# Hydrothermal synthesis of strontium sulfide/nitrogen-graphene quantum dot composites for next-generation supercapattery devices

W. Abbas <sup>a,\*</sup>, A. Mahmood <sup>b</sup>, W. Al-Masry <sup>b</sup>, C. W. Dunnill <sup>c</sup> <sup>a</sup> Department of Physics, COMSATS, Lahore Campus, Pakistan <sup>b</sup> Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia <sup>c</sup> Energy Safety Institute (ESRI), Swansea University Bay Campus, Swansea, SA1 8EN, UK

A supercapattery merges the advantageous characteristics of batteries and supercapacitors (SCs). During this research, we synthesized strontium sulfide (SrS) using the hydrothermal method, and then we doped it with nitrogen/graphene quantum dots (N-GQDs). For SrS/N-GQDs, the Brunauer-Emmett-Teller (BET) analysis determined the total surface area to be 15.50 m<sup>2</sup>/g. Using the three-electrode assembly, the composite strontium sulfide (SrS/N-GQDs) revealed a specific capacity (C<sub>s</sub>) of 737 Cg<sup>-1</sup>. Battery-graded SrS/N-GQDs was utilized as anode and activated carbon (AC) as cathode to assemble a hybrid supercapacitor (SC). It delivered a remarkable power density of 1440 Wkg<sup>-1</sup>, the SrS/N-GQDs//AC supercapattery displayed 167 Cg<sup>-1</sup> in terms of capacity and an energy density of 35.7 Whkg <sup>-1</sup>. SrS/N-GQDs//AC maintained 91% of its initial capacity after 5000 cycles. SrS/N-GQDs has remarkable electrochemical performance, indicating its potential use as a nanostructured electrode in next-gen electrochemical energy storage (EES) devices.

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#### 1. Introduction

This era has seen the increasing degradation of finite fossil fuels, which has led to an energy issue. The need for highly efficient energy storage and transition technologies is growing in order to keep up with the demand for energy [1-4]. Capacitors store charges electrostatically, whereas batteries store charges through faradic interactions between electrolytes along with electrodes [5, 6][5, 6]. Supercapacitors, sometimes known as ultra-capacitors, offer several benefits over conventional chemical storage technologies, including a long cycle life with a high power density [7]. They challenge to offer high density, though. Intermediate energy and power can be produced via pseudocapacitors (PSc), which use reversible diffusion-controlled mechanisms to store electrical energy at the boundary of electrode materials [8]. Two essential components that allow S.C.s to regulate the energy density include cell potential as well as electrode capacitance [9]. Designing a nanoscale, porous electrode material having higher energy density values is one way to boost capacitance. Constructing asymmetric or hybrid energy storage devices, which raise the cell's overall potential, is a further strategy. Two forms of asymmetric/hybrid S.C.s are further classified. Two capacitive electrodes are used in the first kind of hybrid devices, such as EDLCs and PCs. Single capacitive electrodes along with a battery-graded electrode are used in the second kind of hybrid device [10, 11]. We refer to this kind of hybrid device as called supercapattery [12]. The advantageous electric as well as conductive properties of metal sulfides, oxides, especially phosphates/phosphides have made them popular choices for use as active materials in electrode design. These features also make them suitable for use in charge-storage devices.

The use of strontium phosphate in supercapacitor technologies has attracted a lot of interest. Its potential is found in its ability to build novel nanostructures with exceptional conductivity that

<sup>\*</sup> Corresponding author: waseemabbas9883@gmail.com https://doi.org/10.15251/CL.2024.2111.953

greatly increase surface area vital aspect for numerous applications and boost efficiency. The exceptional ionic as well as electronic conductivities, along with their robust reactivity, have made strontium-doped materials a highly regarded choice for solid oxide electrochemical device electrode materials. [13, 14]. Because of their outstanding mechanical qualities, low density, simple functionalization, high electrical conductivity, as well as changeable porosity and surface area, flexible carbonaceous materials are widely utilized in this context. It is also affordable and available [15].

Numerous methods have been developed up to this point for making GQDs (Graphene Quantum Dots) more effective. [16]. Recently it is shown that chemically doping using hybrid atoms provides an efficient way to influence the properties of nanomaterials. [17, 18]. N-GQDs arise when chemical bonding effectively modifies the chemical as well as optical characteristics of nitrogen-doped atoms due to edge effects and quantum limitations [19]. Nitrogen groups may be added inside the GQDs' framework using a variety of methods, including as solution chemistry via electrochemical activation [20].

