Insights into the surface chemistry and electronic properties of sp² and sp³-hybridized nanocarbon materials for catalysis†

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Ultra-dispersed nanodiamond and its derivatives (UNDDs), including bucky nanodiamond and onion-like carbon, offer superior catalytic behavior relative to other nanocarbons. However, a systematic study of their unique properties has been rarely achieved. Their surface chemistry and electronic properties are therefore studied to reveal the essential differences of UNDDs compared to other nanocarbons for catalysis.

Nanocarbon catalysis has been considered as a potential candidate to meet the goals of sustainable and green chemistry over the past few years.1 Numerous achievements have demonstrated that carbon materials, such as nitrogen-doped activated carbon, reduced porous graphene oxide and nitrogen-doped carbon nanotube arrays, exhibit excellent catalytic activity as compared to some industrial transition-metal based or noble-based catalysts in the liquid phase, in the gas phase, as well as in electrochemical reactions.2 Unlike these sp³-hybridized carbon materials, sp³-hybridized ultra-dispersed nanodiamond (ND) and its derivatives (UNDDs), including sp³/sp²-hybridized bucky nanodiamond (BND) and sp²-hybridized onion-like carbon (OLC), have emerged as a new category of the nanocarbon family.3 ND has abundant surface oxygen species including carboxylic acids, ketones, phenols, lactones and so on.4 BND consists of a sp³ carbon core covered with a few sp² graphite-like shell layers that can be directly synthesized by the graphitization of ND in an inert atmosphere or under vacuum (T < 1500 °C, Fig. S1, ESI†). It not only benefits from the remarkable surface properties of graphene-based nanomaterials but also combines the intrinsic characters of a diamond core. Upon increasing the annealing temperature (T ≥ 1500 °C, Fig. S1, ESI†), BND will further phase transfer into OLC, which is a fascinating non-planar-related material with multiple sp² curved closed concentric graphite-like shells.

As new members in the carbonous family, UNDDs possess interesting physicochemical properties, such as superior thermal and chemical stability, high surface energy and unique electronic structure. These properties have made UNDDs competitive candidates for catalytic reactions beside conventional metal-based catalysts.5 Moreover, some recent achievements have highlighted that UNDDs exhibit superior catalytic behavior in comparison to other sp³-hybridized nanocarbon materials (e.g., nanographite, nanotubes, activated carbon, graphene) for some important catalytic reactions, such as ethylene dehydration and phenolic oxidation.6–8 It should be pointed out that the essential differences between a UNDD system and conventional sp³-hybridized nanocarbons in catalytic reactions have rarely been studied, and the origin of the catalytic behavior remains elusive and controversial. As such, it is therefore highly desirable to clarify the structure–property relationship in more detail in an effort to elucidate their underlying catalytic applications. In this work, we compare the surface chemistry and electronic structures of representative sp³- and sp³-hybridized nanocarbon materials by using XPS, temperature programmed desorption (TPD) and ultraviolet photoelectron spectroscopy (UPS), and attempt to give insights into the distinct physicochemical properties of UNDDs and other nanocarbons. Moreover, two probe reactions (nitrobenzene reduction and selective oxidation of 2,3,6-trimethylphenol) are used to reveal the direct correlation between the electronic structure and the catalytic activity.

By using electron energy loss spectroscopy (EELS), the surface electronic structure and graphitization transformation of UNDDs were firstly studied. As shown in Fig. 1a, the main peaks located at about 292 eV in the carbon K-edge of UNDDs correspond to the characteristic 1s → σ* transitions and the shoulder peaks at 285 eV, which are assigned to the 1s → π* transition, indicate the...
B N Dt os p2-hybridized OLC. Interestingly, the G-bands shift from sp2 carbon readily calculated by EELS (with highly oriented pyrolytic synthetic temperature reaches 1500\(\text{ }\)C, the corresponding sp2 content of OLC is 96%, suggesting that the phase transformation from sp3 to sp2 carbon is almost complete. In addition, the fraction of sp2 carbon of representative graphene (GR) and multi-walled carbon nanotubes (MWCNTs) is around 84% and 80%, respectively. The sp2 graphitization degree of OLC is much higher than that of GR and MWCNTs. With respect to specific surface area, there is a good linear relationship among ND, BND and OLC. The specific surface area of ND may involve an amorphous core–shell structure that is functional oxygen groups causes the formation of dangling functional groups such as carboxyl (–COOH, \(\sim 285 \text{ cm}^{-1}\)) and phenol (C–OH, \(\sim 3200 \text{ cm}^{-1}\)) will be effectively removed, leading to the release of both CO and CO2 gases. When the annealing temperature is above 800 \(\text{ C}\), the surface C=O is the only existing oxygen group in theory. The obvious signals of CO and CO2 of ND represent the richer surface chemistry properties as compared with other carbon materials. Actually, the gradual detachment of functional oxygen groups causes the formation of dangling bonds on carbon atoms, which can reconstruct and combine to form π-bonds, indicating that the onset temperature of graphitization (namely, phase transformation) approaches to 800–900 \(\text{ C}\). The HRTEM result of the 900BND sample further
supports this speculation (Fig. S2b, ESI†). The reconstructive phase transformation generates \( \text{sp}^3 \)-hybridized carbon shells on the outside of the ND, followed by continuous graphitization to the inside of the particle upon increasing the temperature.\(^{11}\) Structural defects of the ND surface, inherent or derived from the detachment of surface functional groups, increase the reactivity of the surface carbon atoms, which greatly facilitates the phase transformation process.\(^{12}\) As the temperature exceeds 1300 °C, the initially highly disordered graphite-like shells become increasingly more graphitic with a lower defect density. A fully transformed highly ordered OLC could be obtained when the temperature is above 1500 °C (Fig. S2d, ESI†). Compared with ND, GR and MWCNTs do not exhibit the competitive signals of CO and CO\(_2\) that can be ascribed to the lower concentration of oxygen groups and the highly ordered graphitic structure.

