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Graphitic Carbon Nitride and Polymers: A Mutual Combination for Advanced Properties

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The sheet-like material graphitic carbon-nitride (g-C₃N₄) is one of the most promising metal-free photocatalysts and utilized for various purposes, e.g. energy conversion, waste water remediation or organic synthesis. g-C₃N₄ features a suitable band gap in the visible light range and outstanding physicochemical stability. However, g-C₃N₄ features drawbacks such as structural disorder, low conductivity, poor dispersibility and in turn low processability. Amongst the strategies to improve g-C₃N₄ properties, combination with polymers is a promising avenue toward advanced materials. The present critical review highlights the development and investigation of g-C₃N₄/polymer combination, including (1) g-C₃N₄ as photoinitiator for polymer synthesis, (2) polymer modified g-C₃N₄ for improved dispersibility, (3) g-C₃N₄/polymer hybrid materials fabricated via physical or covalent attachment and (4) g-C₃N₄ based hydrogels. The fabrication methods and application of these areas will be critically reviewed and the advantage of g-C₃N₄/polymer combination comprehensively presented. Moreover, the broad range of applications is highlighted, e.g. photocatalysis, batteries, biosensors, H₂ evolution and films. Finally, the review will conclude with a summary and perspective on future directions as well as current challenges of this research area. In order to stimulate new research regarding the design and construction of g-C₃N₄/polymer materials.

1. Introduction

Sustainability has an increasing impact both on academia and industry, orienting many research fields such as biomass conversion, batteries, polymers and photochemistry.⁵ A significant direction is the integration of free and abundant sunlight into current technology, such as energy harvesting via photovoltaic devices or photo-mediated material synthesis. Semiconductors (such as Si, TiO₂, CdS, hybrid perovskites, polythiophenes) absorb light which results in the formation of excited electrons, and are promising candidates for photovoltaic devices, transistors and for photoinduced reaction catalysis.⁶⁻⁸ Many factors should be considered for the efficiency of a semiconductor materials, such as suitable absorption and bandgap values, lifetime of excited electrons, and charge migration which delays recombination. Even though excessive research has been conducted on these materials, their metal content, possible toxicity and synthesis from non-abundant sources restrict applications. Therefore, suitable candidates which have at least similar photoactivity but are formed via sustainable synthetic conditions are highly sought after.⁹

Graphitic carbon-nitride (g-C₃N₄) is a sheet like material that is traditionally formed from a regular arrangement of tri-s-triazine units (Scheme 1).¹⁰,¹¹ It features a variety of modifications, which have direct influence on the band gap resulting in photoactivity in the visible and UV range of light.¹²⁻¹⁵ Thus, g-C₃N₄ is utilized frequently as visible light induced heterogeneous photocatalyst, for example for organic transformations,¹⁶,¹⁷ hydrogen evolution,¹⁸⁻⁲⁰ pollution degradation¹¹ or CO₂ reduction.²²,²³ Moreover, g-C₃N₄ is utilized in ion transport membranes,²⁴,²⁵ photoelectrochemistry²⁶ or in organic photovoltaics²⁷⁻²⁹ as well as for emulsion stabilization.³⁰ The synthesis of g-C₃N₄ is usually performed from metal-free, oxygen-free, abundant and nitrogen-rich precursors, for example cyanamide,³¹,³² guanidine hydrochloride,³³,³⁴ melamine³⁵,³⁶ or cyanuric acid.³⁸ The process can be realized via several methods. Amongst them, thermal condensation is the most common method for fabrication of bulk g-C₃N₄, which proceeds under inert atmosphere between 400 and 600 °C. Recently, other methods like chemical vapor deposition or electrochemical deposition were introduced for fabricating film or membrane g-C₃N₄.³⁹ The microwave method was utilized as well, e.g. to produce fluorescent g-C₃N₄.⁴⁰,⁴¹ However, the type of the precursors and treatment can significantly influence the physicochemical properties of as-prepared g-C₃N₄. Compared to traditional semiconductors which have defined formulas, g-C₃N₄ represents a large family of materials with a variety of properties. For example, one way to obtain well-defined g-C₃N₄ is the utilization of a
supramolecular precursor complex of cyanuric acid and melamine that already resembles the final g-C$_3$N$_4$ structure. As such, porosity, surface charge, light absorption, photoluminescence, and band gap can be tailored according to the needs. Recently, also the overall shape of g-C$_3$N$_4$ could be tuned via various synthetic methodologies, e.g. a control over precursor crystal structures/shapes. As summary, g-C$_3$N$_4$ seems to satisfy sustainability requirement as semiconductor by being metal-free and synthesis from benign precursors, in addition it possesses tunable properties, however it has some major drawbacks such as structural disorder, as well as being non-processable in bulk.

