standard was added to the solution. The reaction solution was sampled periodically, analyzed and quantified by gas chromatography (Agilent 7890A).

Characterization High resolution transmission electron microscopy (HRTEM) images and electron energy loss spectroscopy (EELS) spectra are recorded by a FEI Tecnai G2 F20 microscope. The X-ray photoelectron spectroscopy (XPS)

spectra are carried out on an ESCALAB 250 XPS system with a monochromatized Al K α X-ray source. The data fitting is performed by fixing the peak maximum within ± 0.15 eV for all spectra and applying a full width half-maximum (FWHM) of 1.2–1.6 eV by means of Avantage analysis software. The value of the mixed Gaussian-Lorentzian is maintained at 30 %. Raman spectra are recorded with a LabRam spectrometer. A He/Ne laser at 532 nm is used as the excitation source. Elemental analysis (EA) was recorded on a TCH-600 analyzer at 2200 °C.

Results and Discussion

The structure of the representative samples was investigated by HRTEM. The surface of OLC and doped OLC samples composes of multiply quasi-spherical concentric graphitic shells (Fig. 1b). The identified interlayer spacing of 0.34 nm in the shells is assigned to the (002) of graphite. Figure 1c–e illustrate that there are some clear surface defects (red arrows) on all the doped samples. However, no distinctive difference in the mean size of particles (ca. 5–6 nm) and morphology is observed among the undoped and doped OLC samples. The N₂ adsorption-desorption analysis indicates that there is no obvious change of the specific surface area and the pore size of all the samples (see Fig. S1, supporting information).

XPS was used to analyze the surface chemical components of different samples. As shown in Fig. 2a and 2c, the XPS spectra of N1s and O1s can be divided into the following regions: N1 (398.2 eV), N2 (399.2 eV), N3 (400.2 eV), N4

