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Synthesis, characterization, and electrochemical properties of the modified graphene oxide with 4,4′-methylenedianiline

Shiva Nikkhah, Hasan Tahermansouri *, Fereshteh Chekin

Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran

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ABSTRACT

Graphene oxide (GO) was modified by 4,4′-methylenedianiline to form a nanocomposite material (GO-amine). Materials were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, derivative thermogravimetric and field emission scanning electron microscopy. The electrochemical behavior of modified carbon paste electrode (CPE) with GO-amine (GO-amine/CPE) was studied by electrochemical methods. The results showed which GO-amine/CPE catalyzes oxygen evolution reaction in alkaline media with an onset potential of 0.4 V (vs. Ag|AgCl|KCl_{3M}), showing a synergistic effect between GO and amine nanocomposite. The high electrochemical stability confirmed the improved electrocatalytic performance of GO-amine. This study affords us a GO-amine based electrocatalyst with high performance and strong durability under alkaline conditions, which can be applied to energy conversion and storage.

1. Introduction

Graphene is considered two dimensional carbon nanofiller with a one-atom-thick planar sheet of sp2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene oxide (GO) is a kind of important derivatives of graphene which has same structure as graphene. In fact, GO nanosheets are highly hydrophilic because it holds various oxygen containing functional groups on basal planes and the sheet edges [1]. Graphene and GO are predicted to have remarkable properties, such as high thermal conductivity, superior mechanical properties, excellent electronic transport properties and energy storage [2–4]. Functionalization of GO may occur via chemical bond formation, hydrogen bonding, or π-π interactions with available unoxidized parts of GO [4]. For example, the amino groups of 4,4′-methylenedianiline can interact with oxygen-containing functional groups of GO(hydroxyl, carboxyl and epoxy groups) in the following ways: (i) hydrogen-bonding interactions(C—OH···H_2N—R), (ii) the protonation of amine groups by the carboxylic groups of the GO layers (—COO^{-}···$^{+}H_3$N—R) and (iii) chemical bond formation on the GO surfaces via nucleophilic substitution reactions on the epoxy groups of GO (Fig. 1). In addition, 4,4′-methylenedianiline bearing aromatic rings can interact with graphene sheets by π–π interaction.

The oxygen evolution reaction (OER) plays an important role in the devices of energy conversion and storage, such as fuel cells and metal-air batteries [5-8]. The anodic OER has slow reaction rate owing to multi-steps transfer of four electrons with high activation energy and large overpotentials [9,10]. Therefore, we need a stable electrocatalyst with high performance so as to lower the large overpotential and accelerate the OER. It is worth noting that designing different nanostructure and crystal phase of electrocatalysts may increase the number of active sites to enhance the electrocatalytic activity.

In the present work, GO was modified with 4,4′-methylenedianiline to prepare GO-amine (Fig. 1). Then, the electrochemical properties of GO-amine indicate prominent improvements of OER activity and electrical conductivity compared to GO, and also revealing a long-term stability in basic media.

2. Experimental

2.1. Materials and methods

4,4′-Methylenedianiline, hydrazine hydrochloride, sodium hydroxide and sulfuric acid from Merck Chemical Inc. and graphene oxide nanoplatelets (99%, Thickness 3.4–7 nm with 6–10 Layers) were purchased and used as received. Analytical reagent-grade chemicals were used as well as deionized water from a Milli-Q system (Millipore). Field emission scanning electron

* Corresponding author.
E-mail address: h.tahermansuri@iauamol.ac.ir (H. Tahermansouri).