In this research article, the hydrothermal technique was employed to synthesized SrS and then doped it with nitrogen-graphene quantum dots (N-GQDs). SEM analysis was executed to observe morphology. Structural properties of SrS/N-GQDs were examined by the means of X-ray diffraction (XRD). The material structure was examined using the X-ray photoelectron spectrum (XPS). Mostly researchers focused on replacing battery-grade electrodes in previous investigations. We adjust combined capacitive as well as battery-graded electrodes during this work. SrS/N-GQDs was used as anode and AC was used as cathode for preparing an asymmetric device. Galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), specific capacity ( $C_s$ ), and stability testing were used in the electrochemical testing of SrS/N-GQDs.

# 2. Methodology

#### 2.1. Materials

We bought potassium hydroxide (KOH) pellets and activated carbon (AC). Additionally, sodium sulfide hydrate (Na<sub>2</sub>S.nH<sub>2</sub>O) from Sigma Aldrich, carbon black (CB), strontium nitrate (SrNO<sub>3</sub>), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>), NMP, and PVDF are included. Urich Technology Malaysia facilitated the acquisition of this nickel foam. Each chemical had been acquired from market and utilized without any sort of purification. The Hg/HgO and platinum (Pt) wire were used as counter and reference electrodes, respectively, and were bought from Japan (ALS Co. LTD).

#### 2.2. Synthesis of strontium sulfide

Hydrothermal method was used to make strontium sulphide. The hydrothermal process was selected as the method of synthesis since it was simple and efficient. Moreover, it offers more crystallinity than alternative methods like the co-precipitation process [21]. An optimal range of temperature in hydrothermal process is 120–250 °C. 0.8 mol solution of sodium sulphide hydrate (Na<sub>2</sub>S.9H<sub>2</sub>O) and strontium nitrate hex hydrate (SrH<sub>12</sub>NO<sub>9</sub>) were prepared using the 30ml of deionized water (DIW). After that, we added drops of Na<sub>2</sub>S.9H<sub>2</sub>O and continually stirred the hex hydrate strontium nitrate (SrH<sub>12</sub>NO<sub>9</sub>) solution for 30 minutes. Subsequently, the resultant solution was autoclaved for six hours at 120 °C. To remove impurities, this synthetic material was repeatedly cleaned with ethanol and water. After being dehydrated in an oven for four hours at 50 °C, the material was then retrieved.

#### 2.3. Synthesis of SrS/N-GQDs

The SrS/N-GQDs was synthesized by dissolving 0.5 g of SrS and 0.5 g of N-GQDs in deionized water (30 ml). Subsequently, all formerly outlined processes were performed to obtain the final product.

# 3. Results and discussion

To verify that the materials are crystalline, X-ray diffraction is used to study them. The XRD peaks of SrS doped with N-GQDs are shown in Figure 1(a). The SrS contribution is shown by the XRD peaks seen at  $2\theta = 30.2^{\circ}$ ,  $45.7^{\circ}$ ,  $52.3^{\circ}$ , and  $65.4^{\circ}$ , which correspond to (200), (220), (222), and (400). On the other hand,  $2\theta = 22.8^{\circ}$ ,  $41.6^{\circ}$ , and  $59.3^{\circ}$  were the locations of the N-GQDs XRD peaks, which correlate to (002), (100), and (110). The synthesis of SrS/N-GQDs is validated by these composite conditions XRD peaks.



Fig. 1. (a) XRD of SrS, N-GQDs and SrS/N-GQDs composite.

#### 3.1. Measurement of SrS/N-doped GQDs electrodes electrochemically

The electrochemical properties of SrS doped SrS/N-GQDs are investigated using potentiostat. All three samples' CVs were assessed within the potential window of 0 to 0.8 V, and at different scan speeds ranging from 3 to 50 mV/s. The CV graphs for SrS and SrS/N-GQDs are shown in Figure 2(a-b), respectively.



Fig. 2. Cyclic voltammetry for (a) SrS (b) N-GQDs (c) Specific capacity of SrS and SrS/N-GQDs via CV.

The redox peaks in the graph shapes show the Faradaic performance of SrS/N-GQDs, an indication of materials that are good candidates for batteries. The faradaic reaction takes place when the OH-ions in the electrolyte react with working electrode. As scan rate increases, oxidation/reduction peaks display rising current levels. Using the provided formula, each electrode's specific capacity was ascertained.

$$Q_{s} = \frac{1}{mv} \int_{V_{i}}^{V_{f}} I \times V dV$$
(1)

The variable Q<sub>s</sub> in the calculation given stands for specific capacity,  $\int_{V_i}^{V_f} I \times V dV$  represents the CV curve's area, whereas the m and v stand for and scan rate as well as active mass, accordingly. This formula is divided by the 0.7 V potential range "V" to find the specific capacity (Cs).