In that sense, a combination of carbon nitride with polymers seems to be a promising avenue for advanced materials (Scheme 1). Polymers can introduce processability (e.g. film formation) into materials as well as they enhance dispersibility. Moreover, a plethora of conducting polymers allows a fine tuning of electron transport process in materials. Therefore, polymer can be utilized to introduce new properties to g-C$_3$N$_4$ or to enhance existing properties (e.g. photocatalysis or conductivity). Likewise, incorporation of g-C$_3$N$_4$ into polymer materials is an avenue to tailor mechanical properties of the polymer, e.g. in the bulk or in hydrogels. Another promising property of g-C$_3$N$_4$ is that of significant interest for polymer science is its inherent property to form radicals under irradiation with visible light. As such it acts as photoinitiator and can be used for polymer synthesis (e.g. polymer particles) in a convenient way. Polymers and g-C$_3$N$_4$ have various points of contact, and by hybridization improved or novel materials properties can be synthesized.

In the following review, this combination is discussed. The research in recent years is divided into four parts. At first the photoinitiator properties of g-C$_3$N$_4$ and its application in various polymerization systems is discussed. Next, the dispersibility of g-C$_3$N$_4$ and polymer- or functionalization-based routes towards improved dispersibility are highlighted. As the main part, g-C$_3$N$_4$/polymer hybrid and composite materials are presented with emphasis on H$_2$ evolution, photocatalysis, biosensors, electrochemical energy storage and solar cells, films, nano particles and polymer properties. Finally, the area of g-C$_3$N$_4$-based hydrogels is introduced with a focus on mechanical properties as well as photocatalytic properties. The review is closed with a summary and discussion of future aspects.

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2. Carbon Nitride as Polymerization Initiator

Commonly, g-C₃N₄ has been employed as a highly active photocatalyst. As g-C₃N₄ features a suitable bandgap to absorb visible light, it generates electrons and holes under visible light irradiation. In these cases, the formation of reactive species (e.g., ‘OH, O₂⁻, and HO₂⁻, or also CN-centered species) takes place, which is not only of interest for photocatalysis but also for polymerization processes as well (Scheme 2). Therefore, two ways are depicted in Scheme 2 where g-C₃N₄ acts as initiator for photopolymerization, which is accompanied with various advantages. First of all, g-C₃N₄ polymerizations can be operated in the visible light region, which is a benign and abundant trigger. Several monomers were investigated for polymerization via g-C₃N₄ as photoinitiator, such as styrene, methyl methacrylate (MMA), α-methylene-γ-valerolactone (MeGVL), methyl acrylate (MA). On top, photopolymerizations have various useful features, like spatial and temporal control. Moreover, g-C₃N₄ is a heterogenous catalyst, which allows easy separation and recycling. Albeit, the conditions can be altered in a way that the growing polymer chains are grafted from g-C₃N₄ and as such recycling or separation is not straightforward. In this case grafting polymers from g-C₃N₄ opens up various opportunities for hybrid material formation, which also broadens the utilization in bioapplications due to the inherent photoluminescent properties of g-C₃N₄.

As a proof of concept, Yagci and coworkers utilized g-C₃N₄ as visible light photoinitiator for free radical polymerization. Mesoporous g-C₃N₄ (mpg-C₃N₄) was employed as heterogeneous visible light photoinitiator in the presence of tertiary amine as reactive co-initiator, conducting free radical polymerization with vinyl monomers such as methyl methacrylate (MMA). Based on the photoredox chemistry of mpg-C₃N₄, the photopolymerization process was realized by exposing the monomer mixture to visible light in the absence of O₂. The initiation mechanism is presumably the transfer of the CN-based hole and the amine. The photochemically formed holes oxidize amines to the corresponding radical cations which abstract hydrogen from another amine leading to the formation of initiating radicals. Moreover, mpg-C₃N₄ demonstrated enhanced activity in the polymerization process due to a larger external surface compared to non-porous bulk g-C₃N₄.

