

Chapter 2

Supercapacitor electrode materials: 2D nanomaterials and heterostructures

Contents

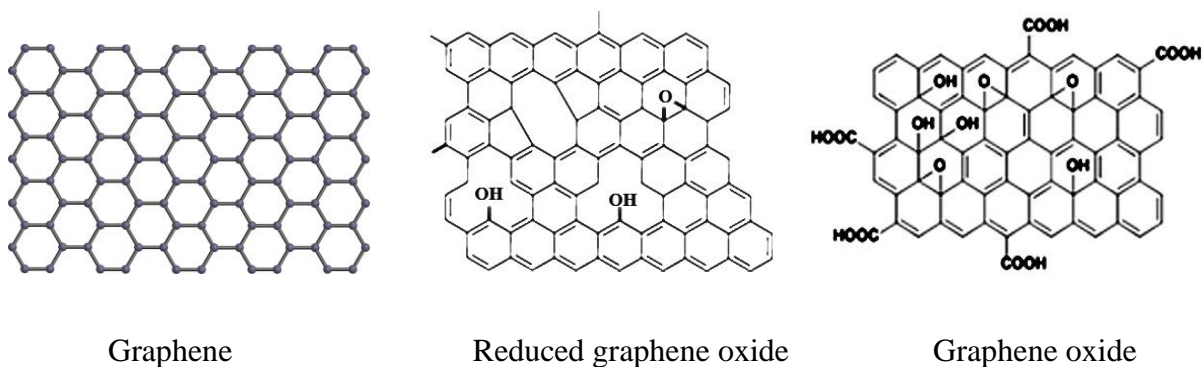
2.1	Introduction
2.2	Graphene
2.3	Graphene/Transition Metal Oxides or Sulphides
2.4	Graphene/h-BN heterostructures
2.5	Graphene/g-C₃N₄ heterostructures
	Bibliography

2.1. Introduction

The charge storage and capacitance of a SC are significantly influenced by the electrode materials. As a result, the ultimate objective for SC devices is to employ newly synthesized nanomaterials with improved capacitance and increased performance over traditional nanomaterials. The key to overcoming issues with supercapacitors' electrochemical charge storage mechanism is to optimize electrical conductivity, band gap, charge carrier mobility and structural flexibility. Numerous 2D materials, including graphene [1], h-BN [2], g-C₃N₄ [3], MoS₂, etc. have been reported in past years for application in energy storage. Like every coin has two sides, these materials have their pros and cons that limit their potential applications. Numerous initiatives have been undertaken to tailor novel electrode materials to enhance their performance. 2D nanomaterials and their heterostructures emerged as the best choices due to the high redox activity, improved ionic conductivity and short diffusion paths produced when active sites and defects are created in the heterostructure materials' grain boundary [4]. Heterostructures are a combination of two or more materials which are physically (Van der Waal's force) or chemically (covalent bond) bonded to each other to form complex geometry with distinctive properties. Heterostructures use the synergetic properties of the constituent materials which will alter the intrinsic properties like band structures, alignment styles, semiconductor types, carrier concentration, and Fermi level difference. Heterostructures can be broadly classified according to the bonding of its constituents as Van der Waal's heterostructures and chemically bonded heterostructures. Van der Waal's heterostructures or Superlattices are formed by stacking different conventional 2D materials like graphene, h-BN, g-C₃N₄, MoS₂, MXenes of similar structure, alternatively to incorporate the merits of different constituents to overcome the cons of each individual block. In order to enhance electrochemical characteristics in chemical bonded heterostructures, transition metal oxides or conducting polymers (PPy, PANI, PEDOT: PSS) are chemically attached to the 2D material.

2.2. Graphene

Graphene, a carbon allotrope, has been actively explored by researchers in past years owing to its amazing qualities like large specific surface area, mechanical strength, high thermal and electrical conductivity, optical properties, and so on [5, 6]. It has a hexagonal honeycomb-like shape with a single atomic layer of sp² hybridised form of carbon [7]. Graphene is highly conductive, transparent, and flexible, making it ideal for use in electronics, solar cells, and other applications.



Graphene is extensively studied in energy storage applications; however, the practical application is limited due its high synthesis cost, processability and self-agglomeration problem of graphene layers. The common route for mass production of graphene is by the oxidation of graphite flakes and further reduction to get few layers graphene which resembles the properties of pristine graphene.