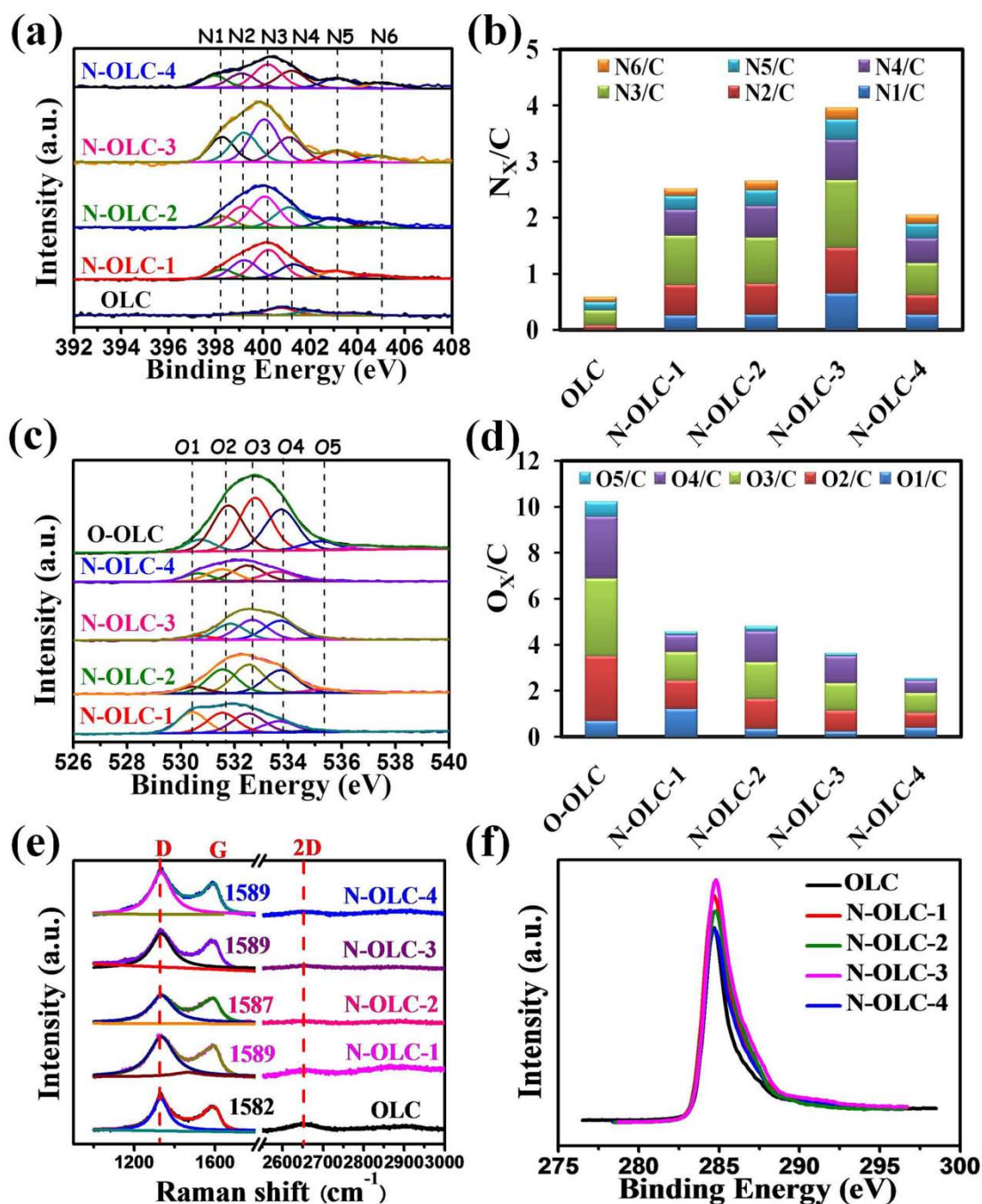


Fig. 2. (a-d) N1s and O1s XPS spectra and distribution diagrams of N_x/C and O_x/C atomic ratio on the undoped and doped OLC samples. (e) Raman spectra of samples using a He-Ne laser ($\lambda=532$ nm). (f) C1s XPS spectra of samples.

(401.3 eV), N5 (402–403 eV) and N6 (405 eV) that are attributed to pyridinic nitrogen, lactam nitrogen, pyrrolic nitrogen, graphitic nitrogen, quaternary nitrogen and nitrate NO_x, respectively. O1 (530.7 eV), O2 (531.8 eV), O3 (532.7 eV), O4 (533.7 eV) and O5 (535 eV) are assigned to quinines or pyrone, unsaturated carbon-oxygen double bond (C=O), carbon-oxygen single bond (ether-like or anhydride), phenolic and adsorbed water, respectively.²⁵ In this work, the nitrogen content in N-OLC can be simply tuned by varying different calcination temperature. Fig. 2b shows that the nitrogen content increases from 0.55 % (atomic percent) for undoped OLC (inherent) to the highest value of 3.95 % for N-OLC-3. On the

contrary, the concentration of oxygen decreases from 10.7 % on O-OLC to as low as 2.55 % for the doped OLC (see Fig. 2d). The similar change feature of bulk content nitrogen and oxygen is found via EA analysis (see Table S1, supporting information). This is well support the XPS results and demonstrate homogenous distribution of nitrogen atoms in the doped samples. Notably, apart from the thermal decomposition of the partial oxygen species,²⁶ the atomic contents of O2, O3 and O4 species in all samples significantly decrease after the introduction of nitrogen, indicating that NH₃ may react with O2, O3 and O4 species and then form all kinds of nitrogen species along with the rearrangement of graphitic layers structure

during the preparation process.²⁷ The detailed analysis of XPS are summarized in Table S2.

The Raman spectra of undoped and nitrogen doped OLC samples exhibit three main features in the 1000-3000 cm^{-1} region (see Fig. 2e), the defect-related D-band ($\sim 1323 \text{ cm}^{-1}$), the G-band ($1582 \text{ cm}^{-1} \sim 1589 \text{ cm}^{-1}$) and the 2D band ($\sim 2653 \text{ cm}^{-1}$). The intensity of D and 2D bands and the peak position of G band are sensitive to the doping state of carbon materials. Comparing with undoped OLC sample, the higher intensity of D band of doped OLC suggests that the increase of the disordered graphite structure in doped OLC due to the formation of the shorter carbon-nitrogen bond.¹³ The extremely low intensity of 2D band in all doped OLC samples reveals the saturation of substitutional nitrogen species doping in OLC.²⁸ The upshift of G band can be explained by the effect of n-