The thermostability and oxidation resistance of UNDDs have been demonstrated to play important roles in gas-phase catalysis. In other previous studies, Barnard and colleague applied a calculated model based on the extrapolated atomic heat of formation, and proposed that the thermostability of BND was better than that of ND.\(^{13}\) Gogotsi et al. studied the standard enthalpies of formation at 25 °C over various nanostructured carbons, assuming that the thermostability of BND was better than that of ND.\(^{14}\) The high stability of BND may be attributed to the oxygen-containing functional groups bonded to the sp\(^3\) structure.\(^{14}\) In the present work, we found that OLC exhibited better thermostability and oxidation resistance compared to other carbon materials, measured using thermogravimetric analysis (TG) under different atmospheres (Fig. S3, ESI†). Although the content of oxygen species among some carbon materials is similar, the weight losses of GR (7.8%) and MWCNTs (4.2%) are higher than those of BND (1.3–3.4%) and OLC (1.0%), but lower than that of ND (13.8%) under an argon atmosphere. Additionally, the oxidation onset temperature of OLC is up to 600 °C, suggesting its feasibility in catalysis under a high-oxidation atmosphere. ND, with the highest concentration of oxygen species, exhibits a similar oxidation resistance to 900BND and 1100BND. The observed behavior may be correlated to their specific core–shell surface.

An ultraviolet photoelectron spectroscopy (UPS) source can excite only valence band electrons and thus it can provide information about the distribution of electrons in the valence band, work function and density of states (DOS) near the Fermi level. As shown in Fig. 3a, the valance band spectra of the carbon materials exhibit three kinds of characteristic peaks located at about 3.0, 7.0 and 8.5 eV, which can be assigned to the C2p–π, π–σ and σ electrons, respectively.\(^{15}\) Using HOPG as a reference, there is no obvious difference in the binding energy of π (~3.0 eV) and σ (~7.5 eV) in the cases of BND and OLC, but the π and σ bands of multi-walled carbon nanotubes (MWCNTs) and graphene (GR) are found to shift to higher binding energies (3.8 eV and 8.5 eV). Moreover, at the region near the Fermi level (Fig. 3b), BND and OLC show a steeper increase in DOS as compared to MWCNTs and GR. These results suggest that the BND with lower π and σ electronic binding energies and enhanced DOS may be more beneficial to be activated than those of MWCNTs and GR under the same conditions. Compared with ND, the BND samples show an increase in intensity at ~3.0 eV, which is suggestive of an increase in the graphitic sp\(^2\) carbon content (Fig. 1a and b). It should be noted that the binding energy of σ of ND (~8.2 eV) is also lower than those of MWCNTs and GR. Here, the signal of the σ band derives from the surface disordered carbon of ND rather than the bulk sp\(^3\) carbon that is deactivated under UPS because of its own insulating properties. These results suggest that UNDDs may be activated at a lower energy cost than those of MWCNTs and GR under identical conditions, that is, UNDDs may have a higher surface energy. This fact well matches the theoretical prediction.\(^{16}\)

The work function (\(\Phi\)) is the minimum energy needed for inner electrons to escape from their nuclei, that is, a lower work function implies that the electrons of the samples have a lower excitation energy barrier.\(^{17}\) As displayed in Fig. 4, regardless of ND, BND and OLC catalysts exhibit lower work function values than those of MWCNTs and GR. In general, the surface groups and electronic structures of the samples are two of the main factors that affect the work function.\(^{18}\) It is noteworthy that compared with GR (2.8 at%) and MWCNTs (0.7 at%), 1200 BND and OLC with similar oxygen contents (2.4 and 0.5 at%, respectively) have lower work functions. Moreover, the result of the fitting curve of BND indicates that the content of sp\(^3\) carbon is not the key factor that affects the work functions of GR, MWCNTs and BND. All these facts demonstrate that the lower work function of BND compared with those of MWCNTs

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**Fig. 3** (a) Valance band spectra of various carbon materials. (b) A magnified region near the Fermi level of carbon materials.

**Fig. 4** Relationship between the fraction of sp\(^3\) carbon and the work function over different carbon materials. Work functions were determined from the secondary electron cutoff of UPS He I spectra using nickel metal as a reference.
and BND could be explained in terms of the destabilization of the π-electrons (lower π electronic binding energy of UNDDs) rather than surface groups or the content of sp² carbon. Such specific π-electrons may be attributed to the curvature of the graphitic shell. A similar result on the effect of the curvature on the catalytic performance.

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Fig. 5 The dependence of the work function on the catalytic activity over different carbon materials for the reduction of nitrobenzene (a) and the selective oxidation of 2,3,6-trimethylphenol (b). Reaction conditions: (a) 25 mg catalyst, 10 mmol nitrobenzene, 6 equiv. N₂H₄, 100 °C, 4 h. (b) 8 mg catalyst, 0.1 mmol 2,3,6-trimethylphenol, 70 °C, 12 h, 3.6 equiv. t-butylhydroperoxide (TBHP), 5 mL trifluorotoluene (TFT).