

Graphitic-Carbon Nitride for Hydrogen Storage

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15.1 Introduction

Carbon nitride (C_3N_4) is the oldest synthetic polymer. The polymeric carbon nitrides were discovered in the late 19th century with general formula of $C_xN_yH_z$ with high N:C ratio, which possess attractive behaviour due to their unique properties in electronic storage for electro and photocatalytic applications. Graphitic carbon nitride materials, denoted as $g-C_3N_4$, have attracted much attention in recent years due to their similarity to graphene structures. Graphitic carbon nitride ($g-C_3N_4$) is comparatively a new type of carbon material with optical band gap energy around 2.7 eV, and has tremendous attention among researchers because of their excellent intrinsic optical properties, such as high photo-absorption and photo-responsiveness, energy storage, semiconductive properties, and thermal and chemical stability. Due to their narrow band gap, it helps to enhance their field emission, photocatalytic, carbon captures, and energy storage properties [1-5]. Moreover, $g-C_3N_4$ is a kind of graphite analogue with a van der Waals layered structures. It has strong covalent C-N bonds instead of C-C bonds in each of their layers. It has nitrogen substituted graphite network, which is fully consisting of π - conjugated sp^2 hybridized carbon and nitrogen atoms. The interlayer distance between carbon and nitrogen atoms can be explained by changing the localization of electrons. There are two different structural models for the $g-C_3N_4$; first is the s-triazine constructed by single carbon vacancies and the second is the tri-s-triazine

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units that are connected via planar tertiary amino groups with larger periodic vacancies [6]. The g-C₃N₄ has many potential applications in catalytic support and gas storage materials, as the addition of nitrogen molecules at their inner carbon nano-layer leads to the formation of strong C-N bond. Usually, carbon allotropes can be formed in α , β , cubic-based C₃N₄ and graphitic structures. While comparing various allotropes of carbon materials, g-C₃N₄ is a promising structure due to their excellent electronic properties and chemical stability [7-11]. The properties of the carbon nitride (CN) materials are controlled by their structure and crystalline properties. Based on their CN frame nano-structure, so far it is classified into five different structures, which are the two-dimensional (2D) graphitic carbon nitride C₃N₄ (g-C₃N₄) and three dimensional nano-frame like structures such as a-C₃N₄, b-C₃N₄, cubic-C₃N₄, and pseudocubic-C₃N₄. Among them, g-C₃N₄ is a stable layered structure, which is similar to graphitic structures. Therefore, it has been used in various fields including catalysis, hydrogen storage, absorption, and desorption of carbon dioxide [12-16]. There are several methods to produce g-C₃N₄ using suitable precursors via cothermal condensation, calcinations, solvothermal, solid state reaction, thin layer deposition, thermal decomposition, and exfoliation. Another important parameters is the functionalization of graphitic carbon nitride, where there are variety of functionalization methods such as impregnation, adsorption-desorption, and photo-assisted reduction have been utilized to functionalize the CNs, for example surface functionalization of CN materials using mesoporous hybrid materials (silica and carbon), organic, inorganic metal or metal oxide nanoparticles and biomolecules. In addition to this, graphitic carbon nanomaterials have also been modified with metal, inorganic-organic, and dyes molecules [17]. Li et al. [18], reported the polyene functionalized graphitic carbon nitride and its application in photocatalytic water splitting process. Many of functional groups (aryl, pyridine, ionic liquids, ferrocene, and aryl acid) were introduced onto g-C₃N₄ at high temperatures. Wu et al. [19] successfully reported the polyoxometalates functionalized mesoporous CNs towards enhancing their electrical properties. These functional groups influence the electron transfer to the electrode, which helps in energy storage as well as photocatalytic systems. Ha et al. [20], reported the MoS₂/g-C₃N₄ composite that prepared by heat treatment at 550°C using thiourea and sodium molybdate and explored for lithium storage applications. The g-C₃N₄ based nanocomposites have also been synthesized in order to store the energetic materials and molecules. Since, the emerging technologies include the electronic devices and electrical vehicles, they require energy storage systems with relatively low cost, high energy density, and improved performance. For examples, lithium ion batteries have limited energy density, it generally depends on the capacity and stability of electrode active nanomaterials. Hence, many

of the elements such as Ge, Si, P, Sn, metal oxide, metal hydrides, and sulfides have been functionalized with $g\text{-C}_3\text{N}_4$, in order to enhance their electrochemical energy, electrochemical kinetics, capacity, and stability and high energy density. Also, these kinds of materials are effective to store the energy including lithium, sodium, and hydrogen etc., [21-27].

15.2 Synthesis of mesoporous graphitic carbon nitride materials

A many attempts have been made to synthesize $g\text{-C}_3\text{N}_4$ materials by condensation of nitrogen rich precursors that comprised of the carbon-nitrogen core structures such as triazine, heptazine derivatives, cyanamide, dicyanamide, thiourea, urea, guanidinium, and melamine [33]. Yan et al. [34] reported that for the synthesis of $g\text{-C}_3\text{N}_4$, melamine can be an excellent nitrogen rich precursors, where it produced the $g\text{-C}_3\text{N}_4$ with enhanced carbon-nitrogen ratios and decreased band gap values. However, the low band gap is found to induce the defects in the $g\text{-C}_3\text{N}_4$ surface during the thermal condensation. Generally, the prepared $g\text{-C}_3\text{N}_4$ through different precursors can be characterized by numerous analytical tools such as diffused reflectance spectroscopy (UV-vis DRS), XRD, XPS, and FTIR. Also, the density functional theory (DFT) can be used to calculate the valence band and conduction band as well. Similar to melamine, thiourea is also nitrogen rich and inexpensive material, which can also be used to synthesize the $g\text{-C}_3\text{N}_4$. Zhang et al. [35], reported the synthesis of $g\text{-C}_3\text{N}_4$ using a simple thermal heating method. They utilized the thiourea as a precursor by heating at various temperatures in the air atmosphere to enable the bulk condensation and polymerization. It was observed that the sulfur species in thiourea played a crucial role in boosting the degree of condensation polymerization.

Further, the mesoporous based $g\text{-C}_3\text{N}_4$ material can be obtained by nanocasting of silica. In order to get the porous $g\text{-C}_3\text{N}_4$, the silica sol and cyanamide are mixed in aqueous solution. After the complete removal of water, it has been transferred into a crucible and heated up-to 500°C -600°C to condense the precursors onto polymeric carbon nitride. Also, the uniformed carbon nitride layer can be obtained through silica sphere template. Several morphologies of $g\text{-C}_3\text{N}_4$ (mesoporous, nanosheets, nanorods, films and hierarchical structures) have been also demonstrated. There are two kinds of templates used in $g\text{-C}_3\text{N}_4$ synthesis namely hard template (nanocasting or replication) and soft template (self assembly) [28]. The $g\text{-C}_3\text{N}_4$ porous materials can be synthesized in two different methods including siliceous and nonsiliceous. Soft template involves the organic agents, which are self assembled with carbon and nitrogen precursors to form

well ordered and thin layered structures. Moreover, porosity can be formed upon elimination of surfactant by heat treatment. In the case of soft template, amphiphilic surfactant, and block copolymers are used to form mesoporous structures.