Synthesis of Graphene Oxide

Graphene oxide which consists of multiple layers of graphene was first synthesized by Brodie by combining Potassium Chlorate (3wt) in Graphite (1wt) in fuming HNO_3 at 60°C for four days [8]. In 1898, Staudenmaier refined the synthesis by substituting a third of the fuming nitric acid with sulfuric acid and adding Potassium Chlorate in multiple additions [9]. 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 combination of conc. H_2SO_4 , NaNO_3 (0.5 wt) and KMnO_4 (3 wt) is used to oxidize graphite [10]. The benefits of the Hummers method are: the entire procedure can be completed in a few hours, replacement of Potassium Chlorate with KMnO_4 thus avoiding the evolution of ClO_2 which is explosive in nature, replacing fuming HNO_3 with NaNO_3 eliminates the formation of acid fog. Although the Hummers technique is commonly employed for the preparation of GO, it has some drawbacks, such as the formation of hazardous gases like NO_2 and N_2O_4 , low yield, residual nitrate which is difficult to remove, etc. To overcome these problems various modifications has been made on Hummer's method in the recent years.

Kovtyukhova and coworkers discovered that a preoxidation of graphite using P_2O_5 and $\text{K}_2\text{S}_2\text{O}_8$ prior to the Hummers method produced highly oxidised GO, although the entire process is extremely time-consuming and costly [11]. Marcano et al. proposed a NaNO_3 free GO process by raising the quantity of Potassium permanganate and employing a 9:1 blend of H_2SO_4 : H_3PO_4 as intercalating agent [12]. This procedure led to a better yield and temperature control is

simple. Chen et al. proposed an improved hummers method by eliminating sodium nitrate and reported that the omission of NaNO_3 has no effect on the total yield of the reaction. This modified approach avoided the emission of hazardous gases and streamlined the treatment of waste liquid, thereby lowering the cost of GO synthesis [13]. Staudenmaier method for GO preparation was modified to study the effect of HNO_3 and H_2SO_4 solution as intercalating agent and HNO_3 - H_2SO_4 in a volume ratio of 1:3 was found to be effective for exfoliation [14]. At room temperature, K_2FeO_4 is also utilised as an oxidising agent to produce single-layer GO [15]. Elimination of NaNO_3 , substitution of KMnO_4 with K_2FeO_4 , and regulation of the quantity of conc. H_2SO_4 employed led to a reduction of reagent usage while giving a high yield at the same time [16]. Panwar et al. have proposed a tri-acidic intercalating agent for GO synthesis by using a mixture of H_2SO_4 : H_3PO_4 : HNO_3 in the ratio 67.5:22.5:10. The outcome demonstrated a substantially larger yield of GO in a very brief processing period [17]. Dimiev et al. have also used a tricomponent solution of H_2SO_4 (4ml), fuming H_2SO_4 (4ml) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1g) as GIC for 100mg of graphite. The results showed a ~100% yield and synthesized 25nm thick graphene nanoplatelets [18].

Table.2.1 Review of existing synthesis methods for graphene oxide

Brodie et al.	Fuming HNO_3 , $\text{KClO}_4(\text{OA})$	<ul style="list-style-type: none"> • Long process (4 days) • Evolution of ClO_2 which is explosive in nature 	[8]
Staudenmaier et al.	Fuming HNO_3 and conc. $\text{H}_2\text{SO}_4(1:3)$, $\text{KClO}_4(\text{OA})$	<ul style="list-style-type: none"> • Formation of acid fog 	[9]
Hummers et al.	conc. H_2SO_4 (GIC), NaNO_3 , $\text{KMnO}_4(\text{OA})$	<ul style="list-style-type: none"> • Most common method • Toxic gases generated ($\text{NO}_2, \text{N}_2\text{O}_4$) • Low yield 	[10]
Kovtyukhova et al.	preoxidation of graphite using P_2O_5 and $\text{K}_2\text{S}_2\text{O}_8$	<ul style="list-style-type: none"> • Better oxidation than Hummer's method • time consuming and expensive 	[11]

Marcano et al.	H ₂ SO ₄ :H ₃ PO ₄ (1:9) (GIC), KMnO ₄ (OA)	<ul style="list-style-type: none"> • avoided the use of NaNO₃ • No toxic gases generated. • High yield 	[12]
Chen et al.	conc.H ₂ SO ₄ (GIC), KMnO ₄ (OA)	<ul style="list-style-type: none"> • Found elimination of NaNO₃ doesn't affect yield. 	[13]
Yu et al.	conc.H ₂ SO ₄ , K ₂ FeO ₄ and KMnO ₄ (OA)	<ul style="list-style-type: none"> • Less reagents required. • High yield 	[16]
Panwar et al.	67.5:22.5:10 mixture of H ₂ SO ₄ :H ₃ PO ₄ :HNO ₃ and KMnO ₄ (OA)	<ul style="list-style-type: none"> • Shorter processing time • Higher yield 	[17]

2.3 Graphene/Transition Metal Oxides or Sulphides

Pseudocapacitance properties is shown by transition metal oxides (TMOs) and conducting polymers (CPs), whereas EDLC behaviour is seen in carbon and carbon-derived materials. Pseudocapacitive materials, in contrast, can store more charge. As the Faradaic charge transfer processes are strongly regulated by electrolyte ions' diffusion, the direct use of pseudocapacitive materials is constrained owing to its poorer electrochemical stability and power density [19].

