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REVIEW ARTICLE

SYNTHESIS OF NiS ANCHORED GRAPHENENANOCOMPOSITES: HIGH PERFORMANCE SUPERCAPACITOR ELECTRODE MATERIAL

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ABSTRACT

Reduced Graphene Oxide (rGO) based Nickel Sulfide (NiS) anchor nanocomposites were developed via hydrothermal approach. We have investigated the effect of different concentration of thioglycolic acid on graphene oxide reduction. More the thioglycolic acid present with the graphene oxide, the reduction is more and high electrochemical activity is also achieved by the composite having high concentration of sulfur. We have achieved specific capacitance of 109.37 F/g at 2.5 A/g for the composite rGO-NiS using 2.7 ml of thioglycolic acid. Energy density and power density of this composites show9.72Wh/kg and 1000W/kg, respectively.

INTRODUCTION

In the twenty first century, fast depleting of fossil fuels or other natural resources, consequently, growing demand of portable energy storage systems, it is the time to move towards clean and sustainable energy resources. So, the great challenges have been taken to innovate small, lightweight, low cost and eco-friendly energy storage materials which can assure us to provide a cheap and safer energy storage system (Patrice Simon and Yury Gogotsi 2008). To fulfil these perquisites, scientists are engaged to develop a new class of energy storage system capable of storing/supplying high energy in a fraction of second. Lithium ion batteries (LIBs) are capable to provide very high energy performance, but limitation is their power performances for high power demanding applications. Super capacitors are these new kinds of energy storage systems having the properties to form a bridge between battery and conventional capacitors (Soumen Giri *et al.,* 2014). They have the excellent property like pulse power supply, long cycle life (>100000 cycles), safety to handle and environmentally friendly. It provides high power density and high energy density as compared with conventional super capacitors. They can be used in memory back up devices, small electronic gadgets, interrupted power supply for industries and energy management system. Now a days, super capacitors have been used in emergency doors on Airbus A380 due to safe and reliable performances (Qian Cheng *et al.,* 2011). There are two types of super capacitors depending on their different charge storage mechanism: (1) Electrical Double Layer Capacitors (EDLCs) where charge store by simple double layer formation and (2) pseudo capacitors where charge store by redox reaction. Using of graphene for the development of super capacitors is the new trends for the versatile properties of graphene which is a 2D dimensional honey comb lattice structure, high surface area, high flexible, and low cost material. Graphene and metal oxide based nanocomposites are one of the most successful candidates for supercapacitor application due to the synergistic contribution of both redox active metal oxide and high surface area containing graphene to improve the overall specific capacitance On the other hand, metal sulfides are also most successful energy storage materials with high performances such as CoS, ZnS, and FeS etc. Among all the sulfides, nickel sulfide has been the subject of considerable interest because of its properties as a paramagnetic-antiferromagnetic transition material, a catalyst for hydrodenitrogenation and hydrodesulfurization, and a transformation toughener in window glass, as well as its potential application in IR detectors, rechargeable lithium battery and solar storage (YaHui Zhang and Qing Wang 2012).

There are several reports on different type of phase formation of nickel sulfide like NiS, NiS_2, β-Ni_3S_2, α-$Ni_{3+x}S_2$, Ni_4S_{3+x}, Ni_6S_5, Ni_7S_6, Ni_9S_8 and Ni_3S_4 andcan formed into different shape such as hierarchical hollow microspheres with different building blocks, archin like 3D nanostructure, hollow sphere assembled from ultrathin nanosheets, nanochains (Ting Zhu *et al.,* 2011) and some phase also used as super capacitors. If the metal sulfides are combined with graphene sheet, there would be the possibility to achieve high specific capacitance by synergistic contribution of both materials. However, there

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are few reports on graphene/metal sulfidenanocomposite for energy storage application. Generally, graphene was prepared by the reduction of graphene oxide. There are several reports to reduce the graphene oxide, mostly $NaBH_4$, hydrazine. Generally, to get the huge amount of graphene, graphene oxide is used which is obtained from chemical modification of graphite.Several reducing agent were used such as hydrazine, $NaBH_4$, hydriodic acid (HI), NaOH, ascorbic acid and glucose which convert GO to rGO. Kaminska *et al.* (2012) also reported the reduction and functionalization of graphene oxide by the using of tetrathiafulvalene (Kaminska *et al.,* 2012). S. Some *et al.* have developed one novel reduction methods that are environmentally friendly, mild, and cost effective ways for mass production of high-quality rGOs by chemical healing (Surajit Some *et al.,* 1929). It is worthwhile pointing out the in-situ reduction of graphene oxide by varying the reductant concentration and should be tuned to optimize the electrochemical performance of the composite, which has not been well studied Here, we have approached a hydrothermal procedure for in-situ reduction of graphene oxide and synthesis of NiS anchored graphene composite. The main trick is the use of Thioglycolic Acid (TGA), a sulfur donating agent work both as reductant for graphene oxide reduction and sulfursource for the formation of NiS. TGA was used previously as a stability reagent to prevent the self-aggregation of chalcogenidesnanocrystal. TGA is a non-toxic template can acts as oriented growth reactant during hydrothermal process.