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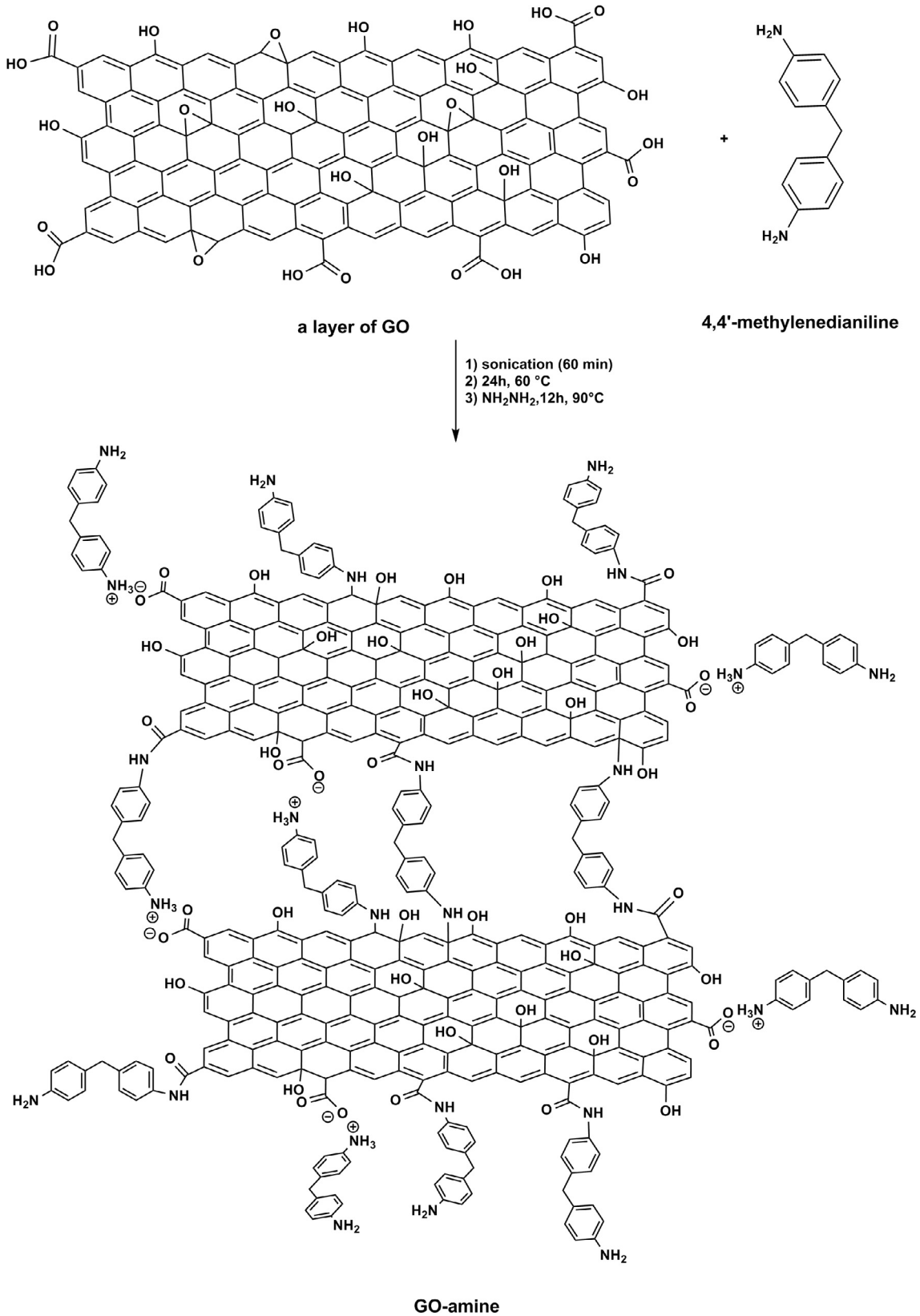

Fig. 1. The modification route of GO layers by 4,4′-methylenedianiline.

microscope (FESEM) measurements were taken using an MIRA3// TESCAN-XMU model. Fourier transform infrared spectroscopy (FT-IR) was recorded using KBr tablets on a Thermo Nicolet Nexus 870 FTIR spectrometer. The samples were studied by thermogravimetric analysis (TGA) (Netzsch TG 209 F1 Iris1) under nitrogen gas atmosphere (10 °C/min).