15.2.1 g-C₃N₄ porous materials by hard template method

Generally, hard template involves nanocasting in order to introduce the meso porosity in carbon, nitride, ceramics, and polymers. Ovcharov et al. [29] reported the synthesis of porous carbon nitride by hard template method for photocatalytic CO₂ utilization. They have studied their different morphology, which is obtained by bulk and hard template of melamine pyrolysis. Moreover, it has enhanced their band gap, high surface area, and high photocatalytic properties. The prepared material has sponge like structures, which is useful to get porous materials. Generally, hard template seems to be the most effective technique to afford a uniformed porous carbon nitride. Also, it creates an effective functionalization of C₃N₄ materials for various practical applications. Introduction of mesoporosity onto solid nanosurfaces, such as nitrides, carbons, and polymers, by nanocasting method provide excellent mold materials such as pipes, plasters, toys, and pots. Nanocasting route involves variety of nanomaterials such as metal oxide nanoparticles, carbon nanotubes, and graphene. Nanocasting methods involve three steps; i) synthesis of mesoporous silica template, ii) infiltration of the template with suitable precursors, and iii) removal of template. Jie et al.[30] reported the synthesis of mesoporous g-C₃N₄ materials using guanidinium chloride based environmental friendly precursors by hard nanocasting method [see Fig. 15.1B]. Lin et al. [31] successfully reported that the carboxylic group modified MCN can be synthesized by hard template method using Santa Barbara amorphous (SBA 15) type of mesoporous silica. These functional groups can be generated bifunctional nanocatalyst using one pot deacetalization-Knoevenagel reaction. In this reaction the ethylenediamine (EDA) and carbon tetrachloride (CTC) were polymerized using porous silica template and further calcined at 90°C to afford the mesoporous CNs (see Fig. 15.1C).

Ryoo et al. [32] reported the preparation of first order mesoporous nanomaterials with 3D structures by nanocasting using MCM-48 hard template. Also, they synthesized the porous materials using sucrose as a carbon rich source and silica hard template. Although, there are different silica (precursors, mesoporous, colloidal, and nanoparticles)-based hard templates have been utilized to synthesize the mesoporous carbon nitride for various applications. However, this template has some disadvantages such as highly toxicity, and

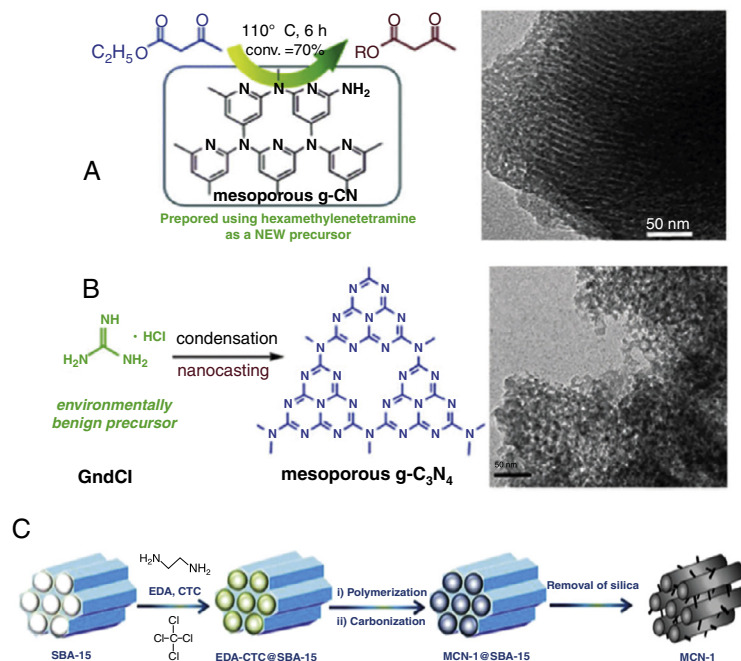


Fig. 15.1. Modification of porous materials by different hard templates (A) synthesis of MPG- C₃N₄ using SiO₂ NPs with cyanamide (B) synthesis of C₃N₄-G-r using SiO₂ NPs with guanidinium chloride (C) C₃N₄ using SBA-15 with EDA and CTC [17].

expensive template, which involve eliminating the hazardous hydrogen fluoride or ammonium bifluorides. Also, it is not environmental friendly material and, hence, still there is some importance to find ecofriendly methods to synthesize MCNs.

15.2.2 Soft templating method to produce g-C₃N₄

Generally, soft templating method reveals the solution-phase based soft molecules such as surfactants in order to precipitate and exploit the self assembly of amphiphilic molecules and guest species, which is determined through natural tendency of low interfacial energies. A soft templating method can be used to synthesize the various mesoporous carbon and inorganic metal oxides. Also, it is called as greener approach to fabricate the porous g-C₃N₄ materials. Usually, surfactants, ionic liquids (ILs), block copolymers or triblock copolymers, and gaseous bubbles are used to produce the better porous g-C₃N₄ materials [36-39]. The MCNs based nanomaterials can be attributed to the thermodynamics of the preparation procedures and condensation of carbon and nitrogen precursors can be decomposed during pyrolysis. This may contaminate the final materials with more carbons during polymerization.

Moreover, the ionic and nonionic surfactant and amphiphilic block copolymers such as P123, P127, Triton X-100, and Brij30, 58, and 76 were used to synthesize the MCNs. Generally, calcinations treatment has to be applied on MCNs materials in order to avoid the collapsed mesoporous structures. While soft templating is being used during polymerization, the main MCNs product at most zero, and this very low yield may be a side reaction between CN polymerized matrix and surfactants, which will provide the self-assemble units [40].

Collins et al. [41] reported that the hollow titania microsphere have been synthesized by using sodium dodecyl sulfate (SDS), which is used as a surfactants in non-aqueous emulsions. Yuan et al. [42] also reported the non-ionic poly(alkylene oxide) amphiphilic as a template for the synthesis of mesoporous titania. The behavior of porous formation and their properties can play a critical role at their template.

Triton X-100 is one of the amphiphilic copolymer based soft template, which offer the mesonanostructured CNs with BET surface area of around $76 \text{ m}^2 \text{ g}^{-1}$ and pore diameter of 3.8 nm respectively. Particularly, soft templates of ionic liquids were used to prepare in MCNs [see Fig. 15.2]. Also, the 1-butyl-3-methylimidazolium tetrafluoroborate was used to prepare the boron and fluorine containing good MCNs [43]. Shen et al. [44] reported the synthesis of MCNs using melamine and Triton X-100 combination of glutaraldehyde through soft template method. By this method, they used the following templates namely, surfactants, ionic liquids (ILs) and block copolymers. Based on the above results, it is suggested that the soft template method mostly offer the disordered MCNs with low specific area and specific pore volume. Moreover, this method is environmental friendly to prepare the MCNs.

