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Amine Functionalized Reduced Graphene Oxide/Tin Sulfide Composite for Supercapacitor Application

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Abstract: Supercapacitors are energy storage devices and varieties of supercapacitors are available. Varieties of electrodes have been synthesized for supercapacitors. In this article Amine functionalized reduced graphene oxide/ Tin sulfide (Am-rGO/SnS) composite for electrode was synthesized by hydrothermal method. The synthesized composite for developing electrode for supercapacitor has been characterized by using different techniques.

Keywords: Composite, Graphene oxide, Hydrothermal, Nanostructure, Supercapacitor.

I. Introduction

Energy storage regulates the efficient management of energy supply and demand [1, 2]. Renewable energy sources such as wind and solar are the intermittent energy sources, can generate energy only when the wind is blowing or the sun is shining. Energy storage involves storing the excess energy during generation, which resolves the high energy demand or when the renewable sources are not available. The energy storage devices can be used to provide power to remote locations or off-grid areas that are not connected to the main power grid [3]. Supercapacitors are a kind of energy storage device, also known as ultracapacitors or electrochemical capacitors that can store and release large amounts of electrical energy quickly.

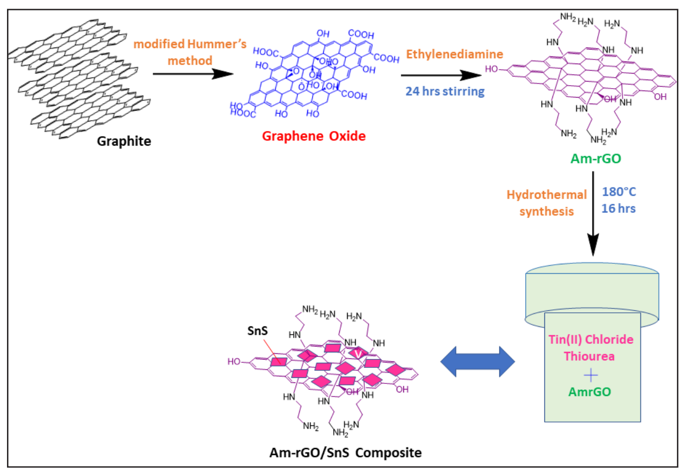
Graphene oxide and reduced graphene oxide-based composites have a wide range of potential applications in the field of energy storage, catalysis and biomedical which can provide a large electrochemically active surface for charge storage, shows excellent electrical conductivity, which permits the efficient charge transfer between the electrode and electrolyte [4, 5].

Nanostructured SnS/carbon composite showed excellent electrochemical performance, with a specific capacitance of 550 F/g at a current density of 2 A/g. The SnS nanoparticles provide high capacitance due to their ability to store charge via redox reactions, while the carbon matrix enhances the electrical conductivity and mechanical strength of the composite [6]. In this work we report a simple one-step synthesis of Am-rGO/ SnS composites as an electrode material for electrochemical supercapacitors.

II. Materials and Methods

A. Materials

Graphite flakes and Tin(II) chloride dihydrate were procured from Sigma-aldrich and used as received. Sulfuric acid, hydrochloric acid, sodium nitrate, Potassium permanganate, hydrogen peroxide, ethylenediamine and thiourea were purchased from SRL Chemicals, Maharashtra, India. Ethanol and Millipore water type I, are used as solvents throughout the study.



Scheme 1: Synthetic Route to Am-rGO/SnS Composite

B. Synthesis of Graphene Oxide

Graphene oxide was synthesized by modified hummers method [7]. About 0.5 g of graphite powder and 0.5 g of $NaNO_3$ were dispersed in 100 mL of H_2SO_4 with stirring in ice bath condition. With the mixture of the aforesaid solution, 3.0 g of $KMnO_4$ was added and continuously stirred for 2 h. After that, the ice bath was removed and vigorously stirred for 6 h. Further, 100 mL water was added and then 6 mL of 30% H_2O_2 was mixed. The pH was maintained to nearly 7. The brown colored turbid was dried in an air oven at 60 °C. The dried graphene oxide was ground to make a fine powder.

C. Reduction and Surface Modification of GO

GO was reduced by adding organic diamine to the ethanolic solution of dispersed GO. The mixture was stirred at room temperature for 24 hours. The resulting black precipitate was collected by centrifugation and washed with distilled water and ethanol several times. Then collect and label the obtained final product as Am-rGO.

