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PREPERATION OF $NiCo_2S_4$ AND NMC NANOBALL ON NICKEL FOAM NITROGEN DOPED MESOPOROUS CARBON (NMC)

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Abstract

Nickel foam, which can be directly used as electrode for supercapacitors application. Nitrogen doped mesoporous carbon (NMC) was prepared by our previous work in chapter 3A. A binary component of $NiCo_2S_4$ at NMC nanoball on Ni foam is prepared by the exfoliation of nitrogen doped mesoporous carbon followed by hydrothermal treatment. The interaction between NMC nanosheets and $NiCo_2S_4$ particles in $NiCo_2S_4$ at NMC nanocomposite is confirmed by powder XRD, Raman spectroscopy, IR spectroscopy and XPS analysis. The UV-Vis diffuse reflectance spectroscopy studied shown that $NiCo_2S_4$ at NMC nanocomposite has smaller band gap as compared to NiCo2S4, which would be a better candidate for charge storage application. The nitrogen doped mesoporous carbon forms highly conductive network and improves the conductivity of the nanocomposite material as well as prevents to the agglomeration of nanoparticles at some extent. Moreover, it has long-term cycling stability with a capacity retention of 88% after 5000 cycles, making it as a material of choice for next generation supercapacitor. The reason of 12% degradation in electrochemical performance was also analyzed by microstructure analysis. Finally, the summary is that the introduction of NMC onto NiCo2S4 array can enhance the charge transfer conductivity, electrolyte penetration, and ion diffusion, which can in turn boost the capacitive behavior of the nanocomposite material.

Keywords: NMC, *Nanocomposite material, Capacitive behavior, Mesoporous carbon.*

SCOPE AND OBJECTIVE: It is necessary to design or develop some new materials which could be fulfilling the requirement of human civilization. The optimum doping of nitrogen (wt%) into the carbon matrix for obtaining high electrochemical capacitance and to understand the different aspects of modifying the surface of these carbon materials bytuning the concentration of the activating agent, carbonization temperatures and doping of heteroatoms. Electrochemical supercapacitors (ESC) are devices that provide transient but extremely high power density compared to normal dielectric capacitors. They are considered as the most advanced next generation energy storage devices. The only drawback in the ESC is the low energy density compared to batteries. Compared to conventional rechargeable batteries, ESCs can be charged and used to deliver charge quite faster, and also work through higher number of charge and discharge cycles. The charge storage in ESCs is through redox mechanism in which variable oxidation states of metal ions are crucial. A number of metal oxides and sulfides containing Co and Ni have been reported as potential electrode materials for pseudocapacitors.

Experimental, Discussion and Result:

Synthesis of NiCo2S4 at NMC composite on Nickel foam

For the preparation of NiCo2S4 at NMC composite on nickel foam, we used nitrogen doped mesoporous carbon synthesized by simple sol-gel method reported in our previous work . This NMC sample has surface area 736 m2 g/m1 and pore diameter of 17.6 nm. In the first step, 20 mg of NMC was dispersed in 20 ml of 1:1 isopropanol/watersolvent followed by sonication for 4 h. In the second step, 20 mg of PVP was dissolved in 20 ml of water followed by stirring for 30 min. To this solution, 0.5 mmol of $Ni(NO_3)_2$·6H2O, 1 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 3 mmol of thiourea and 2 mmol of NH4F were added under stirring. After 2 h, the exfoliated NMC was added to the above solution followed by magnetically stirring for 1 h and then sonicated for 1 h to attain complete homogeneity of the solution. Nickel foam was treated with 3 M HCl solution in an ultrasonic bath for 10 min in order to remove the surface NiO layer, and then cleaned thoroughly using deionized water and acetone for 5 min each. After that, the Ni foam and salt solutions were transferred into a Teflon-lined autoclave and heated at 160 °C an oven for 12 h and then cooled down to room temperature. After hydrothermal growth, the nickel foam was taken out and carefully rinsed several times in distilled water and ethanol, and then dried at 60 °C in an oven for 12 h. For comparison, NiCo2S4 on nickel foam was also prepared in a similar manner without adding nitrogen doped mesoporous carbon (NMC).