doping state on the Fermi level (the level will shift to a higher energy) and the opening of the energy gap.²⁹⁻³⁰ The increase of I_D/I_G ratio for doped OLC samples indicates that the introduction of nitrogen produces much more structural defects than that in pristine OLC (Table 1). Additionally, the ordering of graphitic structure can be revealed by full width at half maximum (FWHM) of C1s (see Fig. 2f and Fig. S2).³¹ Comparing with that of undoped OLC (1.23 eV), the C1s peak of doped OLC (the maximum is 1.6 eV) at 284.6 eV is considerably broadened demonstrating the influence of nitrogen on disordered structure in line with Raman. The broad C1s XPS peak of doped OLC samples at 286.6~288.3 eV can be ascribed to surface trace carbon-oxygen and carbon-nitrogen-containing bond.

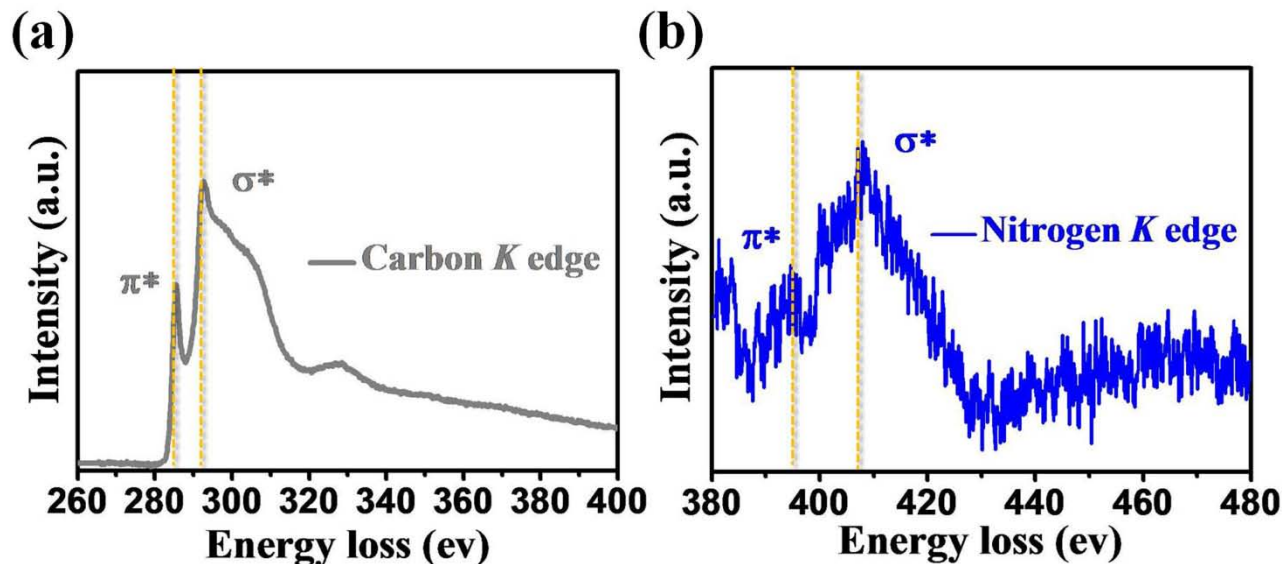


Fig. 3. EELS profiles of representative N-OLC-3 sample. (a) carbon K-edge; (b) nitrogen K-edge.

Electron energy loss spectroscopy (EELS) was considered to be an efficient analysis method for doped carbon materials owing to its spectra correspond to the excitation of the C1s and N1s core electrons to the empty conduction band states and show the local conduction density of states at that site. Fig. 3a shows the carbon K-edge spectra of the N-OLC-3 sample, which exhibits a peak at 285.5 eV due to 1s core level to π^* transitions, and the band starting at 292.5 eV is assigned to transitions to the p-orbits merging with part of the broad σ^* band in well-defined graphite structure, different from nanodiamond sp^3 bounded structure (289.1 eV).³²⁻³³ The characteristic π^* and σ^* transitions in carbon K-edge suggest that a sp^2 hybridization state for carbon. As depicted in Fig. 3b, the π^* peak at about 396 eV in nitrogen K-edge corresponds to the sp^2 bonding of N in hexagonal nitrogen/carbon conformation.³⁴ The σ^* peak at 408 eV is a signature of pentagonal defect corrugations with sp^3 -bonding character.³⁵ The similar spectra feature of C and N K-edge also indicates the incorporation of nitrogen atoms in the carbon sp^2 network.

