

Short communication

Graphene oxide supported copper coordinated amino acids as novel heterogeneous catalysts for epoxidation of norbornene

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ABSTRACT

In this work, we explored whether graphene oxide after modification with copper coordinated amino acids could attain an excellent catalytic activity for the epoxidation of norbornene. Therefore, graphene oxide sheets were functionalized with different amino acids through coordination to copper ions for the synthesis of copper coordinated amino acids-grafted graphene oxide. For this aim, at first amino acids were coordinated to Cu^{2+} . Then, copper ions were complexed with GO. The catalytic activity of the prepared novel catalysts were tested in epoxidation of norbornene. These catalysts showed excellent catalytic performance compared with reported catalysts in other works which demonstrated graphene oxide as a support is superior to other support materials.

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1. Introduction

In the last few years, graphene oxide as a two-dimension (2D) honeycomb carbon nanomaterial has received extensive attention in different catalysis areas such as organic catalysis, electrochemistry and photochemistry [1,2]. Graphene with easy surface functionalization, large specific surface area, intrinsic low mass and abundant oxygen-containing functional groups can be applied as catalyst or support in chemical synthesis [3–5]. The existence of oxygen-containing functional groups on the basal planes and edges of GO allow its modification with different materials such as organometallic compounds, metal nanoparticles and alkaloid [6,7] which are extremely desirable for catalytic applications as catalyst or support. Furthermore, insertion nanoparticles or organometallic compounds on graphene surface for reusability and recovery of catalyst is very significant. Recently, many researches about the synthesis of different catalysts using functionalized GO through physical and chemical methods have been reported [8–11]. For example, after the synthesis of copper (salen) complex onto GO support [Cu(salen)-f-GO], this complex was used as catalyst for the epoxidation of olefins [12]. In 2013, Wang et al. reported the synthesis of N-

heterocyclic carbene-palladium complex (NHC-Pd^{2+}) onto GO support through a chemical method and investigated its role as catalyst in the Suzuki-Miyaura reaction [10]. In 2014, Limei Zhou and his coworker reported the synthesis of copper supported on amino-acid-grafted graphene (A-G-Cu) as catalyst in N-arylation of imidazole with iodobenzene [13].

Due to the existence of good coordination interaction between amino acids and metal ions [14], we first synthesized different amino acids complexes using Cu^{2+} . Then through the coordination of functional groups on the surface and edges of GO (carboxylic acid, epoxy and hydroxyl) with Cu^{2+} ions in the synthesized amino acids complexes, different complexes of GO (GO-Cu-AA) were prepared. Then one of the complexes (GO-Cu-phenylalanine with high conversion) was utilized in the epoxidation reaction, that not only exhibited better catalytic activity for the epoxidation of norbornene but also even after intensive reuse showed good stability. However, since modification of graphene oxide with amino acids through coordination to Cu^{2+} is relatively green and convenient, these samples can be synthesized on a large scale.

2. Experimental

2.1. Materials and instrumentations

All of the information about the materials and instrumentations used in this work was presented in the Supporting information.

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2.2. Synthesis of graphene oxide and GO-Cu-AA

Using modified Hummer's technique [15] graphene oxide (GO) was prepared from natural graphite powder. In a typical procedure, the as-prepared GO (0.0593 g) was good dispersed in 50 mL of distilled water under intense stirring for 30 min. For the synthesis of copper coordinated amino acids, 2 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in the mixture of distilled water-absolute ethanol 50/50 (wt%) and was loaded in a 100 mL round-bottom flask. Then, 2 mmol amino acid in the mixture of distilled water-absolute ethanol 50/50 (wt%) was dropwise added (1 drop in 1 min) to solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ followed by vigorous stirring at room temperature. After drying, the obtained light blue product was recrystallized in diethyl ether and acetone. The solid precipitate was dissolved in distilled water, and was dropwise added to the dispersed GO powder followed by ultrasonication for 5 min and under vigorous stirring for 24 h. Finally, the black solid was collected using the centrifugation followed by washing with distilled water for several times and was dried at 50 °C.

2.3. Catalytic reactions of GO-Cu-AA

At first, 60 mg GO-Cu-AA as catalyst was dispersed in 12 mL of acetonitrile and was placed in a 100 mL round-bottom flask. Then 10 mmol of the substrate and 20 mmol of 30% H_2O_2 was slowly added into the above dispersion under magnetic stirring followed by refluxing in an oil bath for 12 h. At the stated time, the resulting mixture was analyzed by gas chromatography (GC). In order to investigate the recycling experiments, the used catalyst was washed with acetonitrile using the centrifugation for several times, and was reused after each run.

3. Results and discussion

3.1. Preparation of GO-Cu-AA

Amino acids are cheap and environmentally friendly, therefore, they are good candidate for the synthesis of new bio-functionalized graphene oxide. In this work, divalent Cu^{2+} ions as coordinating agent between GO and amino acids were used. For this aim, at first different amino acids complexes were synthesized using the Cu^{2+} ions (Scheme 1).

Then, through coordination of functional groups on the surface and edges of graphene oxide with Cu^{2+} in the synthesized amino acids complexes, different amino acids were located onto GO support (Scheme 2). Thus, various complexes of GO as new catalysts were synthesized, simultaneously. By means of FT-IR, XRD, XPS, Raman spectroscopy, TEM and FE-SEM analysis morphology and structure of the prepared samples were analyzed.