Synthesis Procedure

At first, Graphene Oxide (GO) was prepared from graphite powder by a modified Hummers' method. 40 mg of GO was homogeneously dispersed in 40 ml of milipore water by 30 minutes of sonication at room temperature, followed by the addition of 1 gm urea, Ni $(NO_3)_2$, $6H_2O$, and thioglycolic acid with constant stirring for half an hour. To understand the effect of thioglycolic acid means different sulphur concentration for the reduction of graphene, three different percentage of thioglycolic acid were used while keeping Ni(NO3)$_2$, $6H_2O$ concentration constant. Three different ratio of $Ni(NO_3)_2$, $6H_2O$ and thioglycolic acid were (0.02:0.01), (0.02:0.02), (0.02:0.04) mole. The combination designated as rGO-NiS 0.7,rGO-NiS 1.4,rGO-NiS2.7 for(0.02:0.01), (0.02:0.02), (0.02:0.04) respectively. Then, three different percentthioglycolic acid contain solution were transferred into a 50 ml autoclave, sealed and heated in an oven at 180°C for 24 h. The black precipitate was then collected, washed with water and ethanol five times each and dried in a vacuum oven at 60°C.

FTIR Analysis

FTIR analysis has been carried out to understand the formation mechanism of NiS formation and investigated the effect of thioglycolic acid concentration on the graphene oxide reduction. It would ensure the organic molecules are capped on the NiS surface or not. The FTIR spectra of as synthesized materials are shown in Fig. 1. The broad peak appeared around 3429 cm^{-1} indicates the presence of hydroxyl group or absorbed water molecules. The strong absorption peaks appeared around 1617 cm^{-1} are due to the existence of –COOH which is present in the NiS samples also. Another intense peak for -C-O (alkoxy) group appeared at 1057cm^{-1} and its intensity increases with increasing concentration of thioglycolic acid. From the result of FT-IR analysis, it is suggested that the organic component $–CH_2COOH$ should exist in the composite. The peak for -C-O (epoxy) appeared at 1253cm^{-1} for GO and it completely reduced in GO-NiS composites, indicates the reduction of epoxide ring occurred during the formation of NiS (MasoudSalavati-Niasari *et al.,* 2010). However, the characteristic peak of Ni–S appears at 912 cm^{-1}. The weak absorption peak at 820 cm^{-1} associated with a C–S vibration demonstrate that residual $Ni(S_2COC_6H_{11})_2$ is chemisorbed onto the surface of NiSnanocrystalline. The above results confirmed the reduction of GO and the combination of NiSand graphene in the composite (Shugang Pan 2013).

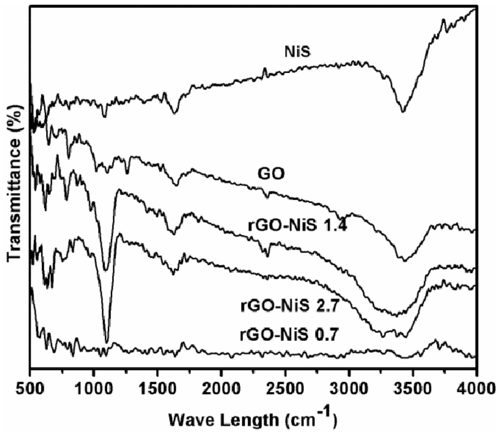


Fig.1. FTIR analysis of the composites

XRD Analysis

XRD analysis of all the as prepared composites was displayed in the Fig. 2. The three composites of NiS/GNS composite show the similar crystalline structure of pure NiS, which are in good agreement with (JCPDS Reference No-02-0693 and 12-0041).