Table 1 shows the catalytic behavior of the undoped and doped samples for the epoxidation of styrene to styrene oxide (SO) under different conditions. In the absence of catalysts, the conversion of styrene is 51.5 % and the selectivity for SO is 4 % after 4 h. This is much lower than that of OLC with the conversion of 85.4 % and selectivity of 12.8 % (entry 2). It should be noted that the doped

OLC samples apparently exhibit higher SO yield than undoped OLC. The introduction of nitrogen improves the catalytic performance. Among all the catalysts, N-OLC-3 exhibits an excellent conversion of 88.4 % with the highest selectivity of 46 % and thus a yield of 40.7 % (entry 6). This result is superior to those recently reported epoxidation catalysts (entry 10, 11 and 12) under the similar conditions.³⁶⁻³⁸ In order to exclude the self-polymerization of styrene under the strong oxidizing environment, tributyl phosphate (TP) is employed as an effective polymerization inhibitor during epoxidation reactions.³⁹ The result (entry 8) reveals that the high conversion for styrene activates from catalysis rather than polymerization. The sp^3 bounded ultra-disperse nanodiamond (UDD) and N-CNTs (prepared by traditionally CVD method at 900 °C) are selected as the reference samples to evaluate the catalytic performance (entry 14 and 15, respectively). Apparently, the catalytic performance of these two referencing samples is much lower than those of all the nitrogen-doped OLC samples. Besides, the effects of the solvents, the molar amount of TBHP/substrate and the reaction time on the catalytic performance of the N-OLC-3 are displayed in Fig. S3. Interestingly, although the conversion of N-OLC-3 increases from 70.5% to 92.9 %, the selectivity decreases from the maximum value of 46 % to 24.2 % when the reaction time prolongs to 12 h. The similar tendency is also observed when increasing the amount of TBHP in the epoxidation reaction. The non-proportional results may due to the further oxidation of the

Table 1. Catalytic epoxidation of styrene by various samples under different conditions.^(a)

Entry	Catalyst	S _{BET} (m ² g ⁻¹)	Time (h)	Con (%)	Sel (%)		Yield (%)		I _D /I _G (area ratio)
					SO	others	SO		
1	--	--	4	51.5	4.0	96	2.06	--	
2	OLC	368	4	85.4	12.8	87.2	10.9	2.4	
3	N-OLC-1	385	4	88	28.0	72	24.6	3.3	
4	N-OLC-2	389	4	88.9	31.3	68.7	27.9	3.2	
5	N-OLC-3	410	2	70.5	40	60	28.2	3.5	
6	N-OLC-3	410	4	88.4	46	54	40.7	3.5	
7	N-OLC-3	410	12	92.9	24.2	75.8	22.5	3.5	
8 ^(b)	N-OLC-3	410	4	87.5	44.1	56.8	38.8	3.5	
9	N-OLC-4	406	4	88	23.2	76.8	20.4	3.4	
10 ^(c)	N-graphene	--	10	58	40	60	23.2	--	
11 ^(d)	Au/TS-1	--	10	19.3	72.4	27.6	14.0	--	
12 ^(e)	Co-OMS-2	--	24	39	50	50	19.5	--	
13 ^(f)	N-OLC-3	410	4	87.5	45.0	55	39.4	3.5	
14	N-CNTs	55	4	75.1	11.1	88.9	8.3	--	
15	purified UDD	305	4	52.5	8.4	91.6	4.4	--	