Recently, our group employed g-C₃N₄ as radical photoinitiator for emulsion photopolymerization. Emulsions of aromatic monomers (styrene and benzyl methacrylate) and MMA in water were formed via g-C₃N₄ (cyanuric acid-melamine-derived g-C₃N₄ (CM)) or 1-decene modified CM as stabilizer. Subsequently, the mixture was exposed to visible light to conduct polymerization. Radicals were formed on the surface of g-C₃N₄. Kinetic studies and in-depth studies of the polymer particles indicated that the g-C₃N₄ surface acted as the reaction locus for polymer chain growth and particle formation. The polymerization mechanism was investigated by addition of hole or electron scavenger to the reaction system, respectively, and it was demonstrated that the emulsion photopolymerization was mainly initiated by the hole. Overall, very well-defined latexes were obtained, which was attributed to the fast nucleation of the latex particles. Moreover, compared to previous works, radicals were formed via holes on the g-C₃N₄ surface directly without co-initiator addition. The direct radical formation leads to crosslinked latex particles directly due to the multifunctionality of g-C₃N₄. Furthermore, our team has employed g-C₃N₄ as heterogeneous photocatalyst for free radical polymerization of MeGVL. At first MeGVL is efficiently synthesized from renewable resources via continuous flow reaction from γ-valerolactone over hierarchical basic zeolite. MeGVL is structurally similar to methacrylic monomers, and further valorization of this compound via efficient polymerization demonstrates the ability to make novel biomass-derived polymer with significant industrial interest.
Scheme 2. Schematic overview of g-C₃N₄ mediated photopolymerization and monomers used in the two approaches: Utilization of g-C₃N₄ as recyclable photoinitiator via radical transfer to an amine compound (top) and g-C₃N₄ initiated grafting of polymers onto the initiator (bottom) (MMA: methyl methacrylate; BMA: benzyl methacrylate; MeGVL: α-methylene-γ-valerolactone; DMA: N,N-dimethylacrylamide; MA: methyl acrylate; HEMA: 2-hydroxyethyl methacrylate).

As a semiconductor, g-C₃N₄ possess a quite high negative position of the conduction band, thus contributing to a high activity of oxygen capture and reduction. Meanwhile, the moderate oxidation potential of g-C₃N₄ efficiently prevents the decomposition of the prepared polymer by the photogenerated holes. Both effects play a crucial role in the photopolymerization process.⁵⁹, ⁶⁰ Thus researchers introduced g-C₃N₄ as a promoter for electron transfer in reversible deactivation radical polymerization (RDRP). For example, Yagci and coworkers⁶¹ utilized mpg-C₃N₄ as photoactivator for reduction of initially loaded copper (II) species, for the in situ formation of copper (I) species, which act as catalytic species in atom transfer radical polymerization (ATRP). Subsequently, polymerization was successfully conducted under sunlight or UV-light irradiation. It was shown that the light-induced electron transfer from g-C₃N₄ is due to the large reduction potential (E_{CB}) of -1.2 eV. Vinyl monomers such as, methyl acrylate (MA), MMA and styrene were successfully polymerized during the reaction with precise control on molecular dispersity (D). A work reported by Qiao and coworkers introduced g-C₃N₄/amine cocatalysts to an photoinduced electron/energy transfer (PET) oxygen-tolerant reversible addition-fragmentation chain transfer (RAFT) polymerization (Figure 1).⁶¹ g-C₃N₄ was employed directly without prior deoxygenation of the reaction mixture to enable electron transfer from added tertiary amines (i.e. triethanolamine TEOA) to dissolved molecular oxygen. Thus, the trithiocarbonate (TTC) chain transfer agents were activated via oxygen reduction, followed by polymerization of acrylic species such as MA, n-butyl acrylate (BA) and water-soluble monomer N,N-dimethylacrylamide (DMA) (Figure 1a). In the mechanism, molecular oxygen takes a prominent part in the photoredox cycle. Thus, benign reaction conditions under visible light, without deoxygenation of monomer solution, are achieved that are time consuming in the common case. Polymers with different polymerization degree could be achieved easily with this process as shown via size exclusion chromatography (SEC) (Figure 1b). Moreover, block copolymer could be synthesized, e.g. PMA-b-PBA (Figure 1c). Such PET-RAFT approach had merits of low toxicity, organic solvent tolerance and facile post-polymerization removal of the catalyst.⁶²