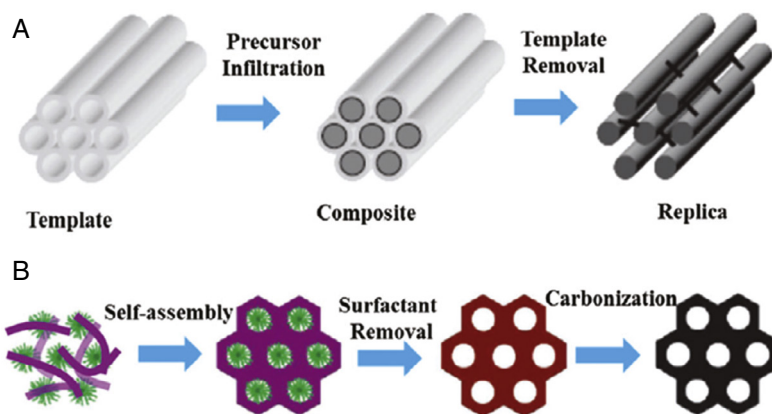


Fig. 15.2. Schematic representation of hard and soft templates to prepare MCNs [45].

15.2.2.1 Ionic liquids (ILs)

Besides block copolymer and surfactants, ionic liquids (ILs) are another alternative materials to be used as soft template to react to the nitrogen containing precursors in order to get $g\text{-C}_3\text{N}_4$. ILs based salts have low evaporation temperature at below 100°C and have no vapor pressure, and hence, it can be easily evaporated without any heating treatment. It can offer good nanoporous structure with reasonable porosity and enhanced physicochemical properties. Mostly, ILs exist with nitrogen based cations and an inorganic anion, the ILs such as alkylammonium, N, N'-dialkylimidazolium, 1-ethyl-3-methylimidazolium (EMIM), 1-butyl-3-methylimidazolium tetrafluoroborate, 1-hexyl-3-methylimidazolium tetrafluoroborate, 1-octyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluorophosphate, and 1-hexyl-3-methylimidazolium tetrafluorophosphate have been used to prepare the $g\text{-C}_3\text{N}_4$ [45,46]. Wang et al. [47] prepared the $g\text{-C}_3\text{N}_4$ materials with 5.6 nm pore size using butyl methylimidazolium dicyanamide ionic liquids. Some of the carbon and nitrogen containing ionic liquid will participate as a co-monomer during thermal polymerization in order to obtain the different heteroatom doped $g\text{-C}_3\text{N}_4$ for photocatalytic application.

Paraknowitsch et al. [48] reported that use of, 1-ethyl-3-methylimidazolium and 3-methyl-1-butylpyridine as organic cation and dicyanamide based anion in order to form the C, N, and H containing ILs. These kinds of ILs are rich in nitrogen and have excellent ionic conductivity, which is similar to graphite. The incorporation of ionic liquid into soft template, a many of the heteroatoms are involved for doping of $g\text{-C}_3\text{N}_4$ during template process. However, there are many limitations found in order to use ILs as soft template. It is high cost as compared to other solvents and some of the ILs is incompatible with water.

15.2.2.2 Block copolymers and surfactants

Block copolymers and surfactants are common templates to synthesize the mesoporous $g\text{-C}_3\text{N}_4$ through soft template method. Surfactants such as alkylbenzene, lauryl sulfate, lignosulfonate, dialkyl sulfosuccinate, sodium deoxycholate, Triton X-100 sodium dodecylbenzene sulfonate, and sodium dodecylsulfate have been used as soft template to prepare the mesoporous $g\text{-C}_3\text{N}_4$. One important challenge is low stability and it is very difficult to form $g\text{-C}_3\text{N}_4$ until $> 500^\circ\text{C}$, which is a long way of decomposition of surfactants. Surfactants are able to produce the amphiphiles nanostructures that could impart the porosity on $g\text{-C}_3\text{N}_4$. These surfactants based soft templates have a common strategy: it has easy hydrolysis, which may cause the redox reaction and relatively has weak interaction

with their precursors. Many of surfactants and block copolymers have been used for the synthesis of carbon nitride materials through template method. Yan et al. [39] reported the synthesis of carbon nitride materials for photocatalytic applications using Pluronic 123 as a block copolymer template. Yan's group results exhibited that the porous materials has improved the BET surface area and better light absorbing behavior for hydrogen evolution. More interestingly, as we know that melamine is a less reactive precursor, which can avoid direct chemical reaction into surfactants under heat treatment and make the melamine preferable material as compared to dicyanamide and cyanamide. However, the combination of melamine and Triton X-100 followed by the addition of sulfuric acid form the solid melamine sulfate. Further, these melamine sulfate materials can form the porous graphitic carbon nitride by the removal of surfactants [49].

15.2.2.3 Gas bubbles

The gas bubbles could be choice for soft templating method to produce g- C_3N_4 . Han et al. [50] reported the heterogeneous nucleation of $CaCO_3$ via bubble template technique, which significantly reduced the nucleation activation barrier. Moreover, the nucleation can be formed at bubble surface. Han's group thoroughly studied the reaction of CO_2 in a gas with Ca^{2+} in solution, which proved an interesting idea in order to use gas bubble-based template for any porous materials. Apart from the surfactants and ILs templates, gaseous bubble templates have potential technique to modifying the polymerization routes for enhancing their optoelectronic properties of graphitic carbon nitride materials. This technique is cost effective, sustainable and environmental friendly technique for the synthesis of porous carbon nitride materials. In addition, this technique is suitable for the large scale or pilot scale synthesis of g- C_3N_4 . He et al. [51] successfully synthesized the nanoporous g- C_3N_4 using sulphur-bubbles based template. Further, it took the advantage of low cost and profuse sublimed sulfur as gas molecules during thermal polymerization of melamine. It exhibited the porous nanostructure with large BET surface area of around $46\text{ m}^2\text{g}^{-1}$ and uniform pore size of 50 nm. Moreover, the prepared the porous carbon nitride materials were found to be good absorbent and mass transfer materials. Further, these materials also exhibited excellent photocatalytic hydrogen production properties under visible light irradiation. In addition, the sulfur mediated mesoporous graphitic carbon nitride was prepared by one step approach using melamine precursors and NH_4Cl as a gaseous bubbles templates and exhibited a high surface area $195\text{ m}^2\text{g}^{-1}$ with uniform mesoporous around 12 nm as shown in Fig. 15.3 [52].

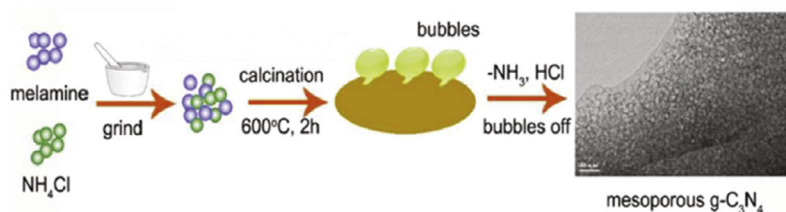


Fig. 15.3. Schematic representation of mesoporous g-C₃N₄ [52].