(a) Reaction conditions: 10 mg catalyst, 1 mmol styrene, 3 mmol tert-butyl hydroperoxide (TBHP), styrene:TBHP:cat = 1:3:10, where the ratio of catalyst is based on catalyst mass. 10 mL solvent, 90 °C. (b) 2 mmol tributyl phosphate (TP) as a polymerization inhibitor is added to reaction system. (c) Ref. 36: 100°C, O₂, reaction time: 10 h. (d) Ref. 37: 60 °C, styrene:TBHP:cat = 1:4:16.7, reaction time: 10 h. (e) Ref. 38: 60 °C, styrene:TBHP:cat = 1:1:10, reaction time: 24 h. (f) The fifth cycle test of N-OLC-3 under same conditions. Desired product: styrene oxide (SO)

intermediate products caused by the active site or the redundant oxidant. Moreover, N-OLC-3 is an excellent reusable catalyst. We can use simple centrifugation to achieve the separation of N-OLC-3 from the reaction solution and reuse it in the next round of

epoxidation reaction (see Fig. S4). After five successive runs, the conversion of styrene on N-OLC-3 is 87.5 % along with the selectivity of 45 % (see Table 1).

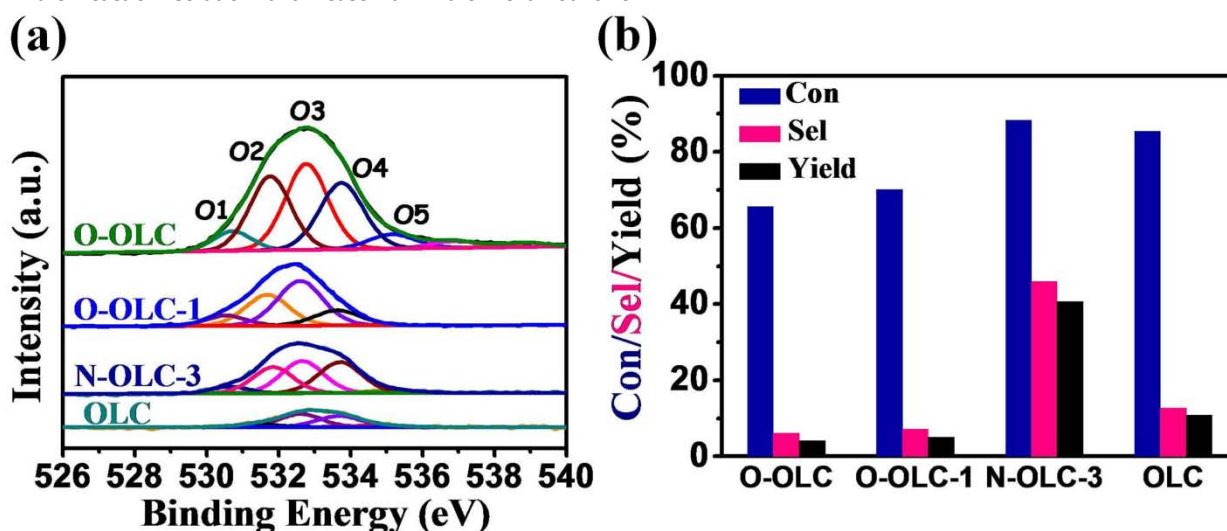


Fig. 4. (a) O1s XPS spectra of undoped and doped OLC samples. (b) Catalytic performance for styrene epoxidation on various samples

In order to understand the nature of above non-metal catalytic process for styrene epoxidation, the role of surface oxygen and nitrogen species was investigated by control experiments. It was reported that for oxidation reactions the catalytic performance of carbon materials activates from the unsaturated C=O groups (O2

species) and carboxylic acid groups.⁴⁰⁻⁴² In this paper, we annealed treatment for O-OLC (at 900 °C) to obtain O-OLC-1 sample that possesses the total oxygen content of 3.7 %, but the content of O2 and O3 species are similar to N-OLC-3 (see Fig. 4a and Table S3). The results of activity measurement indicate that the catalytic

performance of O-OLC-1 is much lower than N-OLC-3, as well as that of O-OLC with the yield of 4.1 % (see Fig. 4b). Obviously, it is nitrogen species that play an important role in the epoxidation reaction rather than oxygen species. The weaker catalytic performance of OLC may be ascribed to the activation of surface defects and/or trace oxygen species for styrene.