3.2. Characterization of copper coordinated amino acids functionalized graphene oxide

3.2.1. FT-IR analysis

The structures of synthesized GO and GO-Cu-AA were characterized by FT-IR analysis (Fig. 1). In the IR spectrum of GO, absorptions peaks at 1734 cm^{-1} and 3430 cm^{-1} are related to $\text{C}=\text{O}$ stretching vibration of carboxylic acids and $\text{O}-\text{H}$ stretching vibration of carboxylic acid and hydroxyl groups, respectively. The peak at around 2922 cm^{-1} is attributed to stretching vibration of aliphatic $\text{sp}^3\text{C}-\text{H}$. Furthermore, bending vibration of $\text{C}-\text{OH}$ [16] and absorptions peaks of epoxy rings [17] appeared at 1058 cm^{-1} and 1228 cm^{-1} , respectively. In FT-IR spectrum of GO-Cu-AA (Fig. 1), after exposing GO to amino acids complexes, the peak for $\text{C}=\text{O}$ is shifted from 1734 cm^{-1} to 1719 cm^{-1} and in addition to, the intensity for this peak is decreased, which these changes confirmed coordination of carboxylic acid groups to divalent metal ion. Similar phenomenon was reported in previous literature [18]. The coordination of carboxylic acid groups to divalent metal ion weakens the $\text{C}=\text{O}$ band and lowers the stretching force constant K , resulting in a lowering of the carbonyl frequency of saturated acid to about 1719 cm^{-1} . Notably, after exposing epoxy groups to Cu^{2+} , due to opening of epoxy rings, a reduction in relative intensity for $\text{C}-\text{O}$ peak of epoxy groups at 1228 cm^{-1} was obvious. With this change, the relative intensity for $\text{C}-\text{OH}$ peak at 1058 cm^{-1} was increased [18].

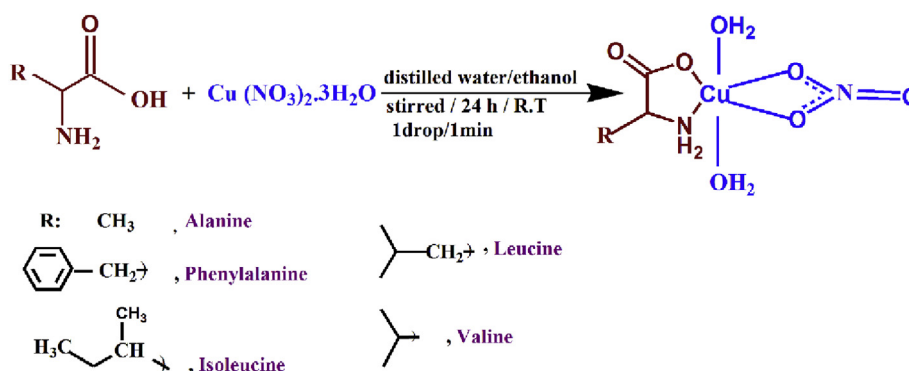
3.2.2. XPS spectroscopy

To provide the qualitative proof for the insertion of copper coordinated alanine onto GO, X-ray photoelectron spectroscopy (XPS) analysis was used (Fig. 2). In the XPS spectrum of GO-Cu-alanine the existence of four peaks at 284, 401, 533 and 942 eV are related to $\text{C}1\text{s}$, $\text{N}1\text{s}$, $\text{O}1\text{s}$ and $\text{Cu}2\text{p}$ signals, respectively (Fig. 2). The deconvoluted $\text{C}1\text{s}$ spectra demonstrated three typical peaks at 287.4, 286.6 and 284.2 eV (Fig. S6b), corresponding to $\text{O}-\text{C}=\text{O}$, $\text{C}-\text{N}$ and $\text{C}-\text{C}/\text{C}=\text{C}$ [19–23]. In contrast with XPS spectrum of GO in literature [24], the $\text{C}=\text{O}$ peak shifted and exhibited partial changes, related to coordination of carboxyl groups to Cu^{2+} ions.

Furthermore, the $\text{O}1\text{s}$ spectrum divided into two fitting curves (Fig. S6c), one peak at 531.3 eV was assigned to $\text{O}-\text{C}=\text{O}$ and another peak at 532.5 eV was ascribed to $\text{C}-\text{OH}$. Owing to the existence of $\text{O}-\text{C}=\text{O}$ functional groups in copper coordinated amino acid, the intensity of $\text{O}-\text{C}=\text{O}$ peak in deconvoluted XPS spectra of $\text{O}1\text{s}$ is higher than of $\text{C}-\text{OH}$ peak [25]. In the deconvoluted XPS spectra of $\text{Cu}2\text{p}$, the dominant curve at 934.9 eV was assigned to $\text{Cu}2\text{p}_{3/2}$, while the small curve at 951.4 eV was assigned to $\text{Cu}2\text{p}_{1/2}$ of copper(II) [11] (Fig. S6d).

3.2.3. Morphology study

The morphology of graphite, GO and different GO-Cu-AA complexes were examined using scanning electron microscopy (SEM) and



Scheme 1. Proposed structure for the copper(II) complexes with different amino acids.

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