Equation (1) obtains specific capacities for SrS and SrS/N-GQDs of 638 C/g and 882 C/g, respectively. The supporting each other impact of both SrS caused an increase in a specific capacity when the SrS sample, which demonstrated a particular capacity via CV, was used. The N-GQDs doping of the SrS composite resulted in an additional increase in the oxidation peaks. [21, 22]. Since the material SrS/N-GQDs predominates over the sample SrS, certain appealing surface areas are not now available for charge storage. One interesting finding from Figure 2(a-b) is that, even though the SrS/N-GQDs show bigger peaks than the SrS sample, the doped material's oxidation peaks move to a higher potential, suggesting that N-GQDs have a reduced oxidation rate capability. In contrast to previous samples, the doped material's broad surface exhibits a greater current response. Figure 2 (c) the specific capacities for SrS and SrS/N-GQDs were determined to be 638 C/g and 882 C/g, respectively.

Figure 3 shows the electrode analysis findings from GCD at 1 Ag<sup>-1</sup>current density to 2.6 Ag<sup>-1</sup> in potential ranges of 0 to 0.65 V. This material falls in battery grade, as shown by the non-linear behaviour of galvanostatic charging and discharging in Figure 3.



Fig. 3. (a) Representation of GCD for SrS (b) GCD for SrS/N-GQDs (c) Specific capacity of SrS and SrS/N-GQDs via GCD.

The results show that the discharge time and, consequently, the  $C_s$ , both decrease with an increase in current density. A limited period of time that the electrolyte ions and electrode material may interact is the cause of the shorter discharge period. At greater current densities, the charge carrier interaction which is the result of increased interest causing internal resistance also contributes to the drop-in discharging time. Following equation may be used to determine specific capacity of GCD electrodes.

$$Q_{s} = \frac{I \times t}{m}$$
(2)

where the current and discharge time are denoted by "I" and "t,".

At 1 Ag<sup>-1</sup>, SrS showed 523 C/g and SrS/N-GQDs 737 C/g. Because of its quicker ion diffusion channel for electrolyte ion contact with the electrode material, SrS/N-GQDs//AC has a higher specific capacity.[23, 24].

Using the BET technique, its pore size, pore volume and surface area were also determined. BET calculate surface area is used to measure the adsorption isotherm. This technique works well with materials that exhibit isotherm curves, however it is frequently applied to a variety of materials [25]. The BET isotherm for SrS/N-GQDs is shown in Figure 4(a). The SrS/N-GQDs have a surface area of 15.50 m<sup>2</sup>/g and a pore volume of 0.038 cm<sup>3</sup>/g. Its 19.72 nm pore size creates the appearance of rapid ion movement. These results suggest that high surface area and a large pore size of SrS/N-GQDs may store a substantial amount of charge rapidly. With cycle stability, this increased surface area immediately improved the specific capacity. Larger surface area facilitates higher charge accumulations, but increased hole volume expedites ion transit. The EIS measurement is shown in Figure 4(b). Because SrS/N-GQDs have the lowest impedance, they are more advantageous for

supercapattery design. Because the components' properties resemble those of a battery, the EIS form in this instance cannot be completely vertical. The reason for this increased conductivity is N-GQDs.



Fig. 4. (a) Nitrogen adsorption desorption isotherm of SrS and SrS/N-GQDs. (b) EIS of SrS and SrS/N-GQDs.

To perform more studies on the material's efficiency, a supercapattery device is made. With the sample SrS/N-GQDs as anode and carbon black as cathode. In order to develop devices that may be used in daily life, the best sample was mixed with activated carbon. After a two-electrodes assembly is developed, the assessment of GCD and CV test performance at different current densities and scan rates is shown in Figure 5(a-c).



Fig. 5. (a) Real device cyclic voltammetry. (c) Real device GCD measurements (c) The Specific capacity for SrS/N-GQDs//AC via CV. (d) Specific capacity for SrS/N-GQDs//AC via GCD.