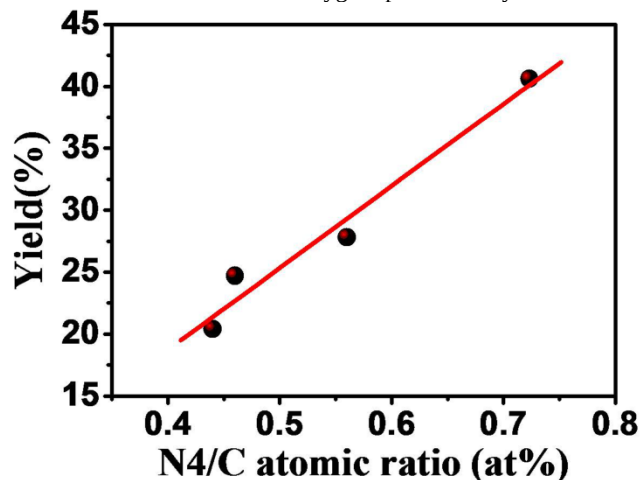
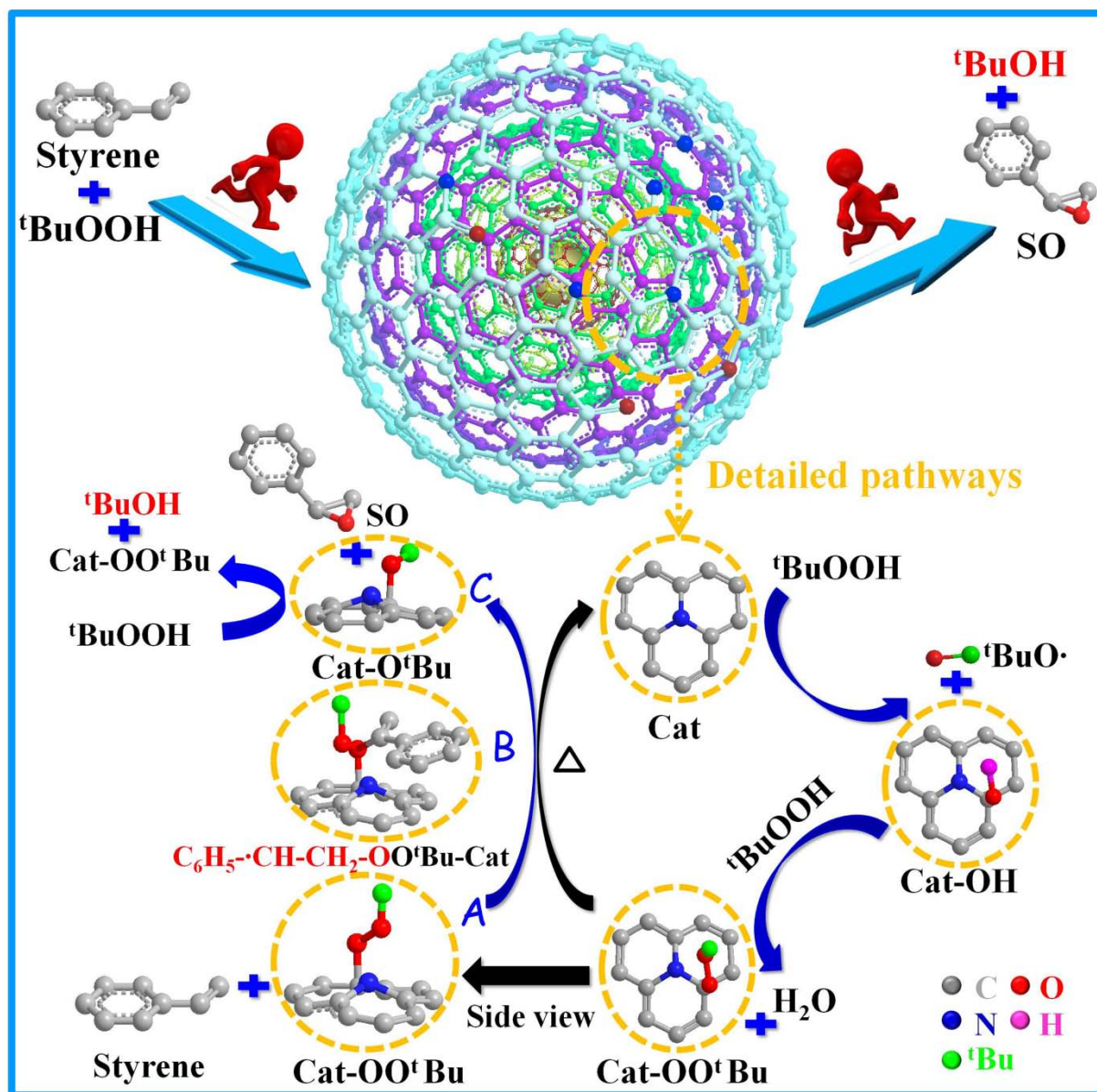


Fig. 5. The relationship between the catalytic activity (Yield of SO) and the concentration of graphitic nitrogen in various doped OLC catalysts.