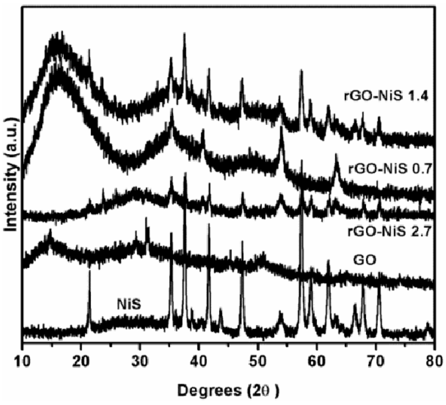


Fig.2.XRD analysis of the as prepared nanocomposites

Additionally, the XRD patterns of the NiS and NiS/GNS composites show that the growth of the (131) plane at $2\theta = 57.44$ was inhibited due to the presence of graphene oxide. The main peak of graphene oxide at $2\theta=14.5$ is shifting to higher by the increasing of sulphur concentration. This may be due to progressive removal of surface oxy-functional groups on the in-plane graphene layers and restacking of reduced GO sheets. At higher concentration of thioglycolic acid, graphene oxide reduce to graphene and a weak broad diffraction peak can be observed at 2θ = 28.96, which is attributed to (002) plane of exfoliate graphene sheet. With the increasing concentration of sulphur in the composite, the exfoliation is more and interlayer gaps gradually increases. Therefore, the increased interlayer space of graphene Nano sheets can contribute larger space for H^+ ion insertion, which also diminishes theH^+ ion mobility inside the vacant space between grapheme nanosheets. As a result,H^+ diffusion is facilitated. Presences of S atom could form a layer of electron cloud. As a result the increased concentration of electron between two layer (Nis and graphene) provide higher electronic conductivity of the ions inside and surface of the composites Hence, the high electrochemical activity of the composites is expected (Kun Changa and Weixiang Chen 2011).

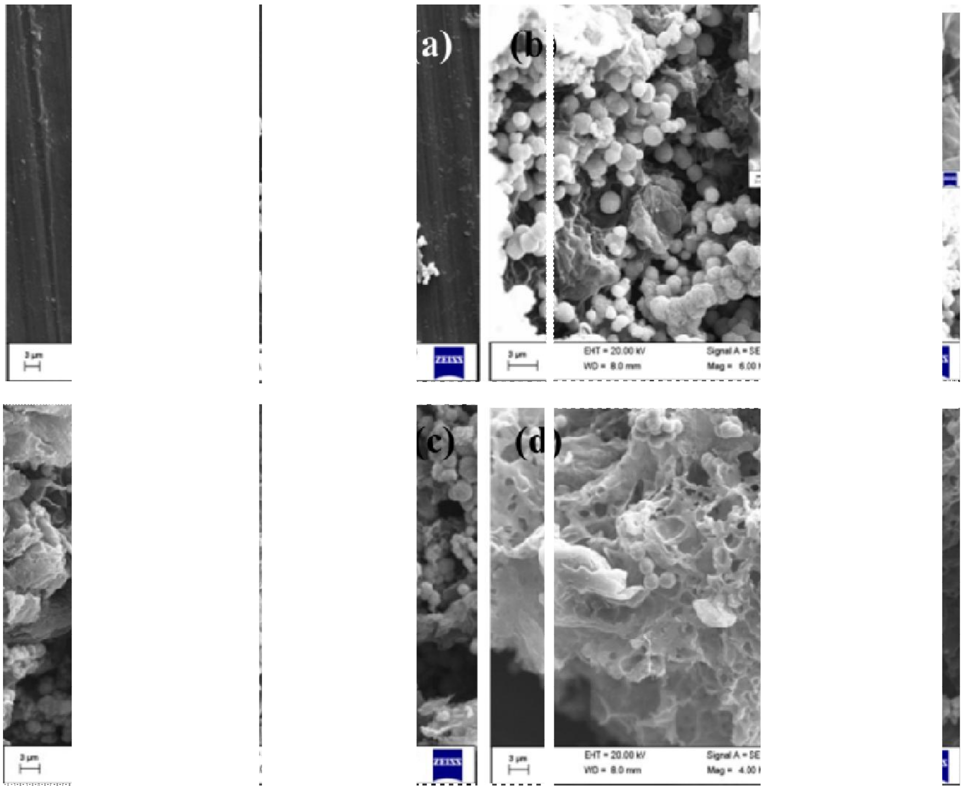


Fig. 3. SEM analysis of (a) NiS (b) rGO-NiS 0.7 (c) rGO-NiS 1.4 and (d) rGO-NiS 2.7

SEM Analysis

The morphology of the as prepared composites were characterized by SEM. It is clearly to see that the bare NiS sample accumulates into a spherical structure with irregular wrinkles. The growth of NiS occurred with continuous contact mood which is observed in the Fig. 3(a). So, continuous frame work was obtained for NiS particle. As can be seen from Figs. 3(b), 3(c) and 3 (d) the morphologies of the NiS anchored graphene composites were clearly observed. The structure of reduced GO exhibited a porous structure with abundant surface wrinkles almost same for Fig. 3(b) and 3(c) but it is completely different in Fig 3(d) which looks like 3D morphology of graphene and shows porous structure. This structure is in the good agreement with XRD and FTIR analysis where graphene oxide was completely reduced to graphene.

