



Confined growth of NiCo₂S₄ on 2D/2D porous carbon self-repairing g-C₃N₄/rGO heterostructure for enhanced performance of asymmetric supercapacitors

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ABSTRACT

In this work, porous carbon self-repairing g-C₃N₄ (pCCN) nanosheets were synthesised using a solvothermal technique followed by calcination and acid treatment. A facile hydrothermal process is employed for the confined growth of NiCo₂S₄ on porous carbon self-repairing g-C₃N₄/rGO heterostructure (pCRNCS) as hybrid material for supercapacitor electrodes. The improved electronic conductivity and activity of carbon self-repairing g-C₃N₄ (CCN) than g-C₃N₄ owing to the creation of extended delocalized π -electrons by the substitutional or interstitial C atoms in the structure and because of acid treatment, the larger planes of CCN are broken down into smaller segments, increasing the edge nitrogen and oxygen functional groups. The introduction of porous CCN led to the strong electrostatic interaction with GO and CCN which aided in the suppression of agglomeration of graphene sheets. The as-synthesised pCRNCS electrode showed remarkably high specific capacitance (1938 F/g at current density of 2 A/g). The excellent electrochemical activity is due to the 2D/2D heterostructure assembly of high surface area rGO and extended highly reactive region and defects in pCCN which facilitated the nucleation and confined growth of NiCo₂S₄ in the framework. The constructed pCRNCS//AC ASC exhibited remarkable electrochemical properties, including a specific capacitance of 211 F/g at 1 A/g, an exceptional capacitance retention of 93.6% after 6000 cycles, and the maximum energy density of 66 Wh/kg at a power density of 751 W/kg. The excellent capacitive behaviour of porous carbon self-repairing g-C₃N₄/rGO@NiCo₂S₄ assure the development of high-performance energy storage device.

1. Introduction

Due to increase in population, dependency on fossil fuel has increased unprecedentedly that eventually has led to huge negative impact on the environment. Need of the hour is to look for alternate renewable sources of energy to meet the perpetual demands of human race [1–3]. In present scenario, the importance of green energy such as wind, solar, tidal energies along with the devices to store such energies has tremendously escalated [4]. Electrochemical capacitors (Supercapacitors) can play a huge role in this context due to higher cycling life and power density than batteries and fast charge/discharge rate [5–7]. However, the major hurdles in the development of supercapacitor are low energy density, narrow potential window and low conductivity of electrode materials [8]. So, it is crucial to develop novel electrode materials with enhanced electrochemical properties for supercapacitor applications.

In the recent years, graphitic Carbon Nitride (g-C₃N₄) has attracted the interest of many scientists due to their moderate bandgap, good chemical stability, interesting optical characteristics, etc. for photocatalytic applications [9]. Nevertheless, there aren't many studies evaluating g-C₃N₄ (GCN) for energy storage applications. GCN has a structure resembling graphene with stacked 2D layers consisting of sp² hybridized C and N atoms forming π -conjugated electronic structures [10]. Despite its high N content with C:N ratio of 3:4, the use of GCN in supercapacitors is limited due to its low surface area and poor conductivity [11]. It has been demonstrated that nanocompositing with graphene improves the conductivity and electrochemical characteristics of GCN [12]. The abundant highly reactive region and defects in GCN acts as a template for crystal nucleation and growth [13]. In addition, g-C₃N₄ possesses a lamellar structure and lattice that is compatible with graphene nanosheets [13]. Chen et al reported a 3D-GCN functionalised graphene for supercapacitors contributing a specific capacitance of 264

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Research papers

Band-gap tuned hexagonal-boron nitride/reduced graphene oxide superlattice wrapped cadmium sulfide/Polypyrrole nanocomposite as an efficient supercapacitor electrode material