Increased electrochemical activity along with high capacitance in transition metal sulphides (TMS) have led to their widespread study as a potential pseudocapacitive material in recent years [20]. Because of its greater electrochemical activity and conductivity than its oxide counterpart [21], nanostructured NiCo₂S₄ has gained a lot of interest among TMSs. When compared to monometallic sulphides such as nickel sulphide (NiS) or cobalt sulphide (CoS₂), the electrochemical activity of nickel and cobalt ions in bimetallic sulphides leads to greater redox properties and, subsequently, a larger specific capacitance [22]. Also, the substitution of sulphur with oxygen in the design is suitable due to sulfur's lower electronegativity in comparison to oxygen, which facilitates simpler electron mobility within the structure and contributes to its improved electrochemical capabilities [23]. Zhu et al. [24] developed a solvothermal technique for the production of mesoporous NiCo₂S₄ nanocomposite with exceptional specific capacitance (1440F/g at 3A/g) and satisfactory cycling stability after 250 cycles. Shinde et al. used the SILAR approach to develop flexible nanoflakes-like NiCo₂S₄ with a capacitance of approximately 1072F/g at 5mV/cm² scan rate [25]. Kulurumotlakatla et al. discussed that a battery-profile NiCo₂S₄ sample exhibited excellent electrochemical

performance, with exceptional specific capacity of around 154.13mAh/g (2A/g) and capacity retention of ~92.5% at 15A/g, and better cycling stability (~95.2% at 4A/g, 5000 cycles) [26]. The charge-discharge process in pseudocapacitive materials leads to volume fluctuation which in turn, limits cycle stability. Therefore, a hybrid of both carbonaceous and pseudocapacitive materials is proved to be effective in improved electrochemical performance.

Because of its larger specific surface area, rGO will offer an abundance of active sites for metal ion growth. Moreover, the in-situ growth of NiCo₂S₄ over the rGO structure will prevent the structural collapse because of the volume fluctuation throughout the charging/discharging operation [27]. The higher conductivity of rGO when composited with intrinsically low conducting NiCo₂S₄ will improve the electrochemical performance and at high current densities it alleviates the sluggish pace of redox reaction [28]. Nevertheless, an excessive quantity of graphene will lead to its own agglomeration, which will severely reduce graphene's utilisation efficiency and inhibit the formation of metal ions on its surface. Furthermore, the contribution of capacitance is relatively restricted in the working voltage range of NiCo₂S₄ electrode (0 - 0.6 V) [29, 30], meaning that the addition of graphene mass lowers the whole device's specific capacitance [31]. Additional issues with NiCo₂S₄ -graphene composites include the non-homogeneous NiCo₂S₄ particle dispersion on graphene surface, graphene's tendency to self-aggregate and re-stack, the lack of pores necessary for rapid ionic exchanges, and so on. Therefore, optimising the material by determining the optimal ratio of metal ions to graphene is crucial for achieving the greatest possible supercapacitive performance.

2.3. Graphene/h-BN heterostructures

Since graphene lacks a band gap, it cannot be employed directly in transistors, despite its potential applications in electronics, transparent conducting films, energy storage, etc. Similarly, graphene derived from reduced graphene oxide with considerable agglomeration lacks the conductivity and capacitance of pure graphene. At the same time, hexagonal-Boron Nitride (h-BN) is a sp² hybridised 2D material with superior thermal conductivity, great mechanical strength, but limited electrical conductivity because of its large band-gap of 6.08 eV [32]. It has similar structure that of graphene. The nano-compositing of h-BN with carbon based materials like graphene enhances electron mobility and increases electrical conductivity due to the creation of heterostructures promoting the defects and free electrons [33]. Moreover, the formation of various band intervals within the hetero-junction establishes new rules for the selection of each quantum well affecting charge flow conditions across the structure. In addition, the formation of hetero-structure increases the defects adjusting charge carriers'