D. Hydrothermal Synthesis of SnS

In a typical synthesis, 1.0 mmol of Tin(II) chloride dihydrate ($SnCl_2$. $2H_2O$) and 3.0 mmol of thiourea ($SC(NH_2)_2$) were dissolved in 40 mL of distilled water. The solution was stirred for 30 minutes to ensure complete dissolution of the precursors. The solution was then transferred to a Teflon-lined stainless-steel autoclave, which was heated at 180 °C for 16 hours. After cooling to room temperature, the black precipitate was collected by centrifugation and washed with distilled water and ethanol several times. The obtained ash coloured product was labelled as SnS.

E. Synthesis of Am-rGO/SnS Composite

For the synthesis of Am-rGO/SnS composite, we have followed the same procedure for the simple one-pot synthesis of SnS. The Am-rGO/SnS composites will be synthesized by mixing 20 mg Am-rGO, Tin(II) chloride dihydrate (1.0 mmol) and thiourea (3.0 mmol) solutions and then subjecting it to the hydrothermal treatment. When the reaction is over, the reaction mixture allowed for work up with same procedure for pure SnS.

F. Characterization

In order to determine changes in the structure of samples, the interlayer d-spacing value was determined using Bragg's Law equation through the use of X-ray diffraction (XRD) analysis. The Shimadzu XRD with CuKα radiation of 1.546 Å was used to characterize the structure and crystalline properties. The FT-IR spectra of the samples were obtained using the KBr pellet method within the range of 400 to 4000 cm^{-1} with a Jasco FT-IR 4600 spectrometer. Meanwhile, the Raman spectroscopy of the samples was recorded on a LabRAM HR instrument. The surface morphological characteristics were determined from Scanning Electron Microscopy using Apreo 2S model.

III. Results and Discussion

A. Powder XRD Analysis

The powder XRD analysis to examine the crystallographic phase's structures of the Am-rGO/SnS composites and the spectra is given in Fig. 1. A distinct diffraction peak is observed at 11.4°, indicating the presence of the (001) plane with interlayer distance of 0.75 nmin the GO, which is consistent with the existing literature [8]. A small additional peak is detected at 42.5° corresponds to (100) plane of some unreacted graphite sheets. The (001) plane of GO has been shifted to lower angle at 10.23° with d-spacing of 0.85 nm is observed in the Am-rGO. The increase in the layer-to-layer distance in Am-rGO indicates that the $-NH_2$ groups have been covalently attached to the GO surface, which attributed the GO is reduced by amine functionalities. A broad diffraction peak is appeared at 22.9° corresponds to (002) plane gives strong evidence for the formation of reduced graphene oxide. The crystal structures of bare SnS and Am-rGO/SnS composites are well matched with standard JCPDS card (JCPDS 39-0354) of orthorhombic phase [9]. An impurity peaks like SnS_2 and SnO_2 is not observed in XRD patterns, reveals highly phase-pure and crystalline SnS particles were produced. Various crystal planes such as (101), (201), (210), (011), (111), (400), (311), (411), (511), (601) and (711) are appeared in for both the pristine SnS and Am-rGO/SnS composite. The decrease in peak intensity is observed in Am-rGO/SnS compared to pure SnS.