Very recently, our group conducted dithiol–ene click reactions between lignocellulosic biomass-derived 4-pentenoic acid (4-PEA) and different dithiols using g-C₃N₄ as photocatalyst.⁶³ Visible light induced click chemistry was utilized for the reactions between 4-PEA and 1,2-ethanediol (EDT), 2,2-(ethylenedioxy)-diethanethiol (EDDT), and 1,4-benzenedimethanol (BDM) leading to polymers in high yields and purities in order to reduce the dependence on petroleum-derived monomers. Moreover, g-C₃N₄ has been utilized as photoinitiator to fabricate g-C₃N₄-based polymer composites under light irradiation via a “grafting from” method, which is defined as chain growth via monomer propagation starting from a surface, i.e. here a g-C₃N₄ surface. As radicals are produced by g-C₃N₄ under visible light irradiation, the grafting occurs presumably via the presence of uncondensed -NH₂ or -NH groups at g-C₃N₄ surface. These groups act as active sites to initiate polymer chain growth from g-C₃N₄ surface. In such a way, g-C₃N₄-based polymer hybrid materials are fabricated, with the firm attachment of polymer on to g-C₃N₄ surface, which facilitates further applications.

Another area where g-C₃N₄ photoinitiation is widely utilized is hydrogel formation. For hydrogel formation the same initiation mechanisms are exploited, i.e. radicals are formed on the surface of g-C₃N₄ with phototreatment and g-C₃N₄ directly participates in the hydrogelation without electron transfer or co-initiator addition. The formation of hydrogels will be covered in detail in Section 5. Most
notably, hydrogels could be formed without addition of external crosslinker, which indicates initiation from the g-C$_3$N$_4$ surface and covalent incorporation of g-C$_3$N$_4$ into the gel network.$^{64}$ As such, these findings support the mechanism found for g-C$_3$N$_4$ initiated polymerization without radical transfer agent addition.

Figure 1. a) Schematic overview over the mechanism of deoxygenation and photoinduced electron/energy transfer-reversible addition-fragmentation chain transfer (PET-RAFT) polymerization employing g-C$_3$N$_4$: (i) photo-induced activation of g-C$_3$N$_4$; (ii–v) electron transfers from amine to g-C$_3$N$_4$ from g-C$_3$N$_4$ to O$_2$, and from g-C$_3$N$_4$ to the trithiocarbonate (TTC), respectively; (vi) initiation and chain propagation of monomers (M); and (vii) reversible degenerative chain transfer (RAFT process). b) a) Utilization of solvent mixtures (e.g. water/ethylene glycol (EG)), b) grafting polymers from g-C$_3$N$_4$ surface and c) grafting polymers to g-C$_3$N$_4$ via double bond containing preformed polymers and d) photofunctionalization with ene containing small molecules. (Reprinted with permission. Copyright 2017 American Chemical Society.)

3. Carbon Nitride Dispersibility

A major issue for the application of g-C$_3$N$_4$ is its poor dispersibility in the pure state. As the strong van der Waals interactions ($\pi-\pi$ stacking) of g-C$_3$N$_4$ sheets causes the agglomeration in the liquid phase. Thus, dispersibility in organic as well as aqueous environment is rather low,$^{65,66}$ and resulting in restricted applicability as well as activity.$^{66,67}$ Especially the formation of thin (2-3 nm) semiconductor films are of great interest for optoelectronics and photovoltaics. However, to form such g-C$_3$N$_4$ films rather elaborate methods like chemical vapor deposition have to be utilized.$^{67,68}$ A solution based process would be simpler and suitable for many real life applications, and therefore, attention has been addressed to enhance g-C$_3$N$_4$ powder dispersibility. Several researchers focused on exfoliation of the bulk g-C$_3$N$_4$ into thin sheets, in which the electrostatic repulsion between g-C$_3$N$_4$ sheets can enable the formation of well-dispersed g-C$_3$N$_4$ colloids. Hence, stable dispersions of g-C$_3$N$_4$ can be prepared, yet the achievable concentration of dispersed g-C$_3$N$_4$ is rather low. A route to disperse g-C$_3$N$_4$ is via additives or physical treatment, e.g. via addition solvents in the dispersion step,$^{69,70}$ hydrothermal treatment,$^{71}$ chemical oxidation,$^{72}$ thermal oxidation$^{73}$ or ultrasonication.$^{74}$ The other option is chemical modification via attachment of molecular moieties. On one hand, with the attachment of charged groups to the g-C$_3$N$_4$ surface, the stability of dispersed g-C$_3$N$_4$ nanosheets can be increased in aqueous environment via electrostatic repulsion. On the other hand, attachment of hydrophilic polymers can stabilize g-C$_3$N$_4$ in dispersion via steric repulsion in aqueous dispersion. In organic solvent, the dispersibility of g-C$_3$N$_4$ can be increased via the attachment of organo soluble small molecules or polymers, where steric repulsion leads to enhanced stability of the dispersion.