mobility and thereby, magnifying the electrochemical activity because of the available free electrons [33, 34]. Hence, the h-BN/graphene composite is an effective supercapacitor material because of EDLC characteristics of graphene and intrinsic pseudocapacitive characteristics of h-BN [33, 35]. Recently, h-BN/rGO has been reported to be n-type after incorporation of rGO into it showing pseudocapacitance through chemi-absorption [35] by contributing C-C bonds, B-N bonds and π -configuration [36]. Moreover, h-BN/rGO shows lower band gap [37] exhibiting excellent capacitance properties due to its non-hierarchical assembly structure [38]. Gao et al. [39] developed a liquid exfoliation process for the creation of randomly stacked h-BN/graphene (h-BN/G) nanomaterial with distinct properties from its parent materials. They altered the optical band-gap by varying the concentration of materials. A band-gap engineering technique by dual doping B and N atoms on CVD graphene was reported by Chang et al. [40]. They were successful in generating a band-gap as high as 600eV in the graphene structure. An improved specific capacitance of 824F/g at 4A/g was observed by Saha et al. [37] using a hydrothermal synthesis process for h-BN/rGO supercapacitor electrode material. The electrochemical properties of h-BN/rGO composite was better than rGO or h-BN individually. Saha et al. [33] further improved the performance of h-BN/rGO nanostructure by varying the amount of graphene content and thereby controlling the structure's band-gap. Boosting the rGO concentration improved the density of states and electrical conductivity, hence lowering the activation energy. The improved h-BN/rGO structure exhibited 960 F/g of specific capacitance at 10mV/s scan rate. Excellent energy and power density (73 Wh/kg and 14 kW/kg, respectively) was shown by an ASC constructed with h-BN/rGO and B, N doped rGO electrodes. In order to create h-BN/graphene hybrid films with desirable properties such as high volumetric capacitance, outstanding life cycle, superior rate capability and good flexibility. Byun et al. [41] devised a straightforward solution-based technique for the synthesis of h-BN/graphene film. The electrode showed 100% capacitance even after 1000 bending tests. Althubaiti et al. [42] reported an h-BN/rGO electrode material through a simple hydrothermal route which exhibited better electrochemical properties than parent materials. They also proved that the capacitance of Co_3O_4 increased significantly when rGO/h-BN composite with Co_3O_4 was used. Excellent capacitance retention of 78% (150 mA/g, 5000 cycles) was seen in an ASC fabricated using rGO/h-BN/ Co_3O_4 . Using vacuum filtering and heat treatment, Li et al. [43] synthesized a rGO/BN composite to use as a binder-free anode electrode in Li ion batteries. The nanocomposite with 2wt.% BN content rGO/BN film presented good rate capability and great capacity retention after 200 cycles, with a reversible capacity of 278 mAh/g at a current density of 100 mA/g. Krishnaveni and co-workers [44] synthesized 3D marigold like

rGO/BN/Ni(OH)₂ composite using hydrothermal method that presented a specific capacitance of 349F/g at 0.5mA/cm² in 0.5M KOH electrolyte. Also, h-BN integrated graphene paper was developed by Rajendran et al. using a simple vacuum filtration technique [45]. After 6000 cycles, the prepared flexible electrode retained 96.3% of its capacitance and a specific capacitance of 322F/g (0.5A/g) was recorded. The above results shows that the h-BN/rGO heterostructures is much beneficial in energy storage applications than its individual materials.

2.4. Graphene/g-C₃N₄ heterostructures

Recent years have seen rise in graphitic Carbon Nitride (g-C₃N₄) researches for photo-catalytic applications due to their moderate bandgap, good chemical stability, interesting optical characteristics, etc. [46]. However, there are few reports assessing g-C₃N₄ (GCN) for use in energy storage. GCN has a structure resembling graphite with stacked 2D layers consisting of sp² hybridized C and N atoms forming π -conjugated electronic structures [47]. GCN has a structure resembling graphite with stacked 2D layers consisting of sp² hybridized C and N atoms forming π -conjugated electronic structures [47]. GCN has a poor conductivity and low surface area, hence its usage in supercapacitors is restricted despite its high N content with C:N ratio of 3:4 [48]. Improvements in GCN's conductivity and electrochemical performance after nanocompositing with graphene have been reported [49]. The abundant highly reactive region and defects in GCN serves as a template for crystal nucleation and growth [50]. Chen et al. reported a 3D-GCN functionalised graphene for supercapacitors which presented a specific capacitance of 264 F/g (0.4 A/g) and better cycling stability [51]. Ding et al. produced a carbon self-repairing g-C₃N₄ (CCN) via homogenous substitution of C for N or by forming new interstitial C-N bonds. Porous framework was generated by cross-linking interactions between rGO layers and the CCN with extended π -conjugated layers. Specific capacitance of the CCN@rGO electrode was computed to be 380F/g at 0.25A/g current density [49]. Subsequent research by Lin and co-workers found that preoxidation of GCN in HNO₃ media trims down the larger planes into smaller segments thereby increasing the edge nitrogen and oxygenated functional groups. Thus, GOOCN₂₄ electrode material so developed exhibited 266F/g and 244F/g at acid and alkali electrolytes respectively at 1A/g [52]. However, the predominant EDLC charge storage method of GCN, graphene, and their nanocomposites results in a poor energy density.