15.2.3 Template free approach

The template free approach reveals that it does not involve any kind of soft and hard template for the synthesis of porous graphitic carbon nitride. Usually, soft and hard templates required the following hurdle synthesis steps; long synthesis time and high cost in order to commercialization the product. There are several efforts made to synthesize the porous MCNs. Reny et al. [53] reported that titania mesoflower based graphitic carbon nitride by template free method for efficient photocatalytic applications. The most outcome of this work is to increase the surface area and reduce charge recombination. This template free technique has the energy reactions such as sonochemical, thermal, and low energy acoustic wave to provide nanoporosity in MCN matrix. Moreover, this technique is a low cost process, which eliminates the expensive templates. Lu et al. [54] reported the template free approach for the synthesis of MCNs using urea by heating at 600°C under ambient pressure. Cui et al. [55] demonstrated that the hollow sphere based graphitic carbon nitride for effective photocatalytic application by template free approach. In this process, the 1,3,5-trichlorotriazine (CC), acetonitrile, and dicyandiamide (DCDA) were kept in autoclave at 180°C for 24 h in order to obtain the graphitic carbon nitride material, where they observed the highest photodegradation behavior of rhodamine B under visible light irradiation (see Fig. 15.4).

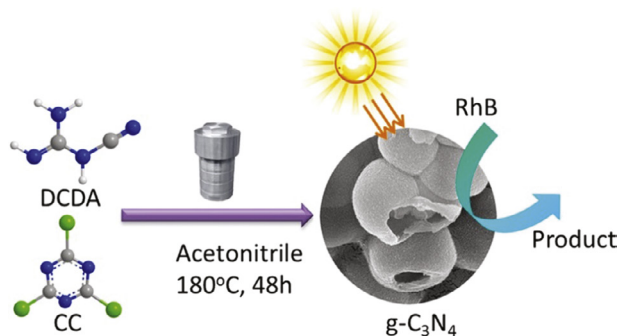


Fig. 15.4. Synthesis of graphitic carbon nitride by template free approach [55].

15.3 Surface functionalization of graphitic carbon nitride

Various mesoporous materials such as mesoporous silica, mesoporous organic/inorganic materials and mesoporous carbons have been functionalized with different inorganic metal or metal oxide nanoparticles, organic molecules, dyes and biomolecules for photocatalytic, sensor, solar cells, electrocatalysis, batteries, supercapacitors, and hydrogen storage applications.

15.3.1 Metal nanoparticles immobilized g-C₃N₄

The incorporation of different metal nanoparticles onto mesoporous graphitic carbon nitride can enhance their electronic and catalytic properties. Few research groups have reported the metal nanoparticles (Pd, Pt, Au, and Ag) based graphitic carbon nitride materials for electro, photo and redox catalyst for energy storage applications.

In situ growth of CuO/O doped with graphitic carbon nitride materials has been achieved by copolymerization process. The porous CuO/O doped with graphitic carbon nitride was used as precursors, which was prepared from dicyandiamide and Cu(NO₃)₂ material. Further, it was mixed with combination of two solvents (acetonitrile/DMF) and heated at 180°C by solvothermal method (see Fig. 15.5). Further, the formation of O-doped g-C₃N₄ allowed the CuO nanoparticles dispersed in homogeneously into their matrix. The outcome of this work, mesoporosity of CuO/O-doped g-C₃N₄ composite can address the following; deficiencies, agglomeration, volume changes, restacking, and limited surface area. Hence, these electrode materials with large number of active sites showed good performance in lithium ion batteries [56]. Anuj et al. [57] also successfully reported the copper nanoparticles decorated g-C₃N₄ materials for the effective photocatalytic applications, which was synthesized from

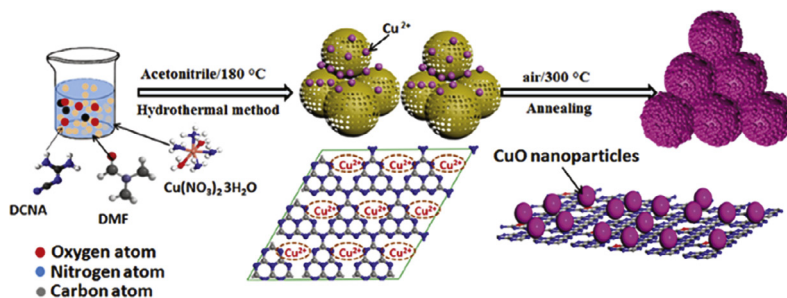


Fig. 15.5. Schematic representation of in situ growth CuO/O-doped g-C₃N₄ nanospheres [56].

ynone, aminoindolizines and pyrrolo [1,2-a] quinoline under mild condition. Further, Lu et al. [58] reported an interesting composite materials, which were prepared by using transition metal oxide nanoparticles and CuO. In addition, the carbon, nitrogen doped graphitic carbon nitride sheets grown onto Ni foil, which is derived from pyrolysis of melamine for efficient electrocatalytic and long-term durability.

Hammers et al. [59] reported the synthesis of CuO/g-C₃N₄ composite using di-indolyloxindols catalyst. Briefly, g-C₃N₄ was synthesized using melamine precursors and heated at 550°C. Further, CuO nanoparticles were dispersed into water dispersed g-C₃N₄ solution and after evaporation of water, a powder sample of CuO doped g-C₃N₄ composite was obtained. Generally, CuO nanoparticles were p-type of metal oxide semiconductor with narrow band gap around 1.36 eV. Also, it is an inexpensive material, which can be used for various photocatalytic applications. CuO has great attention in optical electronics, field emission emitters, lithium ion batteries, gas sensor, and photovoltaic applications. Moreover, CuO nanoparticles show strong interaction with mesoporous materials such as graphene and titania nanotubes, and particularly, it invariably suppresses the recombination rate of photogenerated electron-hole pairs. CuO nanoparticles allow efficient charge separation and promote the electron migration, which is useful to enhance photocatalytic and water splitting properties. Hence, CuO nanoparticles were effective materials in order to functionalize the graphitic carbon nitride for various industrial applications [59-62]. Datta et al. [63], reported the incorporation of gold nanoparticles into mesoporous graphitic carbon nitride materials with different pore diameter, which acted as a multifunctional agent in reducing, stabilizing and controlling the size of the particles, where it also offered a high dispersion behavior along the porous channel.

Lu et al. [64] reported the Pt nanoparticles loaded with mesoporous carbon nitride as bifunctional air electrode materials for rechargeable lithium ion batteries. The electrochemical behavior of the metal functionalized with MCNs showed the high round trip electrochemical efficiencies. Ha et al. [20] also reported that the MoS₂/g-C₃N₄ nanocomposite can be used as an anode materials in batteries, which found to increase the lithium storage capacity. The porous nanocomposite was synthesized using thiourea and sodium molybdate heated at 550°C under nitrogen atmosphere. Hence, the graphitic carbon nitride based mesoporous nanomaterials have found to be very attractive and can be easily functionalized with different metals or metal nanoparticles including Ag, Ni, and Fe for energy storage applications.