Scheme 3. Approaches towards improvement of g-C$_3$N$_4$ dispersibility: a) Utilization of solvent mixtures (e.g. water/ethylene glycol (EG)), b) grafting polymers from g-C$_3$N$_4$ via free radical polymerization, c) grafting polymers to g-C$_3$N$_4$ via double bond containing preformed polymers and d) photofunctionalization with ene containing small molecules.
A reported option is the complex formation with organic modified montmorillonite to facilitate enhanced stability in organic environment, which was utilized to form poly(styrene)/g-C_3N_4 composites.\textsuperscript{77} Exfoliating g-C_3N_4 in 1,3-butadendiol results in graphene-like g-C_3N_4 with around 2 - 6 layers of g-C_3N_4 with a thickness of circa 1-2 nm. However, ultrasonication for 24 hours and possibility to exfoliate only low amount of g-C_3N_4 is the drawback of the approach.\textsuperscript{31}

Another functionalization route to enhance dispersibility of g-C_3N_4 is by pre-condensation or post-condensation. In the case of pre-condensation a specific monomer mixture is used, for example additional phenyl moieties are introduced into the system.\textsuperscript{78} The utilization of a phenyl-functional precursor for g-C_3N_4 synthesis prevents growth of larger g-C_3N_4 sheets which results in quantum dot structure, possessing enhanced dispersibility compared to traditional g-C_3N_4 sheets. Another approach is post-condensation functionalization that allows the introduction of various functional groups via chemical treatment, e.g. oligoethylene glycol (oligoEG) (Figure 2).\textsuperscript{75} Well dispersed colloids (Figure 2a) with high biocompatibility and bioimaging properties could be achieved in that way (Figure 2b). As such Kim and coworkers firstly oxidized g-C_3N_4 via KMnO_4 and exfoliated it via ultrasonication, followed by covalent modification with monomesylated hexahydroxyle glyc. Attachment of oligoEG resulted in oligoEG-modified g-C_3N_4 sheets, which exhibited water dispersibility to be utilized for bioimaging. Oxygen plasma can be employed for introducing protonated hydroxylamine functional groups to g-C_3N_4 surface, which provides extreme hydrophilic character.\textsuperscript{79} Other functional groups such as sulfonic acid,\textsuperscript{80} hydroxyl\textsuperscript{81} or aromatic groups\textsuperscript{48} can also be introduced for enhancing dispersibility of g-C_3N_4 sheets. However, alternative facile and less stringent routes to enhance dispersibility with high g-C_3N_4 solid content yields would be beneficial.

To improve dispersibility, we investigated solvent mixtures (Scheme 3a). The mixture of water and EG in equal volume enabled dispersion with significant g-C_3N_4 weight contents of up to 4 wt.%, compared to a maximum of 0.6 wt. % in pure water. g-C_3N_4 is a photoactive compound that is a semiconductor and thus forms electron/ hole pairs via light irradiation. This feature was exploited to perform photo-initiated polymerization reactions (Scheme 3b). To improve dispersibility of g-C_3N_4 further, a polymerization approach was introduced via g-C_3N_4 photoinitiation. DMA was added to a g-C_3N_4 dispersion in EG/water and treated with visible light, which led to a weakly associated gel. The viscous gel was formed from PDMA grafted g-C_3N_4 and could be easily dispersed in water. In addition, such dispersions possess high stability (up to 2 months) due to steric stabilization of g-C_3N_4 colloids.\textsuperscript{82}

Furthermore, pre-formed one end functionalized polymers could be grafted onto g-C_3N_4 as well (Scheme 3c, refer to Section 4 as well). A way to obtain dispersible-CN via a more exact approach that does not rely on polymerization was also studied. For that, the parent g-C_3N_4 is dispersed in aqueous or organic solution, an one-compound is added, and the mixture subjected to visible light (Scheme 3d).\textsuperscript{76} Due to the radical formation at the g-C_3N_4 surface, addition of the one-compound take place. To prevent polymerization of the added small molecule, aliphatic compounds were utilized as they possess no propagation tendency. Hence, the molecules are grafted on g-C_3N_4 directly. Notable, the modification of the g-C_3N_4 surface chemistry significantly influences the dispersion properties of g-C_3N_4. For example, 3-alloxy-2-hydroxy-1-propanesulfonic acid sodium salt (AHPA) was grafted on g-C_3N_4 to improve water dispersibility with up to 10 wt.% while stable dispersions were obtained, e.g. for 48 hours. Grafting of 11-decene led to organo dispersibility of up to 2 wt.% g-C_3N_4 in solvents like THF, DCM or toluene. In addition, pH-sensitive dispersibility could be introduced via allylamine that leads...
to dispersibility in acidic solution and precipitation at basic pH (Figure 2c). Recently, methyl vinyl thiazole was grafted onto g-C_3N_4, which led to a significant improvement of organo dispersibility via an intrinsic electrostatic stabilization mechanism. The two components create an autonomous donor-acceptor type structure and enhancing excited electron-hole separation.\textsuperscript{83} Moreover, surface functionality has a profound effect on photocatalytic activity as well.