Table 2.2: Review on supercapacitor electrodes on graphene based 2D nanomaterials and heterostructures

Author and year	Nanocomposite	Specific capacitance (F/g)	Power Density (W/kg)	Energy Density (Wh/kg)	Remarks
Chen et al., 2018 [53]	3D-CdS/graphite	511F/g@ 5A/g	800	30.4	Good cycling stability of 90.1% after 5000 cycles was achieved by utilizing graphene.
Patil et al., 2020 [54]	h-BN/reduced graphite oxide	304F/g@ 1A/g	1800	1.25	2wt% h-BN loaded heterostructure exhibits a superior capacitive performance.
Saha et al., 2017 [33]	h-BN/rGO	960F/g@ 10mV/s	14k	73	Band gap of h-BN/rGO structure was controlled by adjusting graphene concentration.
Krishnaveni et al., 2020 [44]	rGO/BN/Ni(OH) ₂	349F/g@ 0.5mA/cm ²	118	48	The use of heterostructure improved the electrochemical properties than pristine ones.
Ding et al., 2016 [49]	carbon self-repairing g-C ₃ N ₄ @graphene	380F/g@ 0.25A/g	--	52.7	The carbon self-repairing g-C ₃ N ₄ (C-C ₃ N ₄) has better electrochemical activity than the pristine g-C ₃ N ₄ . Increases electron mobility and facilitates easy access to electrolytes.
Lin et al., 2017 [52]	3D oxidized g-C ₃ N ₄ @graphene	267F/g@ 1A/g	825	21	Solubility in water as well as edge nitrogen proportion is enhanced by pre-oxidation treatment of g-C ₃ N ₄ , which

					disrupts the polymeric character of the compound.
Li et al., 2020 [55]	Co ₃ S ₄ /g- C ₃ N ₄	415F/g @ 0.5A/g	850	35.7	2D/2D nanosheet heterostructures offers several active sites, short ion diffusion paths, and rapid charge transfer, in addition to enhanced conductivity and mechanical stability.
Dong et al., 2018 [56]	NiCo ₂ S ₄ nanotubes	1005F/g @ 1A/g	484	71	By regulating the ion-exchange temperature, it is possible to obtain and optimize the tubular morphology.
Dong et al., 2020 [28]	NiCo ₂ S ₄ /gra phene	910F/g @ 1A/g	588	48	The synergistic impact of rGO and nickel-cobalt sulphides significantly enhances the material's electrochemical characteristics.

The major hurdles in the development of supercapacitor is low energy density, narrow potential window, low conductivity, etc. of electrode materials [57]. Thus, it is essential to create innovative electrode materials for supercapacitors that have improved electrochemical characteristics. This dissertation focuses on the synthesis of new materials to overcome limitations in traditional electrode materials. Novel high performance nanocomposites for high performance supercapacitor applications are developed by leveraging the synergistic impact of both EDLC and pseudocapacitive materials.

Bibliography

- [1] Tan, Y. B. and Lee, J.-M. Graphene for supercapacitor applications. *Journal of Materials Chemistry A*, 1(47):14814-14843, 2013.
- [2] Kumar, R., Sahoo, S., Joanni, E., Singh, R. K., Yadav, R. M., Verma, R. K., Singh, D. P., Tan, W. K., Perez del Pino, A. and Moshkalev, S. A. A review on synthesis of graphene, h-BN and MoS₂ for energy storage applications: Recent progress and perspectives. *Nano research*, 12(11):2655-2694, 2019.
- [3] Bai, L., Huang, H., Yu, S., Zhang, D., Huang, H. and Zhang, Y. Role of transition metal oxides in g-C₃N₄-based heterojunctions for photocatalysis and supercapacitors. *Journal of Energy Chemistry*, 64:214-235, 2022.
- [4] Saha, S., Samanta, P., Murmu, N. C. and Kuila, T. A review on the heterostructure nanomaterials for supercapacitor application. *Journal of Energy Storage*, 17:181-202, 2018.
- [5] Cai, W., Zhu, Y., Li, X., Piner, R. D. and Ruoff, R. S. Large area few-layer graphene/graphite films as transparent thin conducting electrodes. *Applied Physics Letters*, 95(12):123115, 2009.
- [6] Li, X., Zhu, Y., Cai, W., Borysiak, M., Han, B., Chen, D., Piner, R. D., Colombo, L. and Ruoff, R. S. Transfer of large-area graphene films for high-performance transparent conductive electrodes. *Nano letters*, 9(12):4359-4363, 2009.
- [7] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D.-e., Zhang, Y., Dubonos, S. V., Grigorieva, I. V. and Firsov, A. A. Electric field effect in atomically thin carbon films. *science*, 306(5696):666-669, 2004.
- [8] Brodie, B. C. XIII. On the atomic weight of graphite. *Philosophical transactions of the Royal Society of London*, (149):249-259, 1859.
- [9] Staudenmaier, L. Method for the preparation of graphitic acid. *Ber Dtsch Chem Ges*, 31:1481-1487, 1898.
- [10] Hummers Jr, W. S. and Offeman, R. E. Preparation of graphitic oxide. *Journal of the american chemical society*, 80(6):1339-1339, 1958.
- [11] Kovtyukhova, N. I., Ollivier, P. J., Martin, B. R., Mallouk, T. E., Chizhik, S. A., Buzaneva, E. V. and Gorchinskiy, A. D. Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chemistry of materials*, 11(3):771-778, 1999.