TEM Analysis

To further confirm the formation of NiS anchored graphene composites, TEM analysis was carried out which is displayed in the Fig. 4. As presented in Fig. 4(a), pure NiS mainly consists of spherical nanoparticles which grown like a wreath of flower, and expected a combined path to carry the charge spontaneously. In Fig. 4(b), 4(c) and 4(d), the reduced graphene sheets and spherical nanostructures of NiS can be observed in the composites, indicating that spherical NiS nanoparticles were anchored on the rGO sheets. Moreover, it seems that there is a good combination between rGO and NiS, which favours the more charge accumulation/charge carrier to improve the electrochemical performance. Notably, NiS nanoparticles in the rGO–NiS composites are in the range of 300–500 nm, and the sizes are more uniform compared with pure NiS. These results indicate that NiS can effectively prevent the aggregation of graphene in the NiS/graphene composite. The SAED pattern (Fig. (c))ofNiS shows its single crystalline behaviour and EDX pattern (Fig. (f)) for NiS/graphene confirmed the constituent elementsFrom the above study, we believe that the thioglycolic acid, a complexing agent, plays a critical role on controlling the nucleation and growth of the NiS. There should be considered the formation of $(NiS)_m(NiSHCH2COOH)_k^+$ complex like $(CdS)_m(SHCH2COOH)_k^{2+}$ as confirmed by the FTIR analysis (Hui Zhang *et al.,* 2003). In a homogenous system composed of thioglycolic acid and $Ni(NO_3)_2$ solution, Ni^{2+} can coordinate with thioglycolic acid molecule to form a complex. We can present at the first step, thioglycolic acid was introduced to Ni^{2+} and produce (2), this product generate (3) via the following route:

$Ni^{2+} + HSCH_2COOH \rightarrow NiHS^{+} + CH_2COOH^{+}$
$NiHS^{+} \rightarrow NiS + H^{+}$

$m NiS + k HSCH_2COOH + k Ni^{2+} \rightarrow (NiS)_m(NiSHCH_2COOH)_k^{+} + kH^{+}$

At the final step $(NiS)_m(NiSHCH2COOH)_k^{+}$ changed to the NiS by hydrothermal.

This $(NiS)_m(NiSHCH_2COOH)_k^{+}$complex may be responsible for the chemical reduction of GO. Moreover, thioglycolic acid contains a thiol group which causes to release a proton, act as a nucleophile (Chen *et al.,* 2011).The final product is $(NiS)_m(NiSHCH_2COOH)_k^{+}$ complex which ishydrothermally converted to NiS and anchored on the graphene sheet by synergistic interaction.

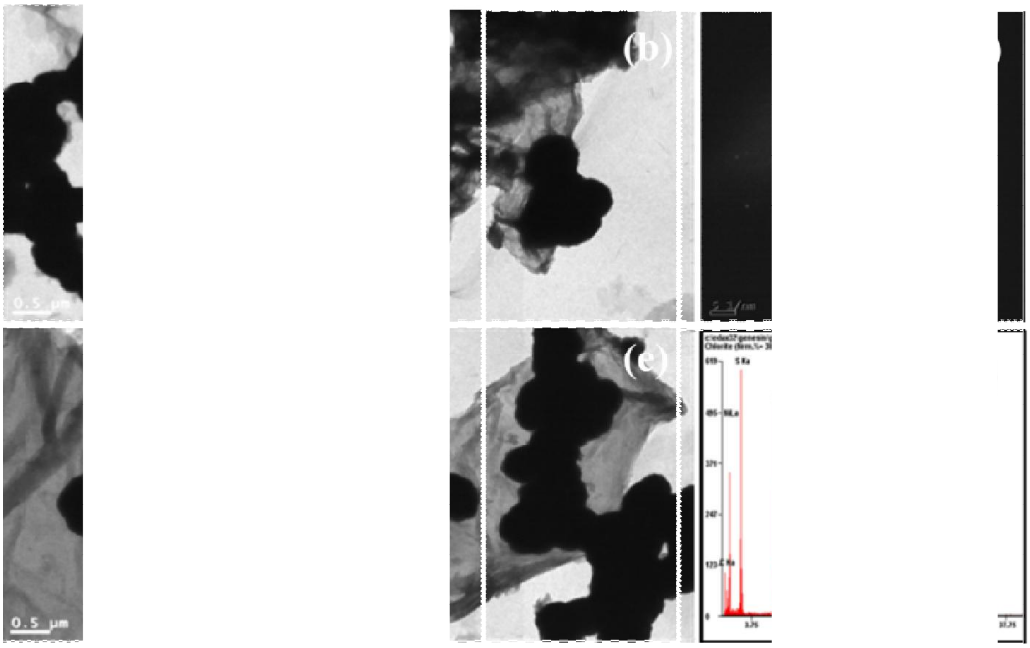


Fig.4. SEM analysis of (a) NiS (b) rGO-NiS 0.7 (c) rGO-NiS 1.4 and (d) rGO-NiS 2.7