15.3.2 Organic molecules functionalized with g-C₃N₄

It is found that the surface charge as well as catalytic behavior can be altered by functionalizing the organic molecules onto g-C₃N₄. Yu et al. [65] reported the amine functionalized g-C₃N₄ using ammonia solution. The highest adsorption efficiency was observed for amine functionalized MCNs due to less nitrogen group on MCNs. Further, these materials enhanced their basicity at their surfaces. Ye et al. [66] reported the synthesis of a polymeric materials using ferrocenecarboxylic acid with -NH₂ terminated group on the surface of mesoporous graphitic carbon nitride materials for the effective photocatalytic application. The resulted material was found to be an effective heterogeneous catalyst towards the selective oxidation of benzene to phenol using hydrogen peroxide under visible light irradiation. Ferrocene functionalized MCNs have better visible light absorption and also accelerated the bulk to surface charge transfer and separation. Li et al. [67] also reported the melon based graphitic carbon nitride, which was synthesized by copolymerization method. The low cost material benzamide and urea were employed to prepare the phenyl functionalized g-C₃N₄ through one pot thermal induction process. Moreover, this phenyl group essentially extent the π conjugation system, which led to the increased visible light absorption and separation of electron-hole pairs. As a result, the end product was found to posses large surface area and excellent photocatalytic properties such as hydrogen generation from water, photo-degradation of dye particularly chromium (VI).

15.3.3 Dye functionalized graphitic carbon nitride

Dye functionalization of graphitic carbon nitride has received great attention because it enhances their photocatalytic activities such as light absorption, conductivity and effluent degradation. In this section, various dyes functionalized g-C₃N₄ have been discussed in detail. Fuchsin organic dye was doped with g-C₃N₄, which enhanced its performance in the photocatalytic production of hydrogen with evolution rate around 1619 $\mu\text{mole g}^{-1} \text{h}^{-1}$, which was found to be four times higher that of the neat g-C₃N₄ under visible light irradiation. Moreover, this dye doped g-C₃N₄ materials acted as electron trap, which enhanced the separation and transportation of photoinduced electron-hole pairs [68]. Further, Lee et al. [69] reported the mesoporous graphitic carbon nitride that investigated by doping the magnesium phthalocyanine in order to expand their absorption at higher wavelengths. Some of the g-C₃N₄ materials have been used to degrade the organic dyes, used for waste water treatment in various industries like leather, textile and chemical. Zhong et al [70] reported

the synthesis of cyclodextrin functionalized graphitic carbon nitride for the removal of organic dyes from industrial wastes. Outcome of this resultant material has dual role in microfiltration and photocatalytic degradation. Xu et al. [71] also reported the graphitic carbon nitride/zinc tetracarboxyphthalocyanine/graphene quantum dots based nanocomposite used to degrade the dyes such as Rhodamine B, sulfaquinixaline sodium and carbamazepine under solar light irradiation. Moreover, solar light absorption and photogenerated electron-hole pair separations are two factors, which involved for the efficient photocatalytic behavior of g-C₃N₄.

15.4 Energy storages in graphitic carbon nitride materials

Graphitic-carbon nitride (g-C₃N₄) has been realized to be a promising material due to their enhanced surface area, layered structure, molecular active sites that provide space for the storage of ions (e.g. Li, Na) and molecules (e.g. H₂). Accordingly, g-C₃N₄ has been physically and chemically modified toward enhancing its energy storage properties.

15.4.1 Hydrogen storage in g-C₃N₄

Hydrogen can be produced from different feed-stocks, these includes fossil resources such as natural gases and coal and also renewable resources such as biomass, sunlight, wind, and hydro-power. There are varieties of technologies used, which include chemical, biological, electrolytic, photolytic, and thermochemical. Storing hydrogen on light weight materials, such as carbon nitride materials, graphene, metal hydrides, and carbon nanotubes-based energy carrier will be useful for automobile applications. For example, during water electrolysis, water is split into hydrogen and oxygen which is used as electrical energy.

There are three generic mechanisms for storing the hydrogen in various materials: absorption, adsorption and chemical reaction.

- i. Absorption: Absorption of hydrogen is directly into the bulk materials by incorporation of atomic hydrogen into interstitial sites at their crystallographic lattice structures.
- ii. Adsorption: Adsorption may be subdivided into physisorption and chemisorptions based on the energetic adsorption mechanism. Physisorption is weaker than chemisorptions, which requires high porous material such as graphitic carbon nitride to maximize the surface area. Moreover, this high surface area can be allowed for easy uptake and release the hydrogen from these porous materials.

- iii. Chemical reaction: Generally, the chemical reaction route for hydrogen storage involves the chemical reaction for both hydrogen generation and storage. Hydrogen generation and hydrogen storages can take place by simple reversible chemical reaction under temperature and pressure (e.g. sodium alanate-based metal complex).

In practice, the mechanism of storing hydrogen involves the interaction between transitional metal atom and hydrogen molecule, where the electrons can be donated to the unfilled orbital of the transition metal atom, which then back donates the electrons to the anti-bonding orbital of the hydrogen molecules [72-74]. For a successful hydrogen economy, it is essential to be able to store hydrogen in large quantities. Generally, In order to store the hydrogen, the gravimetric and volumetric densities should be larger than 5.5 wt % and 81 g/L respectively and also the materials should be operable at ambient thermodynamic conditions. Moreover, adsorption and desorption of the hydrogen should be between 0.2-0.6 eV per molecules [75]. Wu et al. [76] successfully reported the two different carbon nitride materials ($\text{g-C}_4\text{N}_3$ and $\text{g-C}_3\text{N}_4$) with lithium doped composites for storing the high capacity of hydrogen as well used as cathode materials in lithium ion batteries. Moreover, these materials have high density of Li ions, which will be adsorbed over nitrogen triangle in graphitic carbon nitride materials. Beyond these properties, these materials also have excellent storing capacity, where it was found that the gravimetric and volumetric densities of hydrogen in both $\text{Li}_2\text{C}_4\text{N}_3$ and $\text{Li}_2\text{C}_3\text{N}_4$ were greater than 10 wt% and 100 g/L respectively. Currently, to store the hydrogen, pressurized tank provides a gravimetric storage capacity around 5-6 wt.% of H_2 . However, the safety of this storage technique is a major concern, hence, there are alternatives to store the hydrogen in the materials such as reversible metal hydrides, hydrogen adsorbents and chemically hydrogen storage materials such as graphitical carbon, boron nanotubes and light weight metals because, these kinds of nanostructured materials have higher surface area and stability [81]. Koh et al. [77] reported, the hydrogen storage capacity of graphitic carbon nitride using density functional theory. Generally, graphitic carbon nitride materials possess good material for hydrogen sorbent.

This is because the porous structures allow the hydrogen into interior of the nanotubes and pore edges containing double bonded nitrogen provide the active sites for adsorption of hydrogen either physically or chemically. Hydrogen is considered as one of the most promising energy source due to their abundance, easy synthesis and environmental friendly. In order to use the hydrogen one of the energy sources in mobile application, it should be high volumetric/

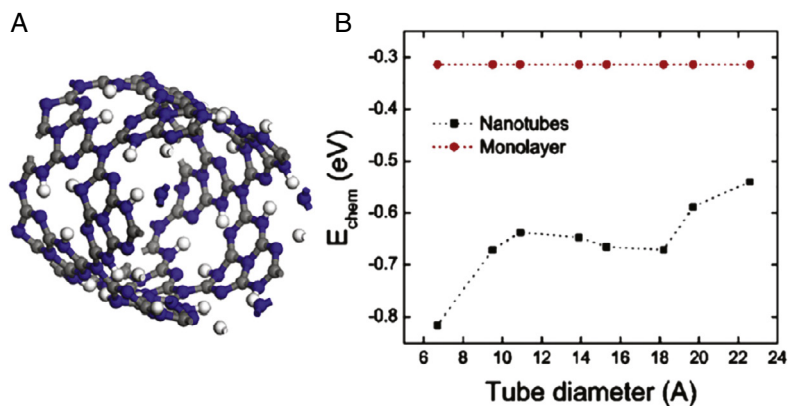


Fig. 15.6. (A) Graphitic carbon nitride (5,0) with three H atoms chemisorbed at each pores (C, N, and H atoms are represented in grey, blue and white), (B) Average H-N chemisorptions binding energy [77].

gravimetric capacity, ultra fast desorption/adsorption capacity and high tolerance to recycling [78–80].