To build the real device, the positive electrode was the binary composite material sample SrS/N-GQDs, while the negative electrode was activated carbon. Electrochemical characterisation of this device was performed in an electrolyte solution containing 1M KOH. Equation (3) below illustrates how the object's Cs and potential range are the only factors that affect the energy density.

$$E = \frac{1}{2}CV^2 \tag{3}$$

where "V" stands for a prospective window and "C" for specified capacity. Consequently, the device needs to operate at a wider potential window to generate high energy density [26]. For sample SrS/N-GQDs, the independent calculations of the CV peaks in a three-electrode assembly are 3 mV/s, and the AC over potential falls between 0 and 0.6 V and -1 to 0 V. Within 0 to 1.6 V range of potential, the scan rates varied from 3 mVs<sup>-1</sup> to 50 mVs<sup>-1</sup> using the SrS/N-GQDs electrodes and activated carbon in the CV graph. The presence of redox peaks at higher potentials and non-rectangular CV curves indicate a non-capacitive, battery-graded character. The CV curves at lower potentials show the capacitive behaviour. The device's remarkable rate capabilities can be explained by the form retention of CV at higher scan rates. Using GCD, the device's behaviour was further examined in the potential range of 0 to 1.6 V at current densities ranging from 1 A/g to 2.6 A/g. These results improve on the potential applications of supercapattery development. The GCD peak's consistent behaviour at higher current density levels and its well-preserved shape demonstrate the device's exceptional rate capacity and stability. The highest Cs of 282 C/g for the device sample SrS/N-GQDs/AC was obtained by CV at a 3 mV/s, whereas the maximum specific capacity of 167 C/g was determined by GCD.

5000 GCD cycles were carried out at a current density of 4.8  $Ag^{-1}$  to assess the supercapattery durability. The charging/discharging time calculated over 5000 cycles is depicted in figure 6(a). The capacity retention graph, which is displayed in Figure 6(b), was discovered to be 84% after 5000 cycles. Figure 6(b) displays the Coulombic efficiency (CE), which is determined using the previously indicated equation following 5000 GCD cycles. 91% was found to be the result. The SrS/N-GQDs/AC b-values that fall within the supercapattery b-value range are shown in Figure 6(c). The b-values support the notion that supercapattery device has been fabricated. The battery's b-values vary from 0 to 0.5, the supercapattery's from 0.5 to 0.8, and the supercapacitors' from 0.8 to 1.0, as shown in Figure 6(d).[27].



Fig. 6. (a) Device stability against 5000 charging/discharging cycles. (b) capacity retention and columbic efficiency versus cyclic stability. (c) Linear fitting for SrS/N-GQDs//AC hybrid device (d) Energy and power densities comparisons with available literature.

Composite Materials	Type of Device	Energy Density (WhKg <sup>-1</sup> )	Power Density (Wkg <sup>-1</sup> )	Specific Capacity (Cg <sup>-1</sup> )	Ref.
Ultrathin Cu <sub>2</sub> P <sub>2</sub> O <sub>7</sub> nanoflakes	Hybrid supercapacitor (HSC)	11.54	7060		[31]
MoS					
	SC	5.42	128		[32]
CoS					
(Nanotubes)	SC	27.7	500		[33]
Morphological Modulation NiCo2Se4 Nanotubes	HSC	25	490		[34]
MnS/ZnS	SC	91	7.78		[35]
Co-MOF/polyaniline					
	SC	23.2	1600	162.5	[36]
SrS/N-GQDs	Supercapattary	35.7	1440	737	This Work

Table 1. Manifestation of the valuation of power and energy densities as reported.

The energy density and power density can be calculated via the following formulas.

$$E\left(Wh\,kg^{-1}\right) = \frac{Q_{s} \times \Delta V}{2 \times 3.6} \tag{4}$$

$$P\left(W\,kg^{-1}\right) = \frac{E\times 3600}{\Delta t} \tag{5}$$

The energy density (E), as shown in Figure 6(d), was found to be 37.5 Wh k/g at a power density of 1440 W k/g. This number is larger than previously published values of un-doped sulphides, suggesting that SrS/N-GQDs performs better in energy storage device applications [28-30]. This study's power and energy densities are compared with those of previous studies in Figure 6(d). Based on the improved performance of the SrS/N-GQDs sample, it was concluded that N-GQD doping enhanced the efficiency of binary metallic sulphide, indicating SrS/N-GQDs an attractive alternative for energy storing and delivering application in term of supercapattery.

# 4. Conclusion

In our work, the hydrothermal method was used for producing SrS. After the binary composite SrS/N-GQDs, a comparison of its electrochemical performance is performed on many samples. The SrS/N-GQDs demonstrated higher capacity because of the N-GQDs wide surface area, which encourages a shorter and stronger path for ion diffusion. An asymmetric 'supercapattery' device with a  $C_s$  of 167 Cg<sup>-1</sup> at 1 Ag<sup>-1</sup> and 91% cyclic stability was attained after 5000 GCD cycles. It was found that the device possesses an energy density of 35.7 Wh/Kg and a power density of 1440 W/Kg. These findings suggest that SrS/N-GQDs can be used in the development of high-performance supercapattery devices.

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