- [12] Marcano, D. C., Kosynkin, D. V., Berlin, J. M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L. B., Lu, W. and Tour, J. M. Improved synthesis of graphene oxide. *ACS nano*, 4(8):4806-4814, 2010.
- [13] Chen, J., Yao, B., Li, C. and Shi, G. An improved Hummers method for eco-friendly synthesis of graphene oxide. *Carbon*, 64:225-229, 2013.
- [14] Sheshmani, S. and Fashapoyeh, M. A. Suitable chemical methods for preparation of graphene oxide, graphene and surface functionalized graphene nanosheets. *Acta Chimica Slovenica*, 60(4):813-825, 2014.
- [15] Peng, L., Xu, Z., Liu, Z., Wei, Y., Sun, H., Li, Z., Zhao, X. and Gao, C. An iron-based green approach to 1-h production of single-layer graphene oxide. *Nature communications*, 6(1):1-9, 2015.
- [16] Yu, H., Zhang, B., Bulin, C., Li, R. and Xing, R. High-efficient synthesis of graphene oxide based on improved hummers method. *Scientific reports*, 6(1):1-7, 2016.
- [17] Panwar, V., Chattree, A. and Pal, K. A new facile route for synthesizing of graphene oxide using mixture of sulfuric–nitric–phosphoric acids as intercalating agent. *Physica E: Low-dimensional Systems and Nanostructures*, 73:235-241, 2015.
- [18] Dimiev, A. M., Ceriotti, G., Metzger, A., Kim, N. D. and Tour, J. M. Chemical mass production of graphene nanoplatelets in~ 100% yield. *ACS nano*, 10(1):274-279, 2016.
- [19] Devi, M. and Kumar, A. Surface modification of reduced graphene oxide-polyaniline nanotubes nanocomposites for improved supercapacitor electrodes. *Polymer Composites*, 41(2):653-667, 2020.
- [20] Wang, X., Zhao, S.-X., Dong, L., Lu, Q.-L., Zhu, J. and Nan, C.-W. One-step synthesis of surface-enriched nickel cobalt sulfide nanoparticles on graphene for high-performance supercapacitors. *Energy Storage Materials*, 6:180-187, 2017.
- [21] Chen, W., Xia, C. and Alshareef, H. N. One-step electrodeposited nickel cobalt sulfide nanosheet arrays for high-performance asymmetric supercapacitors. *ACS nano*, 8(9):9531-9541, 2014.
- [22] Yang, J., Yu, C., Fan, X., Liang, S., Li, S., Huang, H., Ling, Z., Hao, C. and Qiu, J. Electroactive edge site-enriched nickel–cobalt sulfide into graphene frameworks for high-performance asymmetric supercapacitors. *Energy & Environmental Science*, 9(4):1299-1307, 2016.
- [23] Jiang, Y., Yang, Y., Zhu, J., Qiang, L., Ye, T., Li, L., Su, T. and Fan, R. Nickel silicotungstate-decorated Pt photocathode as an efficient catalyst for triiodide reduction in dye-sensitized solar cells. *Dalton Transactions*, 45(42):16859-16868, 2016.

