Research Progress of Organic Functionalized Graphene in Heterogeneous Catalytic Application

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Abstract. Graphene has been applied in many fields as a catalyst with inherent advantages because of its unique structure and properties. Functionalized graphene has been enriched and expanded in the field of performance and application, and has become the current research trend. Organic functionalized graphene is a non-metallic modification of graphene, which has more excellent catalytic performance and is widely used in many reactions. This paper reports the application of organic functionalized graphene in heterogeneous catalysis as the following aspects: of graphene oxide (Go), doped graphene, small organic molecules and modified graphene by organic polymers.

1. Introduction
In 2004, Geim et al discovered graphene with atomic thickness with high light transmittance and electrical conductivity. Because of its high specific surface area and excellent electron mobility, graphene is of great value in the application of catalysts and catalyst carriers [1]. Graphene has become a hotspot of nanometer science research in recent years due to its excellent properties. Through functional modification and composite, the properties and applications of graphene have been further enriched and expanded, it has been widely used in electricity, biomedicine, energy storage materials, catalysis and many other fields, especially in the field of heterogeneous catalysis. At this point, the functionalized graphene can be considered as a nonmetric solid macromolecular catalyst agent. Besides, the huge specific surface area and unique two-dimensional structure of graphene determine that graphene can be used as inorganic nanometer chemical agent ideal carrier, and a variety of inorganic nano-catalytic system has been widely studied and applied such as graphene-based materials immobilized single/polymetallic, metal oxides, metal sulfide nanoparticles.

2. Application of organic functional graphene in the field of catalysis
Organic functionalized graphene refers to the derivative of graphene obtained by nonmetallic modification of graphene by physical or chemical means. The exploration of nonmetallic catalysis has become one of the research hotspots of graphene-based catalysts in recent years [2].

2.1. Graphene oxide (Go)
Go is the most special and important functional derivative of graphene. Which, like graphene, has a typical quasi-two-dimensional structure, but a large number of oxygen-containing groups are connected on the base surface of a two-dimensional space composed of a layer of carbon atoms. The
plane contains -OH and C/O/C, while the lamellar edge contains C=O and COOH. Compared with graphene, Go has larger specific surface area and rich oxygen-containing groups and local conjugation and other characteristics [3].

The unique structure and properties of Go give it the inherent advantage of being a catalyst, and it can play a catalytic role in many heterogeneous catalytic processes as catalytic activator, oxidant and solid acid catalyst (Figure 1).

Bielawski’s research group at the university of Texas was the first to research the catalytic properties of Go. In 2010, Bielawski reported [4] that go could be directly used to catalyze the oxidation of alcohols, alkenes and alkynes. In the 100°C, Go can directly catalyze the reaction that benzene methanol was oxidated to generate formaldehyde, and give a yield as high as 98%, further comparative experiments show that reduction of graphene and graphite oxide have the catalytic activity and reaction could be carried out only in the air. This result suggested that oxygen in the air is the essence of antioxidant, Go have the effect of the activated oxygen molecules, subsequent research has shown that Go under aerobic conditions can also make cis styrene oxidated to the corresponding diphenyl diketone.

Bielawski’s findings offer fresh insights into the nonmetallic catalysis of Go. Besides, Go is also a mild oxidant. In 2011, Liu et al. [5] used porous Go as an oxidant to oxidize sulfur dioxide (SO₂) to sulfur trioxide (SO₃) at room temperature. After reaction, it was found that Go was partially reduced (Figure 2).

Trunschke et al. [6] found that Go can catalyze the insertion of organic molecules into oxygen, and the oxidation of acrolein to acrylic acid can reach half the activity of traditional molybdenum vanadium oxide catalyst. Bielawski [5] also studied the oxidation of Go and successfully oxidized distyrene and diphenylnmethane into corresponding ketone. Go can also be used for oxidation of sulphydryl groups with corresponding disulfide and sulfur oxides [7]. Most of the experimental reaction conditions with Go as oxidant were very harsh, and a large amount of Go was required,
indicating that Go could only be used as a weak oxidant. For the edges of Go are rich in carboxyl groups, and certain sulfonic acid groups are produced on the surface during the preparation process [8]. Therefore, oxidation Graphene can be used as a solid acid catalyst. Bielawaki[4] took advantage of the acidity of Go to catalyze the hydration of alkyne, and the yield of phenylacetylene was up to 98%, and other series of alkynes also achieved good catalytic results. Besides, it was reported by Garcia [9] that Go could catalyze ring opening reaction of epoxide group at room temperature. When only use 0.19wt% of Go, good conversion effect was obtained. In addition, Bao et al [10] prepared the reduction of graphene oxide through the chemical reduction and used the reduction of graphene oxide to catalyze the reduction reaction of nitrobenzene to aniline with hydrazine hydrate as reducing agent, the product yield can reach 97% under room temperature, but only 0.4% yield was obtained with graphite as catalyst. With density functional theory (DFT) simulation, the author argues that the catalytic active site is unsaturated carbon atoms at the edge and defect (Figure 3), this conclusion is then confirmed by related research [11].