Based on above findings, we next explore the correlation between the concentrations of different nitrogen species and catalytic activity. As shown in Fig. 5, a good linear relationship is found between the yield of SO and N4/C atomic ratio obtained from XPS. There is no correlation between the catalytic activity with N1, N2 or N3 species (Fig. S5). This suggests that the graphitic nitrogen species is closely correlated with the epoxidation reaction. In previous work for ethylene oxidative dehydrogenation reactions on nanostructured carbocatalysts, we presented that nitrogen doping not only decreased the adsorption energy of ethylene, but also had a larger barrier for dissociation and more favorable to improve the selectivity of ethylene than the undoped sample.⁴³ Ma and coworkers reported that graphitic nitrogen did not directly participate in the activation of substrates,

but instead changed the electronic structure of the adjacent carbon atoms, finally exhibited a metal-like d band electronic phenomena.⁴⁴ These unique electronic properties of carbon atoms make them a superior position for the adsorption of reactive oxygen species such as peroxide. Recently, with regard to various epoxidation reactions, Sakaki et.al proposed a detailed olefin epoxidation mechanism over the transition metal Ru/porphyrin complex on the basis of the electronic structures of olefin adduct and the transition state via theoretical study. The author assumed that the bonding between the metal Ru and oxo species would form a kind of active species containing a new Ru-oxo σ bond.⁴⁵ Catalytic reactions traditionally using TBHP have been reported to proceed via a free radical mechanism ($^t\text{BuOOH} = ^t\text{BuO}^\bullet + ^\bullet\text{OH}$).⁴⁶ In this paper, due to the formation of a metal-like d band electronic structure, the adjacent carbon atom of the graphitic nitrogen in N-OLC (Cat) may undergo a one-electron oxidation in the presence of TBHP to form Cat-OH species which can be further converted to Cat-OO ^tBu species under the reaction conditions. Besides that, based on the specific properties of free radicals,⁴⁷ the chemical interaction (Scheme 1A) between the double olefinic bond of the styrene and the α -oxygen of the Cat-OO ^tBu species can lead to the breakup of double bond and the formation of a transition state (Scheme 1B) with a new C-O bond and $\text{C}_6\text{H}_5\text{-}^\bullet\text{CH-CH}_2$ intermediate species. In the final step, a ring-closure process (Scheme 1C) essentially leads to the formation of epoxide product since the ring-closure barrier is much smaller than the C-O bond formation barrier.⁴⁸ In addition, we observed the abounding existence of the $^t\text{BuOH}$ after reaction using the gas chromatography verifying indirectly the rational of the process C (Figure Table S4). The detailed mechanism of epoxidation reaction is displayed in Scheme 1.



Scheme 1. The Proposed Mechanistic Pathways for Epoxidation on the Doped OLC.

Conclusions

In summary, a class of nitrogen-doped onion-like carbon (OLC) materials has been controllably synthesized and the total concentration of nitrogen ranges from 2.06 at % to 3.95 at %. We describe that such doped OLC samples as novel metal-free catalysts for epoxidation reaction using TBHP as an oxidant exhibit more excellent catalytic performance than undoped OLC and other recently reported metal-related materials under mild conditions. The best olefin conversion and epoxide selectivity reach to 88.4 % and 46 %, respectively. The possible reaction mechanism is proposed on the basis of the unique properties of graphitic nitrogen and the free radical theory. Our study also highlights a new approach for the design of doped carbon materials with excellent catalytic properties and sets the foundation for the further industrial application.

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Notes and references

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†Electronic Supplementary Information (ESI) available: The materials of additional data and figures about the BET analysis, XPS spectra and

catalytic reaction conditions for various samples. See DOI: 10.1039/b000000x/

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