Electrochemical Characterizations

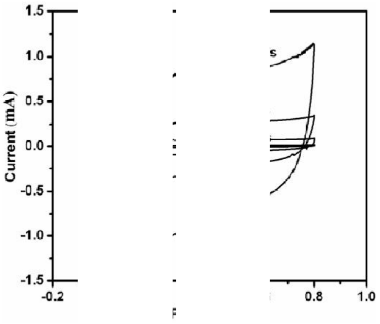
To explore the advantages of NiS/graphene materials and their potential applications as electrodes for supercapacitor, the capacitive properties of NiS/graphene electrodes were measured in 1 M H_2SO_4 by a three-electrode system.

Cyclic Voltammetry

Cyclic Voltammetry (CV) is an effective method to determine the faradic and non-faradaic process involved during the capacitive performance. It was performed at the various scan rate ranging from 1 mV/s - 200 mV/s within the potential range of 0-0.8V. As we know, the CV curve of an ideal supercapacitor should be rectangular in shape and capacitance comes from mostly double layer formation. The specific capacitance of the composite rGo-NiS 2.7 which contain higher thioglycolic acid convert graphene oxide exclusively towards graphene. The CV curves of the as prepared composites are quite rectangular shape which indicates an excellent capacitive behaviour with excellent ion response and a low contact resistance. Specific capacitance are calculated by the following equation (SoumenGiri *et al.,* 2013; Debasis Ghosh *et al.,* 2013):

$$Cs = \frac{\int_{V_1}^{V_2} i(v)dv}{(V_2 - V_1)vm}$$

Where the term in the numerator, of the above equation represents the area of I-V curve and V_1, V_2 are the switching potential in cyclic voltammetry. v and m are scan rate and mass of the sample respectively.The energy density was calculated using the following equation(Shugang Pan *et al.,* 2013; Kun Changa and Weixiang Chen2011): $E = ½ C_sV^2$The energy density reduces slowly with power density. Power density was calculated using the equation: $P = E/t$,Where, P is the power density in W/kg, E is the energy density in Wh/kg and t is the time in hours. The specific capacitance was also calculated by the equation (Shugang Pan *et al.,* 2013; Kun Changa and Weixiang Chen2011):

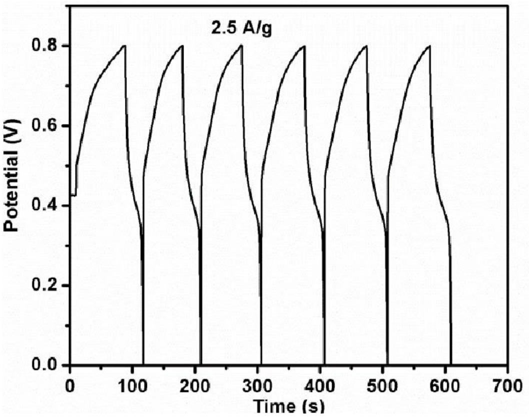


$C_{cc} = (i * \Delta t) / (\Delta V * m)$

The highest specific capacitance of this composite was obtained 114 F/g at 1 mV/s.

Cyclic charge-discharge test

We have also tested its charge-discharge (Fig.) ability at 2.5 A/g constant current density. The "V" shaped curve indicates the capacitive behaviour of the material and from discharge curve we can calculate the specific capacitance which is 109.37 F/g at 2.5 A/g. we have also calculated its energy and power density i.e. 9.72Wh/kg and 1000 W/kg, respectively.



Conclusion

In this work, we have explored the hydrothermal synthesis of NiS anchored graphene nanocomposites. We have observed that the graphene oxide reduction was occurred by the thioglycolic acid which is confirmed by the FTIR and XRD analysis. The SEM and TEM analysis confirmed the successful formation of the nanocomposites. We have also investigated its possible supercapacitor application. The specific capacitance for the composite is 109.37 F/g at 2.5 A/g. The calculated energy and power density of the composites are 9.72Wh/kg and 1000 W/kg, respectively.

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