- [24] Zhu, Y., Wu, Z., Jing, M., Yang, X., Song, W. and Ji, X. Mesoporous NiCo₂S₄ nanoparticles as high-performance electrode materials for supercapacitors. *Journal of Power Sources*, 273:584-590, 2015.
- [25] Shinde, S., Jalak, M., Ghodake, G., Maile, N., Kumbhar, V., Lee, D., Fulari, V. and Kim, D.-Y. Chemically synthesized nanoflakes-like NiCo₂S₄ electrodes for high-performance supercapacitor application. *Applied Surface Science*, 466:822-829, 2019.
- [26] Kulurumotlakatla, D. K., Yedluri, A. K. and Kim, H.-J. Hierarchical NiCo₂S₄ nanostructure as highly efficient electrode material for high-performance supercapacitor applications. *Journal of Energy Storage*, 31:101619, 2020.
- [27] Yang, J., Yu, C., Fan, X., Zhao, C. and Qiu, J. Ultrafast self-assembly of graphene oxide-induced monolithic NiCo-carbonate hydroxide nanowire architectures with a superior volumetric capacitance for supercapacitors. *Advanced Functional Materials*, 25(14):2109-2116, 2015.
- [28] Dong, M., Wang, Z., Yan, G., Wang, J., Guo, H. and Li, X. Confine growth of NiCo₂S₄ nanoneedles in graphene framework toward high-performance asymmetric capacitor. *Journal of Alloys and Compounds*, 822:153645, 2020.
- [29] Shen, L., Wang, J., Xu, G., Li, H., Dou, H. and Zhang, X. NiCo₂S₄ nanosheets grown on nitrogen-doped carbon foams as an advanced electrode for supercapacitors. *Advanced Energy Materials*, 5(3):1400977, 2015.
- [30] Chen, J., Xu, J., Zhou, S., Zhao, N. and Wong, C.-P. Nitrogen-doped hierarchically porous carbon foam: a free-standing electrode and mechanical support for high-performance supercapacitors. *Nano Energy*, 25:193-202, 2016.
- [31] Fan, Y.-M., Liu, Y., Liu, X., Liu, Y. and Fan, L.-Z. Hierarchical porous NiCo₂S₄-rGO composites for high-performance supercapacitors. *Electrochimica Acta*, 249:1-8, 2017.
- [32] Wickramaratne, D., Weston, L. and Van de Walle, C. G. Monolayer to bulk properties of hexagonal boron nitride. *The Journal of Physical Chemistry C*, 122(44):25524-25529, 2018.
- [33] Saha, S., Jana, M., Samanta, P., Murmu, N. C., Kim, N. H., Kuila, T. and Lee, J. H. Investigation of band structure and electrochemical properties of h-BN/rGO composites for asymmetric supercapacitor applications. *Materials Chemistry and Physics*, 190:153-165, 2017.
- [34] Qi, J., Yan, Y., Cai, Y., Cao, J. and Feng, J. Nanoarchitected Design of Vertical-Standing Arrays for Supercapacitors: Progress, Challenges, and Perspectives. *Advanced Functional Materials*, 31(3):2006030, 2021.
- [35] Saha, S., Samanta, P., Murmu, N. C., Banerjee, A., Ganesh, R. S., Inokawa, H. and Kuila, T. Modified electrochemical charge storage properties of h-BN/rGO superlattice

through the transition from n to p type semiconductor by fluorine doping. *Chemical Engineering Journal*, 339:334-345, 2018.

[36] Mazov, I., Kuznetsov, V., Romanenko, A., Suslyayev, V. and Hu, N. Properties of MWNT-Containing Polymer Composite Materials Depending on Their Structure. in *Composites and Their Properties*. 2012, InTech.

[37] Saha, S., Jana, M., Khanra, P., Samanta, P., Koo, H., Murmu, N. C. and Kuila, T. Band gap engineering of boron nitride by graphene and its application as positive electrode material in asymmetric supercapacitor device. *ACS applied materials & interfaces*, 7(26):14211-14222, 2015.

[38] Kumar, S., Saeed, G., Zhu, L., Hui, K. N., Kim, N. H. and Lee, J. H. 0D to 3D carbon-based networks combined with pseudocapacitive electrode material for high energy density supercapacitor: A review. *Chemical Engineering Journal*, 403:126352, 2021.

[39] Gao, G., Gao, W., Cannuccia, E., Taha-Tijerina, J., Balicas, L., Mathkar, A., Narayanan, T., Liu, Z., Gupta, B. K. and Peng, J. Artificially stacked atomic layers: toward new van der Waals solids. *Nano letters*, 12(7):3518-3525, 2012.

[40] Chang, C.-K., Kataria, S., Kuo, C.-C., Ganguly, A., Wang, B.-Y., Hwang, J.-Y., Huang, K.-J., Yang, W.-H., Wang, S.-B. and Chuang, C.-H. Band gap engineering of chemical vapor deposited graphene by in situ BN doping. *Acs Nano*, 7(2):1333-1341, 2013.

[41] Byun, S., Kim, J. H., Song, S. H., Lee, M., Park, J.-J., Lee, G., Hong, S. H. and Lee, D. Ordered, scalable heterostructure comprising boron nitride and graphene for high-performance flexible supercapacitors. *Chemistry of Materials*, 28(21):7750-7756, 2016.