Furthermore, pre-formed end functionalized polymers could be grafted onto g-C_3N_4 as well (Scheme 3c, refer to Section 4 as well). A way to obtain dispersible-CN via a more exact approach that does not rely on polymerization was also studied. For that, the parent g-C_3N_4 is dispersed in aqueous or organic solution, an ene-compound is added, and the mixture subjected to visible light (Scheme 3d).\textsuperscript{76} Due to the radical formation at the g-C_3N_4 surface, addition of the ene-compound take place. To prevent polymerization of the added small molecule, allylic compounds were utilized as they possess no propagation tendency. Hence, the molecules are grafted on g-C_3N_4 directly. Notable, the modification of the g-C_3N_4 surface chemistry significantly influences the dispersion properties of g-C_3N_4. For example, 3-allyloxy-2-hydroxy-1-propanesulfonic acid sodium salt (AHPA) was grafted on g-C_3N_4 to improve water dispersibility with up to 10 wt.% while stable dispersions were obtained, e.g. for 48 hours. Grafting of 11-decene led to organo dispersibility of up to 2 wt.% g-C_3N_4 in solvents like THF, DCM or toluene. In addition, pH-sensitive dispersibility could be introduced via alkylation which leads to dispersibility in acidic solution and precipitation at basic pH (Figure 2c). Recently, methyl vinyl thiazole was grafted onto g-C_3N_4, which led to a significant improvement of organo dispersibility via an intrinsic electrostatic stabilization mechanism. The two components create an autonomous donor-acceptor type structure and enhancing excited electron-hole separation.\textsuperscript{83} Moreover, surface functionality has a profound effect on photocatalytic activity as well.

4. Carbon Nitride/Polymer Hybrid Materials

Polymers are playing a significant role in industry as well as daily life and are widely investigated. Especially, polymer materials with functional properties are of focal interest today, such as self-healing,\textsuperscript{84} stimuli response,\textsuperscript{85} biodegradability,\textsuperscript{86} electrical conductivity,\textsuperscript{87} a combination of traditional polymers with the novel metal-free semiconductor g-C_3N_4 materials is highly worthwhile (Scheme 4). g-C_3N_4 is widely investigated as a metal-free semiconductor, but poor processing inhibits a scale-up of utilization, which is a problem for applicability.\textsuperscript{88, 89} A combination of g-C_3N_4 with polymers appears to be a useful combination.\textsuperscript{90, 91} as properties of both material classes can be coupled via combination of the individual parts.\textsuperscript{92} Due to g-C_3N_4 photocatalytic, photoluminescence, as well as enhanced physical and mechanical properties are obtained, while the polymers bring improved processability or conductivity. There are several ways to fabricate g-C_3N_4/polymer hybrid materials (Scheme 4a). (1) Physical absorption or deposition, mostly prepared in the liquid phase. In the same way, one can also list blending of both materials. (2) “Grafting from” method, in which monomers are polymerized from the g-C_3N_4 surface. (3) “Grafting to” method that is based on chemical bond formation between reactive sites on g-C_3N_4 and active polymer end groups.

Such g-C_3N_4/polymer hybrid materials can be utilized for various applications as discussed in Section 4.1, e.g. photocatalytic H_2 evolution, photocatalysis, biosensors, electrochemical energy storage according to different type of the hybrids (Scheme 4b). As film and membrane materials are commonly applied to electrochemical area and particles are mostly used in biosensors, Table 1 shows the summary of specific g-C_3N_4/polymer compositions and their application area as well as the specific enhanced properties and performance compare to the single component g-C_3N_4. In addition, polymers can be utilized to include g-C_3N_4 into specific material morphologies, e.g. spherical particles or thin films as presented in Section 4.2. Moreover, g-C_3N_4/hybridization enables the improvement of polymer properties, especially mechanical properties as shown in Section 4.3. As such, polymers and g-C_3N_4 can be utilized for mutual benefit. On one hand, polymer improve processing of g-C_3N_4 amongst other properties. On the other hand, g-C_3N_4 improves the properties of polymer materials, e.g. the mechanical properties.