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ABSTRACT

The supercapacitor is focused as a highly sustainable and capacity energy storage device to meet the demand of energy in day-to-day life. Here, a band-gap tuned highly stable h-BN/rGO wrapped CdS/PPy is presented as a supercapacitor electrode material to obtain excellent specific capacitance, high power density and long cycling stability. It was synthesized via hydrothermal method combined with chemical oxidative polymerisation mechanism. The liquid exfoliated h-BN and graphene layers are restacked randomly by properly sandwiching alternate layers to form band gap tuned h-BN/rGO hetero-structure contributing as a conducting framework due to formation of Van der Waals stacked superlattice. The h-BN/rGO-CdS core-shell structure prevents the swelling and shrinking of CdS which improved the electrochemical performance and stability of the supercapacitor electrode. The highly conducting PPy nanowires acts as a backbone for the fast conduction of ions and the porous structure exhibiting superior specific capacitance of 1435F/g at a current density of 1A/g. The asymmetric supercapacitor (ASC) fabricated using h-BN/rGO/CdS@PPy//AC showed a specific capacitance of 102F/g at 1A/g and maximum energy density of 32 Wh/kg at a power density of 750 W/kg. Furthermore, the device showed a capacitance retention of 88.50 % after 5000 cycles assures it as a promising material for supercapacitor application.

1. Introduction

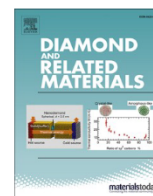
The past few years have witnessed expeditious exploration and advancement of renewable energy sources owing to the depletion of fossil fuels having its negative impact on the environment. Energy storage is a crucial factor to fulfil the increasing global energy demand with long-term sustainability for modern *E*-devices. In this direction, the supercapacitor, as an energy storage device, has garnered popularity due to its excellent specific capacitance, high power density, fast charge-discharge rate and long cycling stability [1]. The metal sulphides have drawn researcher's attention as a new promising class of supercapacitor electrode material due to its higher electrical conductivity [2] and more electrochemical activities than that of metal oxides/hydroxides [3]. Moreover, in alkaline electrolyte, metal sulphides exhibit reversible redox reactions ($MS + OH^- = MSOH + e^-$, where M = transition metal). The existence of valence states in materials such as NiS, CoS, CuS and CdS improves energy density and demonstrates excellent specific

capacitance [4]. Among these sulphides Cadmium Sulfide (CdS) is an outstanding pseudocapacitive material owing to its larger specific area, superior electrical conductivity, cost-effective, low toxicity and environmental stability [5]. Even, nanocomposites of CdS such as WO_3 -CdS provide high capacitance with 133 % capacitance retention [6]. The porous CdS grown on Ni foam substrate using one-step hydrothermal method was conveyed to show 909 F/g specific capacitance at 2 mA/cm² [7]. However, the theoretical capacitance of 1675 F/g using CdS electrode is much higher than that obtained experimentally [5]. There are many ways to enhance the electrochemical performance of CdS based supercapacitor - one way to improve the supercapacitor performance is to use the composite of CdS and EDLC like graphene, CNT and activated carbon as an electrode material [8,9]. In this direction, Graphene based CdS composite has been extensively studied by researchers due to its high specific capacitance and conductivity, large surface area and high mechanical strength [10–12].

The hexagonal-Boron Nitride (h-BN) is a sp² hybridized 2D material

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Synthesis and optimization of N, S doped reduced graphene oxide-NiCo₂S₄ hybrid active material for all-solid-state asymmetric supercapacitor

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ABSTRACT

The optimal use of materials leads to the overall increase in electrochemical performance of SCs. In this work, a novel hierarchical porous N, S doped reduced graphene oxide-NiCo₂S₄ hybrid nanocomposite was synthesized by in-situ growth of NiCo₂S₄ over porous rGO framework by a facile hydrothermal process. The materials are optimized by determining the proper ratio of metal ions to graphene in order to obtain optimal supercapacitive performance. The optimum use of materials showed improved nucleation and confined growth of NiCo₂S₄ nanoneedles over rGO by taking the advantages of high specific surface area and porosity of rGO. The N,S dual doping further enhanced the electrochemical activity by introducing defects in the crystal structure by replacing the lattice C atoms thereby rendering the graphene structure more disordered. The prepared GNCS3 electrode exhibited high specific capacitance (1640F/g at current density of 1A/g). The improved electrochemical activity is due to the synergetic impact of NiCo₂S₄ and rGO, wherein rGO served as an excellent conductor and ideal framework. The all-solid-state GNCS3//AC ASC fabricated showed excellent electrochemical properties with a specific capacitance of 135F/g at 1A/g, excellent capacitance retention of 92.5 % after 5000 cycles and highest energy density of 27 Wh/kg at a power density of 600 W/kg. The facile synthesis and excellent capacitive behaviour of NiCo₂S₄/rGO makes it an ideal electrode material for supercapacitor applications.