Koh et.al. [77] described the hydrogen storage capacity by density theory calculation. The size effect on the hydrogen storage capacity of graphitic carbon nanotubes has H-chemisorption of binding energy increase with increase the tube diameter. They have observed the lowest binding energy for g-C₃N₄ with tube diameter 9.5 to 18 Å.

Moreover, the binding energy for hydrogen chemisorptions is significantly lower than monolayer, which clearly indicates that the nanotubes are able to store the hydrogen in efficient way as shown in Fig. 15.6. Nair et al. [78] also reported the palladium decorated g-C₃N₄ synthesized by cost effective method towards hydrogen storage. They have reported that the Pd decorated graphitic carbon nitride possessed a better storing capacity of hydrogen. The kinetic results of both g-C₃N₄ and Pd-g-C₃N₄ have been plotted in Fig. 15.7. It is clearly reveals that the Pd doped g-C₃N₄ increase the kinetic of adsorption and gravimetric capacity while decrease the saturation time. This is due to metal catalyst that dissociates the hydrogen molecule into hydrogen atoms. In this context, they clearly explained that the dispersion of Pd NPs on g-C₃N₄ is able to convert the hydrogen molecules into hydrogen atom under spill over mechanism. Due to this reason, the Pd NPs based graphitic carbon nitride has excellent chemisorption and physisorption of hydrogen. Moreover, the low energy barrier of graphitic carbon nitride materials, their hydrogen storing and releasing behavior will also be faster at low pressure and temperature as well [78]. Sayyed et al. [79] demonstrated the hydrogen storage capacity of multilayer graphitic carbon nitride and palladium doped graphitic carbon nitride by computational technique, which also included quantum mechanics calculations and grand canonical Monte Carlo simulation in order to predict the hydrogen storage

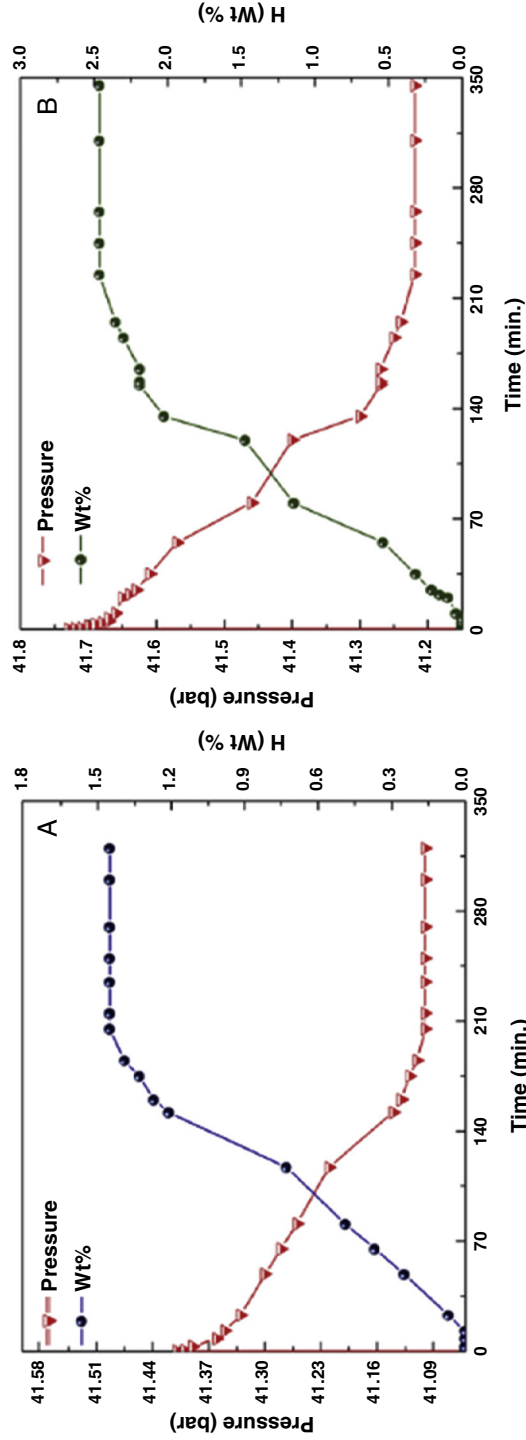


Fig. 15.7. Kinetic studies of (A) g-C₃N₄ and (B) Pd-g-C₃N₄ [78].

behaviors. Generally, hydrogen can be stored in five different techniques which including, (i) storing H_2 inside the high pressure gas cylinder (up to 80 MPa), (ii) liquefaction in cryogenic tank at 21 K, (iii) storing at ambient temperature and pressure, (iv) chemically attached in ionic liquid and (v) oxidation of metals with water. These methods are some of the disadvantages such as unsafe, low capacity, nonreducibility, and high cost [80].

In order to enhance the hydrogen molecules in carbonaceous materials, there are various hetero atoms have been doped, such as sulfur, boron, nitrogen, and phosphorous into graphitic carbon nitride. The electronegativity between atoms and dopants, tend to induce their dipole movement as well as increase the hydrogen storage efficiency. Again, Nair et al. [81] reported the palladium-cobalt decorated graphitic carbon nitride material for their hydrogen storage capacity. These porous nanocomposite materials, while treating with hydrogen gas at room temperature, showed a high uptake capacity of around 5.3 at 3 MPa pressure.

They studied the storage capacity of those porous materials at 0.1-3 MPa and 0°C - 1000°C , the pressure-composition isotherm of $\text{Pd}_3\text{Co/g-C}_3\text{N}_4$, while treating with H_2 gas molecules, where it was found that almost 90 % of the gas molecules were getting back under desorption process. A maximum hydrogen storage capacity was observed around 5.3 ± 0.1 wt.% at room temperature under 3.3 MPa pressure for bimetallic alloy doped graphitic carbon nitride [81]. Also, the mechanism of hydrogen storage on alloy based graphitic carbon nitride worked under spill over mechanism. The Pd_3Co alloy clusters acted as catalyst spill over sites, which dissociated the hydrogen molecules into atoms as shown in Fig. 15.8A-C. Siroos et al. [82] also reported that adsorption of hydrogen in graphitic carbon nitride and graphene oxide sheets and observed that the hydrogen storage capacity for graphene oxide isotherm at 22 bar, 1.06 mmol/g and adsorption isotherm for graphitic carbon nitride is 296 K and 1.27 mmol/g respectively.

15.4.2 Lithium ion storage in graphitic carbon nitride

As we know that the graphitic carbon nitride has large number of porous defects that can able to store more lithium ions, which will eventually increase the capacity. Furthermore, their porous defects can act as transmission channels, where the lithium ions can be migrated into graphitic carbon nitride surfaces, which lead to the fast mobility of lithium ions.