Figure 3. (a) Structure of defect free one-layer graphene; (b) The optimized structure of the nitrobenzene molecule reacting with one-layer graphene through two C-O bonds

2.2. Doped graphene
Heteroatom doping can not only widen the band gap of graphene, which makes graphene from conductor transform to semiconductor, but also affect the spin density and charge distribution of carbon atoms. For example, nitrogen doping will bring about an increase to local electron cloud density, leading to enhanced alkalinity on the surface of graphene, thus generating catalytic activity sites. Doped graphene could be prepared simply and has high catalytic activity to oxygen reduction reaction (ORR), so it is an ideal material to replace precious metals such as platinum, gold and palladium.

Shao et al. [12] prepared nitrogen doped graphene with plasma injection method, and the prepared doped graphene showed very high electrocatalytic oxygen reduction activity, with higher stability and selectivity than platinum metal catalyst. Wei group [13] prepared pyrrole type nitrogen-doped graphene using the space-restricted induction protocol, and nitrogen-doped graphene showed excellent electrocatalytic activity for ORR. Qiao and his colleagues [14] studied synergistically doped graphene with sulfur and nitrogen and found that for ORR, synergistically doped graphene was more active than either sulfur or nitrogen doped graphene alone.

Dai group [15] prepared boron and nitrogen synergistically doped graphene by heat treatment with boric acid and ammonia as heteratomic sources, and this synergistically doped graphene showing higher electrocatalytic activity than commercial platinum/carbon (Pt/C) catalysts.

2.3. Organic small molecule, polymer modified graphene
By modifying the organic functionalization of graphene and Gor, more active groups or small organic molecules can be derived on the surface of graphene materials, making them become non-quantitative macromolecules and serve as solid acid or solid base catalysts. Su et al. [16] used strong acids to pretreat Go and to carboxylate the graphene. Then, the modified graphene was an efficient catalyst for primary amine oxidation, and can get a conversion rate of 98% under mild reaction conditions and had excellent reusability.
Chang's research group [17] used chlorosulfonic acid to modify Go, which can effectively catalyze the hydrolysis reaction of hexose, glucose and fructose (Figure 4), and its reuse performance is very stable.

Figure 4. Chemical conversion of hexose sugars to LA and LA-derived chemicals

Ji et al. [18] prepared graphene solid acid catalyst, by the free radical addition method to introduce benzene sulfonic acid onto the surface of graphene (Figure 5), which had very high activity for the hydrolysis of ethyl acetate, and the catalytic effect was higher than that of Nafion NR50 commercially. The catalytic activity decreased only slightly after repeated use for 5 times.

Figure 5. Illustration for the preparation of sulfonated graphene.

Based on the same idea, Yuan et al. [19] modified Go with amination through protonization and carbon-metallization nucleophilic substitution reactions to produce graphene solid base catalyst, which also showed high catalytic activity for the hydrolysis of ethyl acetate. Li et al. [20] Introduced sulfonic acid group and amino group into graphene surface simultaneously through free radical addition and silanization reaction, and prepared graphene-based acid-base dual-function synergistic catalyst (Figure 6), and achieved excellent conversion and yield for continuous reaction of Deacetalization--Nitroaldol.

Figure 6. Illustration for preparation of GO–AEPTMS/SO$_3$H hybrids

In addition to small organic molecules, organic polymers and graphene-based materials can also serve as excellent heterogeneous catalysts. As shown in Figure 7, Wang [21] used poly (3-hexyl thiophene-2, 5-2) (P$_3$HT) to non covalent functionalized Go, and tested the complex activity through the Mannich reaction. The results showed that the product yield is as high as 93%, far higher than that of homogeneous P$_3$HT (about 65%), and traditional titanium dioxide photocatalyst can only get a yield of 58%, the researchers believe that the electron transfer of graphene substrate during the reaction process is the main reason for the catalytic enhancement effect.
Figure 7. Oxidative Mannich Reaction catalyzed by graphene-ploymer hybrid as heterogeneous catalyst

3. Conclusion
Graphene materials are widely used in a variety of unique catalytic systems. Organic functionalization modification has improved the catalytic effect of graphene materials and made them become composite catalysts with synergistic catalytic properties. However, the functional graphene catalyst still faces many challenges, such as the catalytic mechanism of the catalyst, the relationship between the catalytic activity and its functional groups, conjugated structure and defect sites, which need to be studied. In addition, while actively developing graphene catalytic reaction system, we should also synthesize more functional graphene composites and use them to develop more green and efficient catalytic reaction systems.

Acknowledgments
We gratefully acknowledge support for this work provided by Self-financing projects for key R&D projects in Hebei Province (Grant NO. 18214911) and the Doctor Foundation of Shijiazhuang University of Applied Technology (Grant NO. 15YB1002).

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