1. Introduction

In the past few decades, increased environmental pollution and global warming has led to the use of renewable energy sources and the corresponding energy storage [1–4] and conversion devices are in focus of many researchers [5–7]. Among the many energy storage devices, electrochemical capacitors or supercapacitors have gained much attention due to its excellent specific capacitance high energy density, power density, cycling stability etc. [8]. Supercapacitors (SCs) are mainly classified as electrical double-layer capacitors (EDLC) and pseudocapacitors based on their charge storage mechanism [9]. In EDLCs, charge storage is due to the reversible adsorption or desorption of electrolyte ions in the electrode surface but in the case of pseudocapacitors energy storage mechanism is due to the fast and reversible Faradaic redox reactions [10]. Carbon and carbon derived materials shows EDLC behaviour while transition metal oxides (TMOs) and conducting polymers (CPs) shows pseudocapacitive properties. Comparatively, pseudocapacitive materials have higher charge storage properties. However, direct application of pseudocapacitive materials are limited due to its lower

electrochemical stability and power density, as the Faradaic charge transfer reactions are significantly controlled by diffusion of electrolyte ions [11].

Recently, transition metal sulphides (TMS) with improved electrochemical activity and high capacitance have been investigated extensively as pseudocapacitive material [12]. Among TMSs, nanostructured NiCo₂S₄ has garnered much attention due its better electrochemical activity and higher conductivity than its oxide version [13]. The electrochemical activity from both nickel and cobalt ions in bimetallic sulphides results in higher redox characteristics and consequently superior specific capacitance when compared to monometallic sulphides like nickel sulphide (NiS) or cobalt sulphide (CoS₂) [14]. Also, the replacement of sulfur with oxygen in the architecture is applicable as a result of sulfur's reduced electronegativity compared to oxygen, facilitating easier electron movement in the structure and contributing its superior electrochemical capabilities [15]. Zhu et al. reported a solvothermal method for the synthesis of mesoporous NiCo₂S₄ nanocomposite with excellent specific capacitance (1440F/g at 3A/g) after 250 cycles and desirable cycling stability [16]. Shinde et al. synthesized a flexible

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Green reduction of graphene oxide using phytochemicals extracted from Pomelo Grandis and *Tamarindus indica* and its supercapacitor applications

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ABSTRACT

Green synthesis method is an effective approach for reduction of graphene oxide (GO) and the surface tuning of graphene nanosheets. In this work, facile green approach for the reduction of graphene oxide was adopted by utilizing phytochemical extracts of *Citrus grandis* (Pomelo) and *Tamarindus indica* (Tamarind). FTIR analysis showed significant reduction/elimination of the peaks that corresponds to the oxygen containing groups. XRD and Raman analysis confirmed the successful reduction of GO after treating with fruit extracts. The morphological analysis by SEM and TEM images further confirmed the formation of graphene nanosheets. The conductivity of both Pomelo-rGO (P-rGO) and Tamarind-rGO (T-rGO) were found to be 10^4 -folds higher than that of GO. The electrochemical characterization of the synthesized rGO was done by cyclic voltammetry (CV). Specific capacitance of 65.25 F/g and 47.33 F/g were recorded for T-rGO and P-rGO, respectively. The results showed that this green synthesis route is promising for the large-scale production of rGO.

1 Introduction

Graphene-based research have gained new heights after the successful isolation of single-layer graphene from graphite via Scotch Tape method in 2004 by A. Geim and, K. Novoselov. Graphene, a carbon allotrope is a wonder material with high thermal and electrical conductivity, mechanical strength, high-specific surface area, optical properties, etc. [1, 2]. These properties of graphene have proved to be

beneficial for wide range of applications which includes nanoelectronics, polymer composites, solar cell, transparent electrode energy storage systems such as supercapacitor, hydrogen storage etc. Graphene is said to have brought revolution to the material technology. There are many methods for the synthesis of graphene such as mechanical exfoliation, thermal exfoliation, chemical vapor deposition etc. However, the most effective method for mass production is the oxidation of natural graphite into