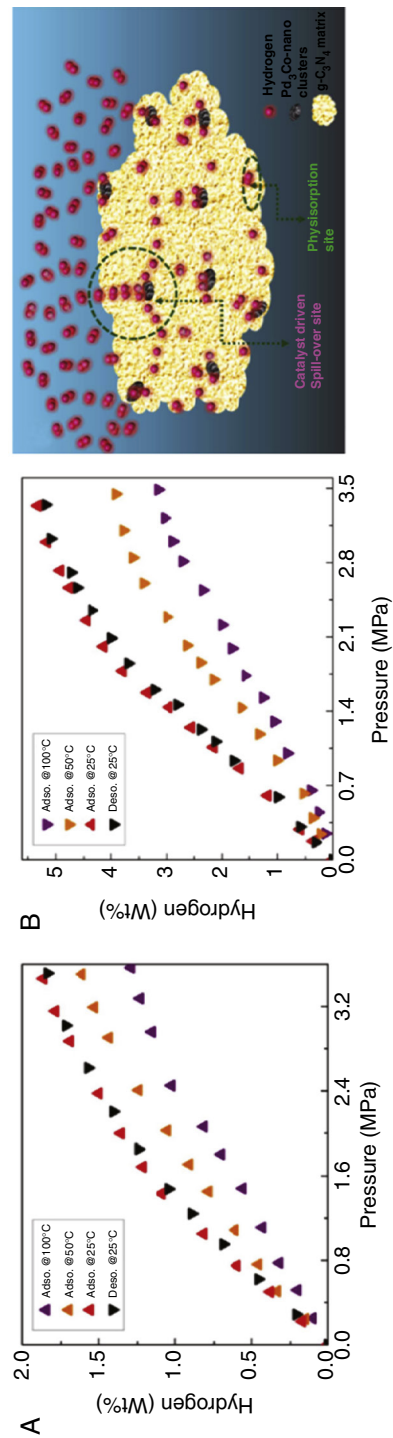


Fig. 15.8. Hydrogen pressures of (A) Isotherm of g-C₃N₄, (B) Pd₃Co/g-C₃N₄ and (C) Schematic representation of hydrogen adsorption mechanism [81].

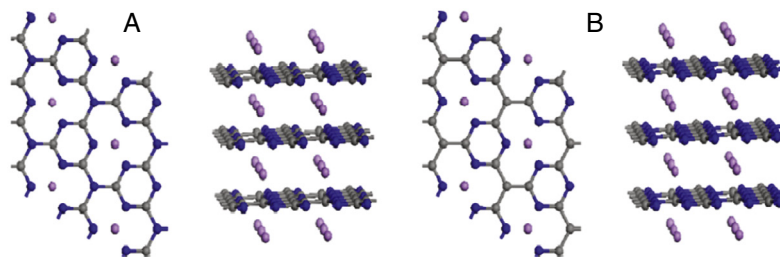
15.4.2.1 Application of graphitic carbon nitride in lithium ion battery

Lithium ion batteries are considered as one of the appropriate rechargeable batteries for portable electronic, electrical vehicles and other industrial applications. There have been many works done, in order to upgrade the batteries properties such as high energy density, light weight and durability. Generally, lithium ion batteries have three parts namely, solid or liquid electrolytes, cathodes, and an anode. Usually, all kinds of batteries prefer to store the chemical energy and convert into electrical energy, therefore rechargeable batteries with high energy density materials have great attention. Lithium ion storage in different nanostructure materials such as graphene, carbon based porous materials has been proved to be significant strategy for increasing their high energy density [83]. They are variety of nanomaterial based electrodes used in LIBs, especially one-dimensional materials such as carbon nanotubes and silicon nanotubes/nanowires. The theoretical value of charge and discharge capacity for silicon nanowires is around 4200 mAh/g. The main disadvantage for Si based battery is instability. Therefore light weight materials such as carbon and carbon nitride have great attention because of their high energy density and more over, the theoretical Li storage capacity of LiC_2 , is around 1250 mAh/g for carbon nanotubes whereas, graphite has 372 mAh/g, LiC_6 . To determine the suitable location of Li atoms in triangular N holes and hexagonal rings onto graphitic carbon nitride ($\text{g-C}_3\text{N}_4$ and $\text{g-C}_4\text{N}_3$) with their respective binding energies are 2.2 eV and 4.3 eV per atom [84,85].

Wu et al. [76], successfully reported, the Li ion doped with two different kind of carbon nitride materials ($\text{Li}_2\text{C}_3\text{N}_4$ and LiC_4N_3), which is useful for lithium ion anode and cathode materials with specific capacity. They have investigated the specific capacity of $\text{Li}_2\text{C}_3\text{N}_4$ and found that it does not suitable for anode materials since the binding energy of Li atom is large. But in the case of its usage as cathode materials, the specific energy is around 0.961 kW*h/kg, which is almost twice than LiCoO_2 (0.518 Kw*h/kg).

Each Li ion is placed between two holes of two adjoining layers and half of the specific capacity is reduced for bulk $\text{Li}_2\text{C}_3\text{N}_4$ and bulk LiC_4N_3 and cohesive energies of lithium are 3.6 eV and 5.2 eV as shown in Fig. 15.9. Marlies et al. [86] also reported that the sodium and lithium ion storage on graphitic carbon nitride materials. Lithium adsorption was observed over their triangular pores into graphitic carbon nitride (C_3N_4 , C_6N_8 and bulk C_3N_4). Recently, Li storage capacity of graphene is one Li per six carbon atoms (LiC_6) with their specific theoretical capacity is 372 mAh/g. Generally, graphene based

Fig. 15.9. Geometric structure of (A) bulk $\text{Li}_2\text{C}_3\text{N}_4$ and (B) bulk LiC_4N_3 [76].



materials will be able to store the Li ions on both side surfaces and also it has large surface area, enhanced electrical conductivity, high chemical and thermal stability, which make it as suitable alternative materials [87].

Marlies et al. demonstrated the charge and discharge curve of C_6N_8 , which is effective storage for sodium and lithium ion batteries as shown in Fig. 15.10. Both batteries was tested and observed the discharge plateau from around 1.3 V to 0.2 V. It is experimentally proved that the lithium atoms are intercalated and stored in both the outside and inside of the graphitic carbon nitride surfaces.

During intercalation, the lithium ions are used to occupy the pores of the graphitic carbon surface. Beside porosity, heteroatom doping is another strategy in order to improve the electrochemical performance in various graphene based materials, which can be used as electrode materials. Meng-yao et al. [88] also reported that the adsorption and storage of sodium and lithium ion on $\text{g-C}_2\text{N}$ using first principle calculation. They observed that the capacity of lithium ion and sodium ion was found to be 596 and 276 mAh/g in LiC_2N and NaC_2N respectively. Li ions are located into each side of the pores and they will be able to interact with neighboring three nitrogen atoms of the graphitic carbon pores surfaces. In order to introduce the Li ion one by one on monolayer, they found that each pores are hold six Li ions with the specific capacity of 596 mAh/g.