A significant issue with polymer hybrids and composites is the compatibility of polymer and the mixed-in material. In the case of g-C_3N_4, favorable interactions are present in many cases. For example, g-C_3N_4 is prone to establish π–π interactions with polymers like PS or BMA. On the other hand, g-C_3N_4 contains polar groups at the edges, which allows interactions (mostly hydrogen bonding) with polar polymers like PDMA or poly(2-hydroxethyl methacrylate) (PHEMA).

4.1 Applications of g-C_3N_4/polymer hybrid materials

g-C_3N_4/polymer hybrids as photocatalysts for H_2 evolution and CO_2 reduction

One of the major applications of g-C_3N_4 for photocatalysis is their employment as visible-light-driven water splitting photocatalyst for H_2 evolution. Low conductivity and high recombination rates of photoinduced electrons and holes significantly limits the production of H_2 and merging of g-C_3N_4 with conductive polymers is one of the efficient strategies to overcome these issues. Due to the excellent solubility, processability and long-term stability of polymer semiconductors, such hybrid materials can significantly improve the photoelectric properties of g-C_3N_4. The combination of g-C_3N_4 with conductive polymers, e.g. poly (3-hexylthiophene) (P3HT),\textsuperscript{93} poly(pyrrrole) (PPy)\textsuperscript{94} or poly(aniline) (PANI),\textsuperscript{95} is usually achieved via physical interactions, self-assembly or thermal deposition methods. As g-C_3N_4 possesses a stacked 2-dimensional (2D) structure and van der Waals interactions between g-C_3N_4 sheets, with the presence of -NH_2, -NH or -OH on the edge with a slight negative surface charge,
Physisorption of polymers to g-C$_3$N$_4$ surface via weak van der Waals or electrostatic interactions is enabled.

For example, Yan and coworkers combined P3HT and g-C$_3$N$_4$ by impregnating g-C$_3$N$_4$ with a chloroform solution of P3HT overnight, followed by evaporation of the solvent, which resulted in physical attachment of P3HT to g-C$_3$N$_4$ surface (Figure 3a). With the increased deposition of P3HT, a remarkable increase of H$_2$ evolution of 300 times was achieved using Na$_2$S and Na$_2$SO$_3$ as electron donors. The improved catalytic activity was attributed to the enhanced electron conductivity after P3HT incorporation. Later, the same group established a g-C$_3$N$_4$/Au/P3HT/ Pt layer structure using a self-assembly method. A tight g-C$_3$N$_4$/Au conjugation was formed by photodeposition, then P3HT/Pt was combined with g-C$_3$N$_4$/Au due to the formation of Au-sulfur association between Au on g-C$_3$N$_4$ and sulfur in the P3HT structure. Thus, chemical bonds were used instead of physical adsorption to ensure a tight junction between the individual g-C$_3$N$_4$ and P3HT layers. Such layered structures were demonstrated to be efficient for the effective separation of photoinduced electron-hole pairs and for H$_2$ evolution.

Nevertheless, P3HT has the drawback of a limited processability in aqueous media, which is the preferred choice for g-C$_3$N$_4$ so far. An option to circumvent that problem is to switch to polymer PPy. PPy is a typical conductive polymer which possesses high stability in the oxidized state as well as high conductivity. For example, Chen and coworkers reported the loading of highly dispersed PPy nanoparticles onto the g-C$_3$N$_4$ surface via sonochemical approach in a physical attachment (Figure 3b). PPy-g-C$_3$N$_4$ suspension was treated with ultrasonication for 12 hours and drying at 80 °C. The addition of PPy nanoparticles showed no effects on the absorption edge of g-C$_3$N$_4$ but influenced the intensity of the g-C$_3$N$_4$ emission peak, indicating the more effective separation of photogenerated electrons and holes in PPy-g-C$_3$N$_4$ compared to pristine g-C$_3$N$_4$. The activity of H$_2$ evolution was dramatically improved with the increasing loading amount of PPy. Furthermore, graphitized-poly(acrylonitrile) (g-PAN) nanosheets were deposited on g-C$_3$N$_4$ via one step thermal condensation method reported by Hao and coworkers (Figure 3c). Simple mixing of g-C$_3$N$_4$ precursors with PAN and thermal treatment under 650 °C led to graphitization of PAN. Thus, a layered structure of g-PAN/g-C$_3$N$_4$ was obtained. Compared to aggregated polymer morphologies, the g-PAN with aromatic conjugated structure possess more reactive sites and short diffusion distance, which decreases the recombination rate of photogenerated charge carriers. Hence g-PAN acts as an effective electron transfer channel in the g-PAN/g-C$_3$N$_4$ composites and obviously enhanced the photocatalytic performance for H$_2$ evolution.