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Synthesis of highly oxidized graphene (HOG) by using HNO₃ and KMnO₄ as oxidizing agents

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ABSTRACT

A fast and efficient route is a key challenge in synthesis of graphene oxide (GO). In the present work, we report the synthesis of highly oxidized graphene (HOG) via 2 step chemical oxidation method by using a mixture of H₂SO₄ and HNO₃ as the intercalating and initial oxidizing agent followed by KMnO₄ as the final oxidizing agent. The XRD results of HOG showed peaks at 2θ = 9.7 (d spacing = 9.1 Å) which is the largest ever reported in such a short synthesis time. Raman spectroscopy confirmed the XRD results which proved that HOG is highly oxidized. UV-vis spectra provided evidence of the presence of an ample number of oxygen functionalities, such as hydroxyl, carboxyl, epoxide, and carbonyl on graphene oxide. SEM results exhibited the presence of wrinkles and folds along with a rough surface in HOG. The GO prepared by this method took only 3.5 hrs and is more oxidized compared to the ones prepared by Hummers method.

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1. Introduction

Graphene, an allotrope of carbon has been extensively studied over the past few years by researchers due its extraordinary properties like high specific surface area, high thermal and electrical conductivity, mechanical strength, optical properties, etc [1,2]. Graphene is a single atomic layer sp² hybridized form of carbon with a hexagonal honeycomb like structure [3]. Graphene is insoluble in water or any organic solvents [4] whereas graphene oxide (GO) contains high-density oxygen functional groups, like hydroxyl and epoxy group at its basal plane, and carboxyl at its edge makes it easily soluble in water [5]. Due to good solubility, ease of production, functionalization etc, GO is the most popular precursor of graphene. These properties justify the interest of researchers in the synthesis of eco-friendly, economical and scalable production of GO.

Graphene oxide is a stack of multiple layers of graphene which was first synthesized by Brodie by adding Potassium Chlorate (3 wt) in a mixture of Graphite (1 wt) in fuming nitric acid at 60 °C for 4 days [6]. In 1898, Staudenmaier improved the synthesis by replacing one third of fuming HNO₃ with H₂SO₄ and adding

Potassium Chlorate in batches [7]. In 1958, Hummer and Offeman reported the Hummers method which is widely considered as the best approach for the oxidation of graphite. In this a mixture of conc. H₂SO₄, NaNO₃ (0.5 wt) and KMnO₄ (3 wt) is used to oxidize graphite [8]. The advantages of Hummers method are: the entire process can be finished within a few hours, replacement of KClO₃ with KMnO₄ thus avoiding the evolution of ClO₂ which is explosive in nature, replacing fuming HNO₃ with NaNO₃ eliminates the formation of acid fog. Although Hummers method is widely used for synthesis of GO, it also has some demerits like the generation of toxic gases like NO₂ and N₂O₄, low yield, residual nitrate which is difficult to remove, etc. To overcome these problems various modifications has been made on Hummers method in the recent years.

Kovtyukhova et al. have found that a preoxidation of graphite using P₂O₅ and K₂S₂O₈ before the Hummers method resulted in highly oxidized GO but the whole process is very time consuming and expensive [9]. Marcano et al. proposed an NaNO₃ free GO process by increasing the amount of KMnO₄ and using a 9:1 mixture of H₂SO₄:H₃PO₄ as intercalating agent [10]. This method led to higher yield and the temperature can be easily controlled. Chen et al. proposed an improved hummers method by eliminating NaNO₃ and found that the exclusion of NaNO₃ does not affect the yield of the overall reaction. This improved method eliminated the generation of toxic gasses and simplified the procedure of purifying waste

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Green synthesis of cerium oxide nanoparticles using *Dillenia indica* aqueous extract and its anti-oxidant activity

