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MoO_3-rGO nanocomposites for electrochemical energy storage

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ABSTRACT

We have synthesized the one dimensional (1D) MoO_3 nanorods and MoO_3-rGO nanocomposite by using sonochemical dispersion method at low temperature. The obtained products were characterized by using Raman spectroscopy, FT-IR, SEM, TEM and HR-TEM. We have demonstrated the electrochemical properties of MoO_3 nanorods and MoO_3-rGO nanocomposites. The specific capacitance for MoO_3 nanorods and MoO_3-rGO nanocomposite was calculated to be 3.3 F/g and 22.83 F/g at current density of 0.3 A/g respectively. The nanocomposite of MoO_3-rGO shows the better electrochemical performance as compared to pristine MoO_3 nanorods sample due to improvement in the conductivity. Our result suggests that the MoO_3-rGO nanocomposites material has great potential for electrochemical energy storage and related applications.

1. Introduction

The One dimensional (1D) and two dimensional (2D) nanostructure material currently utilized for the energy storage devices due to high efficiency and good life time[1–4]. The various 1D nanostructure morphology such as nanowires [5], nanorods [6], nanotubes [7] has become attractive for electrochemical energy storage devices such as supercapacitor, Li-ion battery [8–10] and other applications such as chemical sensing, [11–13], photodetector [14–17], field emitter [18], catalyst [19] etc. Recent research focus on development of high energy storage devices such as the supercapacitor due to high power density and fast charge-discharge rate. [20] The 1D metal oxide nanomaterials have advantages to improve the electrochemical and other nanoscale based devices. The various transition metal oxide based nanomaterials such as MnO_2 [21], RuO_2 [22], NiO [23], and Fe_2O_3 [24] have been reported to be used in supercapacitor with high specific capacitance.

Among MoO_3 is one of transition metal oxide material attracted with fascinating properties for electrode material in Li-ion battery [25] and in supercapacitor [26–28]. The MoO_3 has low cost, good structural stability, high electrochemical activity, less toxicity than other transition metal oxide materials [29]. The drawbacks of MoO_3 materials have its low power density with poor electrical conductivity due to narrow operating voltage window. In order to enhance the electrical conductivity and improve the specific capacitance of MoO_3 nanomaterial one can decorate or functionalized the materials or by doping with various suitable materials so as to improve the materials specific properties such as conductivity, capacity to store charges, good cyclic stability, high power density etc.

Graphene the 2D the material discovered in 2004 has extraordinary properties such as high charge mobility, high surface area, high chemical stability and high mechanical flexibility which can be able to improve the electrode conductivity and their performance in energy storage and related devices [30–33].

In present investigation we have synthesized MoO_3-rGO nanocomposite by in-situ reduction of GO in presence of MoO_3 and tested its performance for electrochemical energy storage devices.

2. Experimental section

All chemicals were of analytical grade and used without any further purification.

2.1. Synthesis of MoO_3 nanorods: MoO_3 nanorods were synthesized by simple hydrothermal method as reported earlier [34]

2.1.1. Synthesis of MoO_3-rGO nanocomposite

GO was prepared from graphite powder by modified Hummer's method [35,36]. The Mixture of 0.5 g graphite powder and 0.25 g sodium nitrate ($NaNO_3$) with 12 ml concentrated sulphuric acid (Conc. H_2SO_4) and stirred continuously for 1 h. After that, $KMnO_4$ was added in above reaction mixture and reaction was continued at

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40 °C for 12 h. The reaction mixture was diluted up to 250 ml deionized water and treated with 2.5 ml 30% H_2O_2 solution. The product was collected by filtration, washed several times with conc. HCl and deionized water and finally dried at 80 °C.

For the MoO_3-rGO nanocomposite preparation, 20 mg GO was dispersed in 20 ml deionized water and sonicated for 2 h. After that, 200 μl hydrazine hydrates was added in to the mixture with continuous sonication for 15 min. The 0.1 g of MoO_3 nanorods powder was added in above solution with constant stirring at room temperature for another 2 h. The product MoO_3-rGO nanocomposite was collected by centrifugation and dried in vacuum at 80 °C for 12 h.

2.2. Structural and morphological characterizations

The MoO_3 nanorods and MoO_3-rGO nanocomposite were characterized by Raman spectroscopy (HR-800 Raman spectrometer, Horiba Jobin Yvon, France) using 632.8 nm red laser (NRS1500W). The FT-IR measurements were carried out at BRUKER TENSOR 37. The SEM images were recorded using FEI, QUANTA 200 3D SEM with tungsten filament as electron source. The TEM images were capture with FEI TECNAI TF-20 (FEG instrument).

2.3. Electrochemical measurements

The electrochemical performance of MoO_3 nanorods and MoO_3-rGO nanocomposite were carried out at three electrode system in 0.5 M aqueous solution of Na_2SO_4 used as an electrolyte. The cyclic voltammetry (CV) and gavanostatic charge-discharge curve measurements were carried out on multichannel potentiostat and galvanostat using Metrohm, μAutolab type III electrochemical workstation. Electrochemical impedance spectroscopy was examined on Autolab PGSTAT 30 (ECO Chemie) system.

2.4. Electrode fabrication

Active material for working electrode (~5 mg) was dispersed in 1 ml mixture of deionized water: ethanol solution (7:3) and 10 μl nafion were used as a binder. The Ag/AgCl is used as a reference electrode and platinum wire were used as a counter electrode for electrochemical measurements. The 20 μg of active material (MoO_3 nanorods or MoO_3-rGO nanocomposite) was loaded on to the 3 mm diameter glassy carbon electrode at room temperature.