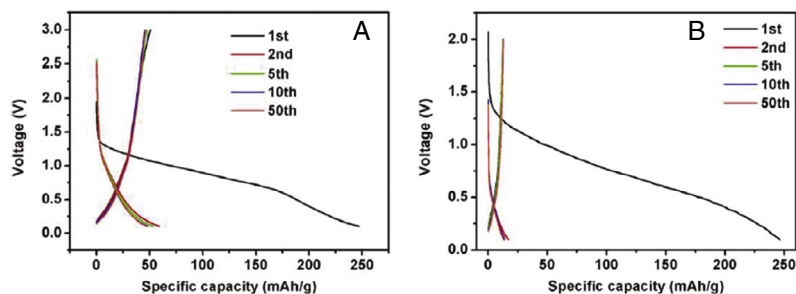


Fig. 15.10. Charge and discharge curve of C_6N_8 (A) Lithium and (B) Sodium [86].

15.4.2.2 Sodium ion storage in graphitic carbon nitride

Electrical vehicles are one of the most capable ways to reduce the carbon emission in environment because of the usage of lithium and sodium ion batteries in electrical vehicles. There is a great interest to develop a high energy density battery. In this direction, the sodium ion battery is also one of the high density rechargeable batteries. However, one of the biggest challenge of sodium ion battery is negative electrode and thermodynamically unstable, therefore storing sodium ion in various carbon materials is very low around <35 mAh/g [90-96]. Guo-Ming et al. [89] depicted the C/g- C_3N_4 composite by one-pot heating of mixer of urea and asphalt for Na storage capacity in Sodium ion batteries. It is low cost, high rate capability and chemically stable. Accordingly, they reported that the C/g- C_3N_4 sodium ion have two times higher than that neat g- C_3N_4 .

Further, the C/g- C_3N_4 sodium ion was characterized by galvanostatic cycling and observed that the cycling capacity at 0.4 A/g (see Fig. 15.11A). These material have also been tested for their charge

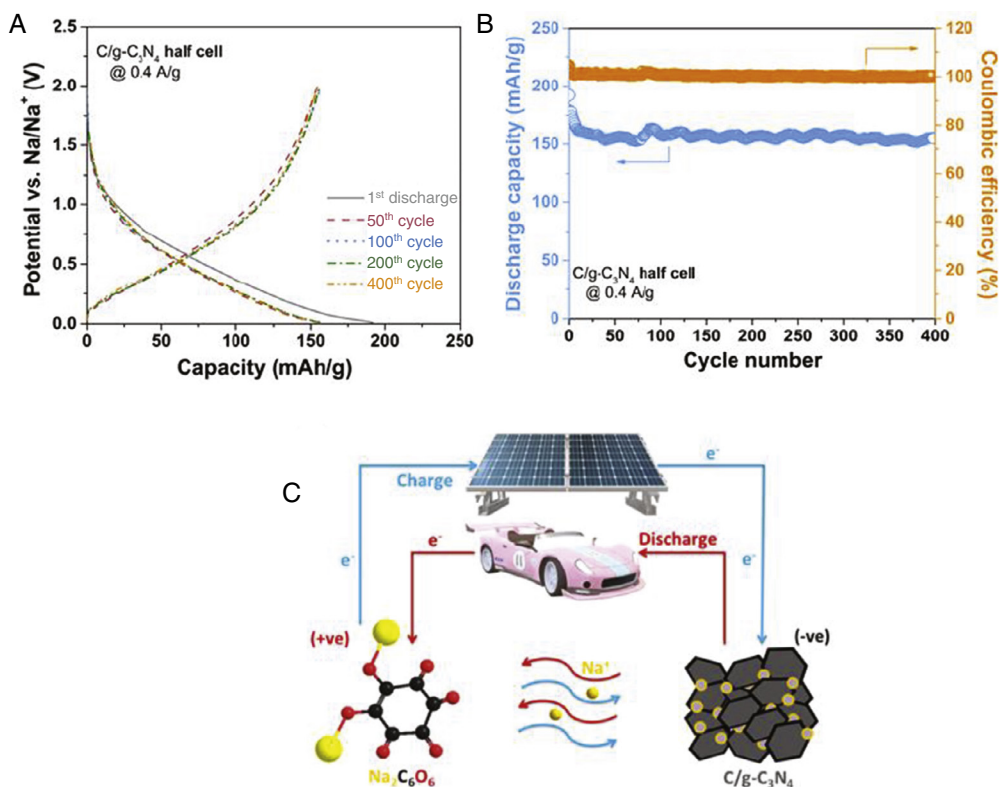


Fig. 15.11. (A) Galvanostatic charge/discharge curve of C/g- C_3N_4 , (B) cycling performance of C/g- C_3N_4 Na and (C) Current and electron flow of C/g- C_3N_4 Na full cell containing positive ($Na_2C_6O_6$) and negative (C/g- C_3N_4), [89].

and discharge study, found that the average capacity of around 160 mAh/g in 400 cycles with Coulombic efficiency > 99.9 % that achieved for sodium half cell as shown in Fig. 15.11B. In order to study the above physicochemical properties, they used the sodium rhodizonate dibasic ($\text{Na}_2\text{C}_6\text{O}_6$) as organic electrode (see Fig. 15.11C).

The graphitic carbon based composite materials (C/g- C_3N_4 sodium ion) used as long life sodium ion battery, which was found to be two times higher than neat g- C_3N_4 and also excellent Columbic efficiency as well as high energy density. The graphitical carbon nitride materials have been used to store different energetic molecules such as hydrogen, lithium and sodium. Apart from these, Hussain et al., [97] successfully reported that the CO_2 capture or storing on graphitic carbon nitride (g- C_6N_8) and different transition metals ranging from Sc to Zn have been tested their storing capacity and calculated *via* density functional theory (DFT) calculations. Graphitic carbon nitride materials are well known for their uniform pore size, high surface area to volume ratio and 2D nanostructure. These materials were already tested for their storing capacity of hydrogen and sodium as discussed in previously. Further, these materials can also be used as excellent storage material for CO_2 . Transition dopants such as Sc and Zn can be used as excellent binder or anchoring elements on g- C_6N_8 , which essentially enhance the storing of the carbon dioxide molecules [98-100].

15.5 Concluding remarks and future prospects

In this chapter, we have described recent progress in energy storage applications using graphitic carbon nitride materials. We have discussed in detail about the synthetic procedures of various graphitic carbon nitride-based materials by soft and hard templates method. Further, the functionalization of g- C_3N_4 (using organic, inorganic, and dyes) has been discussed. Similarly, different elements such as Si, P, Sn, metal oxide, metal hydrides and sulfide functionalized g- C_3N_4 has also been demonstrated for enhanced their electrochemical energy. An updated overview of g- C_3N_4 based batteries such as lithium ion and sodium ion have also been discussed. The theoretical and practical values of charge and discharge capacity have been highlighted as deduced by DFT and galvanostatic methods. Mesoporous graphitic carbon nitride materials are effective to store the various energetic molecules and ions including lithium, CO_2 , sodium and hydrogen. Hence, g- C_3N_4 can be a futuristic material that can be used in different solid state batteries and can be used as promising materials for energy storage applications.

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