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Abstract. Recently, the focus has been on the environment-friendly synthesis of nanoparticles (NPs) due to no chemical processing and generation of toxic and hazardous materials. Here, a novel method has been reported for the synthesis of cerium oxide nanoparticles (CeO₂ NPs) through a green route using *Dillenia indica* aqueous extract. The physico-chemical properties and morphological study of CeO₂ NPs were performed by using X-ray diffraction, field-emission scanning electron microscope imaging, energy dispersive X-ray analysis, Fourier transform infrared spectroscopy, RAMAN and ultraviolet-visible spectra. The nano-polycrystallinity of face cubic lattice structure is formed in CeO₂ NPs samples with an average particle size of 70 nm. The anti-oxidant property study of CeO₂ NPs was carried out using 2, 2-diphenyl-1-picrylhydrazyl (DPPH) scavenging assay. The CeO₂ NPs assure significant DPPH scavenging activity indicating excellent anti-oxidant property. This green synthesis method has the potential for mass production of CeO₂ NPs cost effectively without environmental pollution.

Keywords. Cerium oxide nanoparticles; *Dillenia indica*; anti-oxidant; green synthesis.

1. Introduction

Cerium belonging to rare-earth lanthanide series has two oxidation states (+3 and +4) [1]. The oxide of cerium (CeO₂) represents the cubic fluorite structure with oxygen deficiencies, providing redox reaction sites [2]. The nanoparticles (NPs) with their excellent properties such as miniature size and shape, and high surface to volume ratio have drawn much attraction in industrial, environmental and medical applications [3,4]. Likewise, CeO₂ NPs have also a wide range of applications such as catalyst [5,6], sensors, sunscreen cosmetics, fuel cells with solid oxide, chemicals alteration in the body, antibacterial activity, drug delivery carriers, anti-parasitic ointments, therapeutics agents, etc. [7–9]. Compared to other metal oxide NPs such as TiO₂ and ZnO, CeO₂ NPs possess less toxicity while applying to cell activity [10]. The NPs are efficient in degradation of pollutants from wastewater [11]. Recently, CeO₂ NPs have been tested for antibacterial behaviour using gram-positive and gram-negative bacteria [12]. The CeO₂ NPs with anti-oxidant activity have potential applications in daily human life as evaluated by various researchers [13,14].

There are many methods reported for the synthesis of NPs, such as microwave [15], hydrothermal [16], flame spray pyrolysis [17], sonochemical [18], sol-gel, co-precipitation methods [19]. Although these physical and chemical methods control the size and shape of NPs, these methods use toxic materials also requiring high temperature and pressure, lesser biocompatibility [2,9,20,21]. The green synthesis methodologies in the synthesis of metal and metal oxide NPs offers advantages such as large-scale commercial production and pharmaceutical applications, etc. Furthermore, green synthesis of nanostructures especially metal oxide NPs has emerged as a simple, non-toxic, inexpensive and efficient approach for nanofabrication. In this direction, biosynthesis of inorganic nanostructures such as oxide NPs, sulphide NPs, metallic NPs and other nanostructures have been reported for a wide range of applications such as drug delivery, antibacterial activity, gene therapy, DNA analysis, bio-sensing, magnetic resonance fingerprinting imaging extract [22]. The plant extracts, micro-organism and biological products are used for the biosynthesis of nanostructures, especially metallic NPs where phenolic groups, polyphenols and terpenoids reduce particle size making it

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Research Publications

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2. **Panicker, N. J.**, Ajayan, P. M. and Sahu, P. P. Band-gap tuned hexagonal-boron nitride/reduced graphene oxide superlattice wrapped cadmium sulfide/Polypyrrole nanocomposite as an efficient supercapacitor electrode material. *Journal of Energy Storage*, 56:105901, 2022. (I.F. 8.9)
3. **Panicker, N. J.** and Sahu, P. P. Synthesis and optimization of N, S doped reduced graphene oxide-NiCo₂S₄ hybrid active material for all-solid-state asymmetric supercapacitor. *Diamond and Related Materials*, 136:109936, 2023.
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6. Das, S., **Panicker, N. J.**, Rather, M. A., Mandal, M. and Sahu, P. P. Green synthesis of cerium oxide nanoparticles using Dillenia indica aqueous extract and its anti-oxidant activity. *Bulletin of Materials Science*, 46(1):3, 2022.
7. **Panicker, N.J.** and Sahu, P.P., Could graphene be the solution in the battle against Coronavirus SARS-CoV-2 (COVID-19)? *BioNanoScience* (revision submitted).