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Covalently functionalized graphene sheets with biocompatible natural amino acids

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ABSTRACT

Graphene sheets were covalently functionalized with aromatic–aliphatic amino acids (phenylalanine and tyrosine) and aliphatic amino acids (alanine, isoleucine, leucine, methionine and valine) by simple and green procedure. For this aim, at first natural graphite was converted into graphene oxide (GO) through strong oxidation procedure; then, based on the surface-exposed epoxy and carboxylic acid groups in GO solid, its surface modification with naturally occurring amino acids, occurred easily throughout the corresponding nucleophilic substitution and condensation reactions. Amino acid functionalized graphene demonstrates stable dispersion in water and common organic solvents. Fourier transform infrared, Raman and X-ray photoelectron spectroscopies, X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy were used to investigate the nanostructures and properties of prepared materials. Each amino acid has different considerable effects on the structure and morphology of the pure graphite, from increasing the layer spacing to layer scrolling, based on their structures, functional groups and chain length. In addition, therogravimetric analysis was used for demonstrating a successful grafting of amino acid molecules to the surface of graphene.

1. Introduction

In nanoscience field, carbon-based nanomaterials play an important role and have attracted the scientific community since their discovery [1]. Among these materials, graphene is one of the most exciting materials which has fascinated great interest in the past several years owing to its potential applications. Graphene, a single layer of sp^2-bonded carbon atoms, is a two-dimension (2D) honeycomb nanostructure [2–6]. The outstanding properties of graphene as well as their functionalized forms render it an ideal candidate in a wide range of applications; including composite materials, gas sensors, transparent electrodes and transistors [7–11]. Due to characteristic structures of carbon-based nanomaterials, they can interact with wide variety of organic molecules by covalent or noncovalent forces (hydrogen bonding, π–π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions) [12–15].

However, the existence of high π–π stacking and van der Waals forces due to attraction between adjacent layers facilitates graphene forming, irreversible aggregation or even restacking to graphite which greatly limits the applications of graphene in several areas, as well as fabrication of graphene based polymer nanocomposites, biosensors, drug delivery systems, solar cells, nanomechanical and transistor devices [13,16–21]. Along with numerous approaches that developed to address this obstacle, the most reliable techniques are functionalization of graphene [22–24]. Several methods have been used for the modification of graphene which can be divided into two common categories: covalent and non-covalent functionalization. Utilizing of graphene oxide (GO) as a precursor, has received great attention of a significant number of researchers these days. GO is an oxygen-containing graphene derivative with partial breakage of sp^2–sp^2 bonds into sp^3–sp^3 bonds for inserting some pendent groups like; hydroxy, epoxy, and carboxylic acid. These functional groups facilitate the interaction between the host materials and GO, also they lead to good dispersion of GO in aqueous solutions thanks to the hydrophilic nature of surface functionalities [25–29].

On the other hand, despite GO sheets readily swell and disperse in aqueous media but they cannot be readily dispersed in

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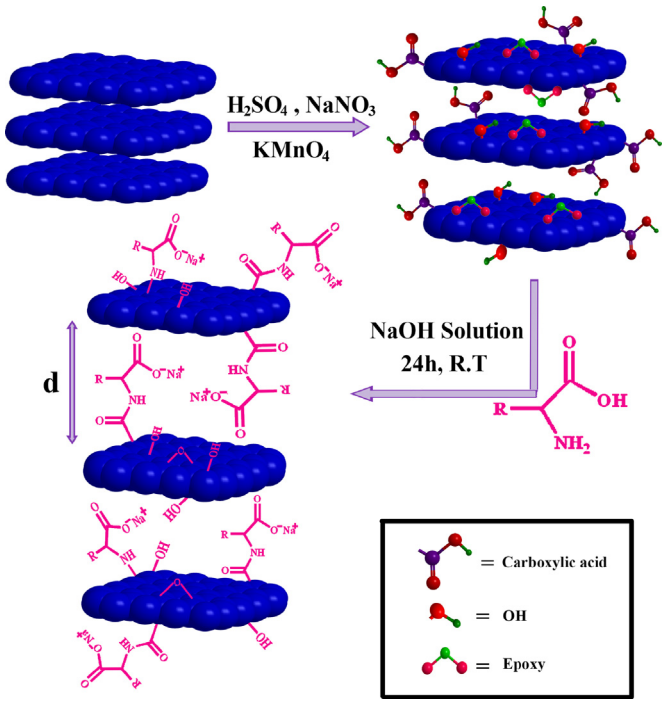