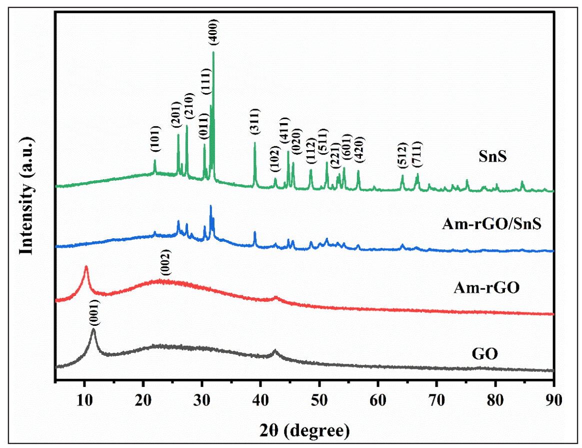


Fig. 1: Powder XRD Pattern of GO, Am-rGO, Am-rGO/SnS Composite and Pure SnS

The synthesized composite is confirmed from the functional characteristics of their corresponding IR bands. The FT-IR spectra of GO, Am-rGO, Am-rGO/SnS composite and SnS alone are shown in Fig. 2. A broad peak observed at 3425 cm^{-1} is attributed to the stretching vibration of O–H groups. The sharp peak observed at 1703 cm^{-1} is assigned to the C=O stretching of the carboxylic acid group, while the peak at 1626 cm^{-1} is attributed to the sp^2 (C=C) stretching [10]. A sharp peak at 3425 cm^{-1} in Am-rGO, corresponds to the N–H stretching vibration. In both the GO and Am-rGO, two intense peaks at 2926 and 2858 cm^{-1} represent the asymmetrical and symmetrical methylene stretching vibrations. Compared to GO, all the absorption bands are significantly shifted in Am-rGO and the C=O stretching vibration is not observed, indicating a reduction in oxygen functional groups, which confirms the reduction of GO into rGO with substituted amino groups [11]. Notably, two peaks at 1625 and 1041 cm^{-1} are observed in Am-rGO, which are attributed to N–H bending and C–N stretching, respectively. Therefore, the FT-IR analysis confirms the amine functionalization followed by reduction occurred on the GO surface. The peak at around 500-550 cm^{-1} in both the pure SnS and the Am-rGO/SnS composite, display the formation and the presence of SnS.

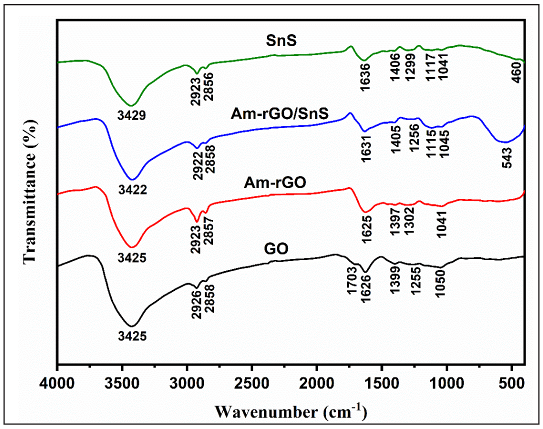


Fig. 2: FT-IR Spectra of GO, Am-rGO, Am-rGO/SnS Composite and Pure SnS

B. Raman Analysis

Raman spectroscopy is an essential tool to identify the electronic structure of carbon-based materials, especially C=C double bonds that lead to high Raman intensities. Raman spectroscopy is a useful technique for characterizing different carbon materials like graphene, graphite, carbon nanotubes and activated carbon. The Raman spectra of GO, Am-rGO, Am-rGO/SnS composite and pure SnS are shown in Fig. 3. It can be distinguished between the ordered and disordered carbon structures by analyzing the characteristic peaks of the D and G bands. The D band is associated with structural defects, while the G band is associated with the degree of graphitization or sp^2 carbon structure. In Fig. 3, the 'D' and the 'G' bands of graphene oxide were detected at 1351 and 1608 cm^{-1} and its respective I_D/I_G value is 0.90. Conversion of GO into Am-rGO by reduction and amine functionalization and formation of Am-rGO/SnS composite, indicates the lower wave number shifting of sharp peaks at 1348 and 1596 cm^{-1} from pristine GO. The intensity ratio (I_D/I_G) increases to 0.99 for Am-rGO and 1.02 for Am-rGO/SnS composite, reveals large number of structural defects, disorders and some oxygen losses occurred on the composite [12].

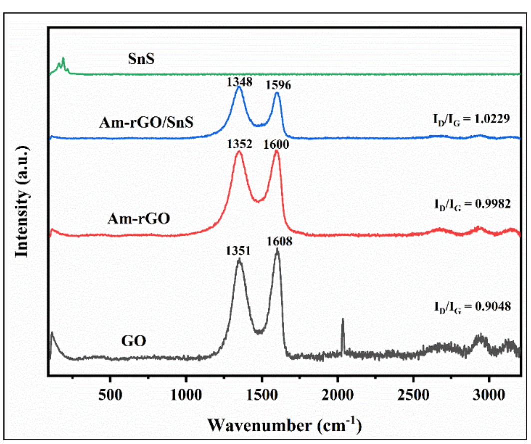


Fig. 3: Raman Spectra of GO, Am-rGO, Am-rGO/SnS Composite and Pure SnS

C. SEM Analysis

The surface morphological characteristics of the prepared composite were examined by scanning electron microscopy. The SEM images of GO, Am-rGO, Am-rGO/SnS composite and pure SnS are shown in Fig. 4.