[42] Althubaiti, N., Mussa, Y., Bongu, C. S., Bayhan, Z., Arsalan, M., Soliman, A. and Alsharaeh, E. Reduced graphene oxide/hexagonal boron nitride-based composite as a positive electrode in asymmetric supercapacitors. *Journal of Materials Science*, 57(30):14371-14385, 2022.

[43] Li, H., Tay, R. Y., Tsang, S. H., Liu, W. and Teo, E. H. T. Reduced graphene oxide/boron nitride composite film as a novel binder-free anode for lithium ion batteries with enhanced performances. *Electrochimica Acta*, 166:197-205, 2015.

[44] Krishnaveni, M., Suresh, C. M., Wu, J. J., Asiri, A. M., Anandan, S. and Ashokkumar, M. Synthesis of 3D marigold flower-like rGO/BN/Ni (OH)₂ ternary nanocomposites for supercapacitor applications. *Sustainable Energy & Fuels*, 4(6):3090-3101, 2020.

[45] Rajendran, J., Reshetilov, A. N. and Sundramoorthy, A. K. Preparation of hybrid paper electrode based on hexagonal boron nitride integrated graphene nanocomposite for free-standing flexible supercapacitors. *RSC advances*, 11(6):3445-3451, 2021.

- [46] Guo, W., Wang, J., Fan, C., Chen, Z., Liu, P., Zhu, D., Xu, Z., Pang, L. and Li, T. Synthesis of carbon self-repairing porous g-C₃N₄ nanosheets/NiCo₂S₄ nanoparticles hybrid composite as high-performance electrode materials for supercapacitors. *Electrochimica Acta*, 253:68-77, 2017.
- [47] Luo, Y., Yan, Y., Zheng, S., Xue, H. and Pang, H. Graphitic carbon nitride based materials for electrochemical energy storage. *Journal of materials chemistry A*, 7(3):901-924, 2019.
- [48] Ashritha, M. and Hareesh, K. A review on Graphitic Carbon Nitride based binary nanocomposites as supercapacitors. *Journal of Energy Storage*, 32:101840, 2020.
- [49] Ding, Y., Tang, Y., Yang, L., Zeng, Y., Yuan, J., Liu, T., Zhang, S., Liu, C. and Luo, S. Porous nitrogen-rich carbon materials from carbon self-repairing gC₃N₄ assembled with graphene for high-performance supercapacitor. *Journal of materials chemistry A*, 4(37):14307-14315, 2016.
- [50] Li, L., Qin, J., Bi, H., Gai, S., He, F., Gao, P., Dai, Y., Zhang, X., Yang, D. and Yang, P. Ni(OH)₂ nanosheets grown on porous hybrid g-C₃N₄/RGO network as high performance supercapacitor electrode. *Scientific reports*, 7(1):1-11, 2017.
- [51] Chen, Q., Zhao, Y., Huang, X., Chen, N. and Qu, L. Three-dimensional graphitic carbon nitride functionalized graphene-based high-performance supercapacitors. *Journal of materials chemistry A*, 3(13):6761-6766, 2015.
- [52] Lin, R., Li, Z., Abou El Amaiem, D. I., Zhang, B., Brett, D. J., He, G. and Parkin, I. P. A general method for boosting the supercapacitor performance of graphitic carbon nitride/graphene hybrids. *Journal of Materials Chemistry A*, 5(48):25545-25554, 2017.
- [53] Chen, L., Zuo, Y., Zhang, Y. and Gao, Y. Cadmium sulfide anchored in three-dimensional graphite cage for high performance supercapacitors. *Applied Physics Letters*, 112(22):223901, 2018.
- [54] Patil, I. M., Kapse, S., Parse, H., Thapa, R., Andersson, G. and Kakade, B. 2D/3D heterostructure of h-BN/reduced graphite oxide as a remarkable electrode Material for supercapacitor. *Journal of Power Sources*, 479:229092, 2020.
- [55] Li, W., Li, Y., Yang, C., Ma, Q., Tao, K. and Han, L. Fabrication of 2D/2D nanosheet heterostructures of ZIF-derived Co₃S₄ and gC₃N₄ for asymmetric supercapacitors with superior cycling stability. *Dalton Transactions*, 49(40):14017-14029, 2020.
- [56] Dong, M., Wang, Z., Li, X., Guo, H. and Wang, J. A smart architecture of nickel-cobalt sulfide nanotubes assembled nanoclusters for high-performance pseudocapacitor. *Journal of Alloys and Compounds*, 765:505-511, 2018.

[57] Yu, X. Y., Yu, L. and Lou, X. W. Metal sulfide hollow nanostructures for electrochemical energy storage. *Advanced Energy Materials*, 6(3):1501333, 2016.