3. Results and discussion

The as synthesized MoO_3 nanorods and MoO_3-rGO nanocomposite were characterized by Raman spectroscopy. The Fig. 1(a) shows the typical Raman spectra of MoO_3 nanorods with vibrating mode of terminal bond Mo=O showing symmetric and asymmetric stretching at 819 cm^{-1} and 995 cm^{-1} respectively. The asymmetric stretching vibration mode of O—Mo—O assigned at 665 cm^{-1}. The Raman peak at 379, 335, 288 and 247 cm^{-1} indicating the vibrating bending modes in MoO_3 [37]. The composite of MoO_3-rGO confirm by Raman spectroscopy. In composite sample asymmetric stretching mode in O—Mo—O slightly shifted to 661 cm^{-1}. The bending vibrating mode shifted to 373, 330, 283 and 238 cm^{-1} respectively. The Fig. 1(b) show the Raman spectra of GO which depicts the D-band and G-band positions[39]1335 cm^{-1} and [39]1602 cm^{-1} respectively [38]. In MoO_3-rGO nanocomposite sample the D-band and G-band slightly shifted towards the lower wavenumber 1327 cm^{-1} and 1595 cm^{-1} respectively [39].

The FT-IR spectra of MoO_3 nanorods and MoO_3-rGO nanocomposites were shown in Fig. 1(c). The FT-IR spectrum of MoO_3 nanorods sample show the band at 873 $cm^{-1}$and 995 cm^{-1} due to symmetric and asymmetric stretching of Mo=O and Mo_2—O vibrating mode respectively [40]. In the FT-IR spectra of MoO_3-rGO

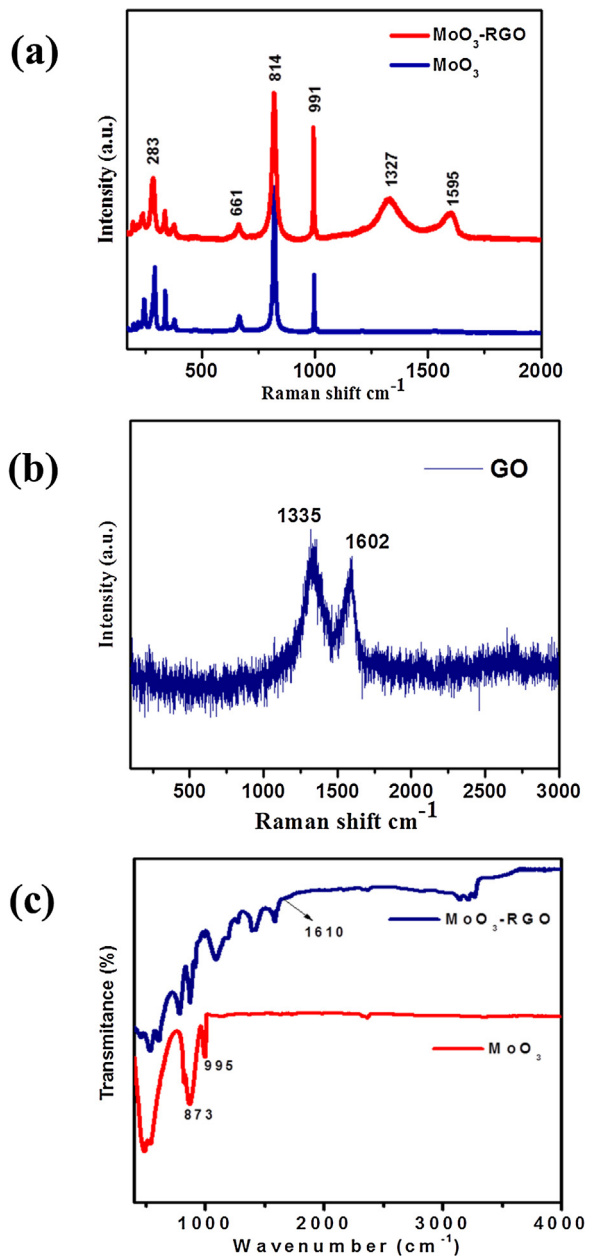

Fig. 1. (a) Raman spectra of MoO_3 nanorods and MoO_3-rGO nanocomposite; (b) Raman spectra of GO and (c) FT-IR spectra of MoO_3 nanorods and MoO_3-rGO nanocomposite.

nanocomposites these stretching vibrating modes shifted towards 870 cm^{-1} and 990 cm^{-1} due to reduction of GO and introducing or decoration of rGO with the MoO_3 nanorods. The band ~537 cm^{-1} appeared in composite material due to the bending vibrating mode in which the oxygen atom link to three Mo metal. In MoO_3-rGO nanocomposite; generally carbonyl (C=O) stretching band can be obtained at around 1700 cm^{-1} is disappeared due to carbonyl group at surface of rGO nanosheets substituted by MoO_3[41–44]. The absorption band appeared ~1610 cm^{-1} (low intense) assigned that the aromatic C—C stretching vibration mode. The broad absorption band observed ~3418 cm^{-1} belongs to O—H stretching vibrating mode. This functional group helpful for the hydrogen bonding between MoO_3 and rGO nanosheets.

The morphology of as synthesized MoO_3 and MoO_3-rGO nanocomposite were characterized by SEM. The Fig. 2(a and b) shows the high and low resolution SEM images of MoO_3 sam-

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