Structure and Morphology

X-ray diffraction patterns of nitrogen doped mesoporous carbon (NMC), $NiCo_2S_4$ and $NiCo_2S_4$ at NMC samples are given in Fig. 4.1. The two broad diffraction peaks at $2\theta = 24.5°$ and 43.7°, indexed to (002) and (100) reflections respectively, are the signatures of amorphous nitrogen doped mesoporous carbon. The $NiCo_2S_4$ phase grown on Ni foam shows well-defined diffraction peaks at 26.5°, 31.8°, 38.5°, 50.6°, and 55.9° corresponding to (220), (311), (400), (511) and (440) planes of the cubic spinel structure (JCPDS No.43–1477). All the diffraction peaks of NiCo2S4 and NiCo2S4@NMC are weak and broad which indicate lower degree of crystallization. The two strong diffraction peaks at 2θ = 45.2° and 52.5° correspond to (111), (200) planes of nickel foam respectively. The NiCo2S4@NMC sample also exhibits similar diffraction peak as NiCo2S4 sample with an additional broad diffraction feature around 24.2° due to the presence of NMC. There are no other peaks present confirming the purity of the samples. The presence of NMC in NiCo2S4 at NMC composite is also confirmed by Raman spectral analysis (Fig. 4.2a). There are two characteristic peaks seen, one at about 1335 cm–1 associated with disordered structure of carbon (D band) and the other at 1573 cm–1 associated with graphite in-plane vibration (G band) of $NiCo_2S_4$ at NMC nanocomposite. The intensity ratio of D to G bands is an indication of the formation of structural defects in $NiCo_2S_4$ at NMC nanocomposites. The ratio is about 1.10 for NMC and it increases to 1.17 for the nanocomposite. This is a small but significant difference which indicates the interaction of $NiCo_2S_4$ nanoparticles with NMC surfaces. Further, the Raman Dband at 1330 cm–1 and G-band at 1575 cm–1 of NMC are also shifted, respectively, to 1296 cm–1 and 1596 cm–1 in NiCo2S4 at NMC nanocomposite. The difference in the peak values of D and G bands for NMC is 245 cm–1 which is increased to 300 cm–1 in NiCo2S4 at NMC nanocomposite. All these changes in the D and G bands clearly point out strong chemical interactions between NMC and NiCo2S4 nanoparticles. The NiCo2S4 at NMC nanocomposite is further investigated to ascertain the nature of bonding, functional groups and interaction of NMC with NiCo2S4 by Fourier transform infrared spectroscopy.

The porous characteristics of $NiCo_2S_4$ and $NiCo_2S_4$ at NMC nanocomposite samples are analysed by N2 adsorption-desorption measurements. The BET isotherms and pore-size distribution plots of these two samples are shown in Fig. 4.3. Both the samples show Type-IV isotherms with H1 hysteresis loops suggesting the presence of mesoporous structure. The specific surface area of $NiCo_2S_4$ at NMC nanocomposite is 42 m2 g/1 while it is 11 m2 g/1 for $NiCo_2S_4$ nanoparticles. The increase in surface area is due to the contribution of high surface area NMC. The interfacial region of NMC and $NiCo_2S_4$ spinel is important which can generate defects and vacancies in the spinel structure.

CONCLUSIONS:

In conclusion, binary component of $NiCo_2S_4$ at NMC nanoball on Ni foam is prepared by the exfoliation of nitrogen doped mesoporous carbon using hydrothermal treatment. The electrode materials are tested for supercapacitor applications. Nickel cobalt suphides when mixed with active carbons seem to favor the formation of nanocompiosites with reduced band gaps. The as synthesized $NiCo_2S_4$ at NMC nanocomposite electrodes provide efficient and quick pathways for ion and electron transport and exhibit outstanding electrochemical performance than NiCo2S4. The nitrogen doped mesoporous carbon forms highly conductive network and improves the conductivity of the material. It also prevents to some extent the agglomeration of nanocomposite which increases the cycling life of the electrode. The nitrogen doped mesoporous carbon supported $NiCo_2S_4$ nanoball on Ni form delivers highest capacitance of 2017 F g/1 and capacity of 281 mAh g/1 at a current density of 3 A g/1. It has long-term cycling stability with a capacity retention of 88% after 5000 cycles, making it as a material of choice for next generation supercapacitor.

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