Fig. 1. Synthesis of GO and functionalized graphene with different types of amino acids.

most common organic solvents [3,12,30]. So, in order to increase the dispersibility of graphene in various solvents (aqueous and organic), further functionalization (amidation, esterification, sulfonation and etc.) is needed [13,15,31–33]. Inserting different kinds of functional groups onto graphene layers leads to various changes on graphene structure such as increasing the interlayer spacing or layer scrolling that possess the structure distinct from graphite and multi-walled carbon nanotubes [34–37]. In addition, nowadays, the biological applications of graphene have also been interested [38–42]. Aiming this goal, biocompatible equipments may be rewarded while using multi-functional natural metabolites such as amino acids. These materials are environmentally friendly and naturally occurring compounds, that make graphene a good candidate for biological activities [43–50].

In this context, bio-functionalized graphene sheets with aromatic–aliphatic and aliphatic amino acids have been prepared through easy and green procedure. For this propose, at first GO was synthesized using the simplified Hummer's method [51], then amino acid functionalized graphene materials were synthesized by condensation and nucleophilic addition reactions between $-NH_2$ groups of amino acid and carboxylic acid or epoxy groups on the GO sheets. All synthesized amino acid functionalized graphene were characterized by several techniques including Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and one of them was structurally characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The thermal properties of graphite, GO and functionalized graphene materials were examined through thermogravimetric analysis (TGA). Moreover their morphology was investigated by field emission scanning electron microscopy (FE-SEM). Furthermore, two of them were examined as representative by transmission electron microscopy (TEM) analysis.

2. Experimental

2.1. Materials

Natural graphite powder (diameter 5–10 μm, thickness 4–20 nm, layers <30 and purity >99.5 wt%), was purchased from Neutrino Co. (Iran). Other chemicals used in this study were obtained from Fluka Chemical Co. (Switzerland) and Merck Chemical Co. (Germany) and were used without further purification.

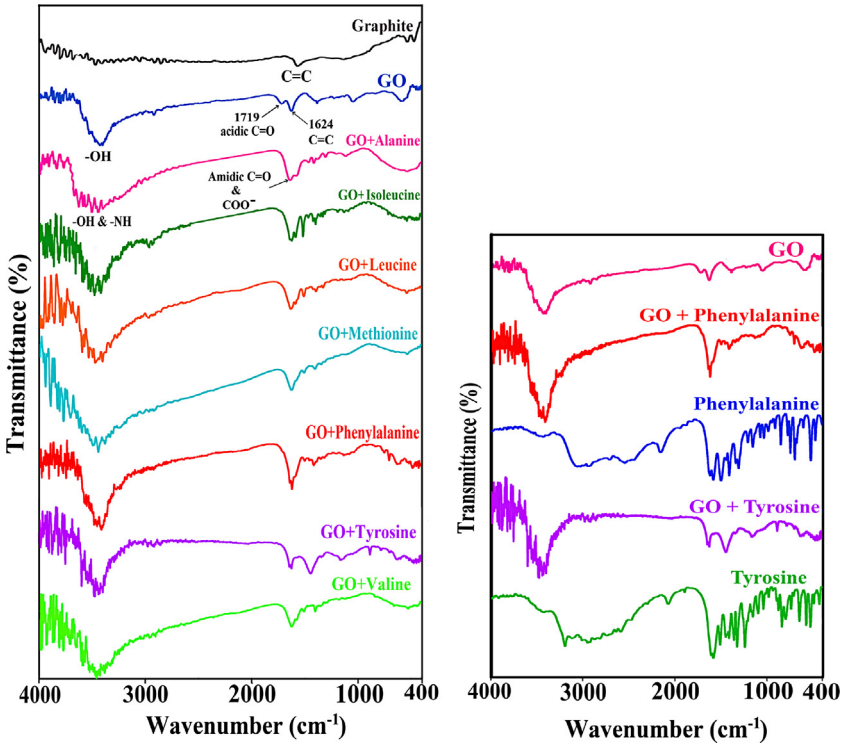

Fig. 2. FT-IR spectra of the pure graphite, GO and different amino acid functionalized graphene and FT-IR comparing of phenylalanine and tyrosine functionalized graphene with their attributed amino acids.