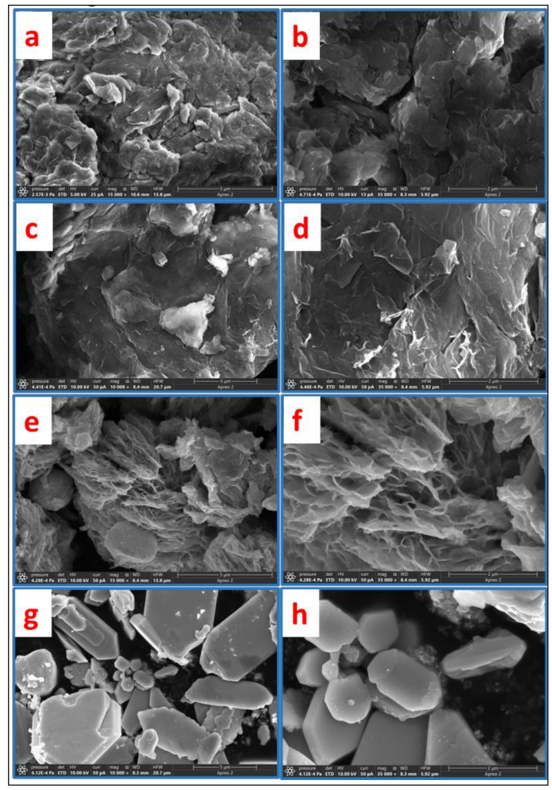


Fig. 4: SEM Images of (a, b) GO, (c, d) Am-rGO, (e, f) Am-rGO/SnS Composite and (g, h) Pure SnS

The prepared GO were displayed stacked layered morphology from Fig. 4a and Fig. 4b. The SEM images of amine functionalized reduced graphene oxide (Am-rGO) possess corrugated and wrinkled layers morphology were observed from Fig. 4c and Fig. 4d. The Am-rGO/SnS composite exhibits stacked layers with fractured surface morphology are shown in Fig. 4e and Fig. 4f. The SEM images of pure SnS evolves different shaped majorly hexagonal shaped plates-like morphology were revealed in Fig. 4g and Fig. 4h.

The chemical composition of the synthesized composite was examined by EDAX analysis are given in Fig. 5. For GO, the C and O elements peaks was appeared, which confirmed the oxidation of graphite sheets and graphene oxide formation. The presence of C, N, and O elements is observed in the EDAX spectra of Am-rGO is shown in Fig. 5b, indicates amine functionalization. In Fig. 5c, the EDAX spectra of Am-rGO/SnS composite reveals the composite formation from the appearance of C, N, O, S and Sn elements. The chemical compositions of pure SnS were also described from EDAX measurement (Fig. 5d).

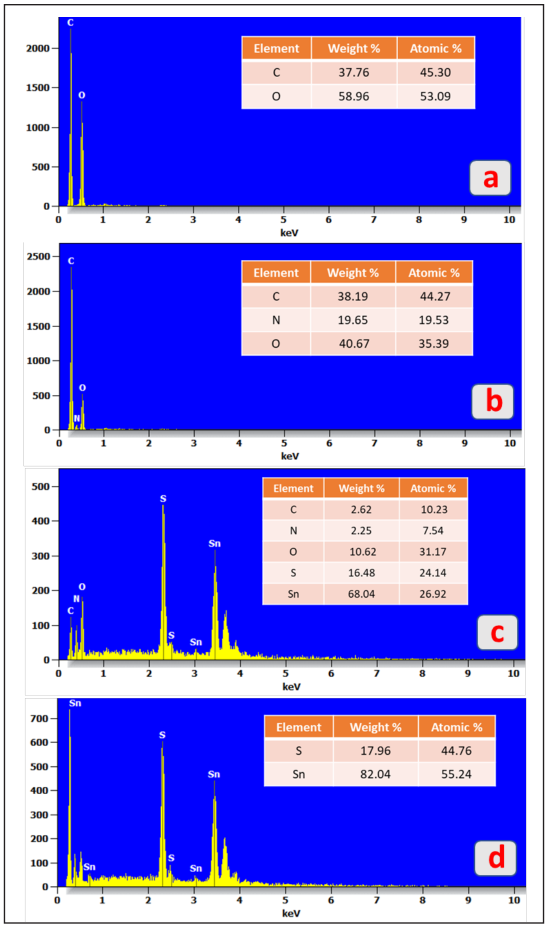


Fig. 5: EDAX Spectra of (a) GO, (b) Am-rGO, (c) Am-rGO/SnS Composite and (d) Pure SnS

IV. Conclusion

Amine functionalized reduced graphene oxide/Tin sulfide (Am-rGO/SnS) composite was prepared by hydrothermal technique. The composite formed was characterized by XRD, FT-IR spectroscopy, SEM and EDAX techniques. It is proposed that electrode fabrication will be carried out using the Am-rGO/SnS composite on stainless steel substrate and its electrochemical supercapacitor performance will be measured.

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