Very recently, hydrophobic polymer grafted g-C$_3$N$_4$ was employed as a three-phase photocatalyst for enhanced selectivity and activity of CO$_2$ reduction. Hydrophobic 1H,1H,2H,2H-perfluorodecanethiol was utilized to modify PGMA grafted on CM (pFe-PGMA/CM) via thiol-epoxy addition reaction. Subsequently, an in-situ photoloading method was applied for loading Pt on the pFe-PGMA/CM surface.
A three-phase contact photocatalyst of CO\(_2\) (gas), H\(_2\)O (liquid) and catalyst (solid) was fabricated to enable a high concentration of CO\(_2\) molecules on the catalyst surface. Moreover, the mass transfer limitation of CO\(_2\) was overcome due to the hydrophobic catalytic surface, which contributed to an enhanced CO\(_2\) reduction reaction and suppressed hydrogen evolution reaction. The observed efficiency was about 34 times higher than can be commonly used as hydrophilic catalysts. Reisner and Roy showed an avenue to CO\(_2\) reduction as well.

Phthalocyanine catalyst in CO\(_2\) photosensitization facilitated remarkable activity of the effect of CN porosity, solar energy harvesting and was polymerized directly in the presence of mpg-C\(_3\) with 1,2,4,5-tetracyanobenzene together with Co\(^{2+}\) ions. To obtain a good interfacial contact, 1,2,4,5-tetracyanobenzene together with Co\(^{2+}\) ions was polymerized directly in the presence of mpg-C\(_3\). A synergistic effect of CN porosity, solar energy harvesting and photosensitization facilitated remarkable activity of the phthalocyanine catalyst in CO\(_2\) reduction under visible light.

![Figure 3](image-url) (a) A proposed mechanism of visible light-induced H\(_2\) evolution on g-C\(_3\)N\(_4\)-poly(3-hexylthiophene) (P3HT) polymer composite photocatalysts (Reprinted with permission.\(^{44}\) Copyright 2011 Royal Society of Chemistry). b) The mechanism to understand the role of the dispersed poly(pyrrrole)(PPy) nanoparticles in enhancing the photocatalytic activity of PPy-g-C\(_3\)N\(_4\) for H\(_2\) evolution (Reprinted with permission.\(^{44}\) Copyright 2013 Royal Society of Chemistry). c) Illustration for the enhanced photogenerated charge carriers separation and transfer in the graphitized-poly(acrylonitrile) (g-PAN)/g-C\(_3\)N\(_4\) composites under visible light irradiation (λ > 400 nm) (Reprinted with permission.\(^{44}\) Copyright 2014 American Chemical Society).

**g-C\(_3\)N\(_4\)/polymer hybrids as photocatalysts for water contamination degradation**

In addition to H\(_2\) evolution, other photocatalytic tasks can be performed with g-C\(_3\)N\(_4\)/polymer hybrids as well. g-C\(_3\)N\(_4\)/polymer hybrid materials show improved performance towards water contaminant degradation as well.\(^{39}\) For example, organic dyes like Methyl Red, Congo Red or methylene blue (MB)\(^{100}\) are responsible for wastewater contamination, as they have been used for dying fabrics. Due to their high solubility in water, effective purification processes are needed as otherwise these dyes cause significant contamination in wastewater. Moreover, they act as easy recognizable substances to probe photocatalytic activity. Several strategies were attempted to degrade dyes so far, such as ion exchange, electrochemical treatment, adsorption, membrane separation and catalytic reduction.\(^{101-103}\)

Amongst the approaches to degrade dyes in water, g-C\(_3\)N\(_4\) based polymer hybrid composites via photocatalytic means show remarkable advantages such as being low-cost, ease of processability and reversibility as well as activity under visible light.\(^{104}\) Zhu and coworkers in situ synthesized PANI nanofibers between g-C\(_3\)N\(_4\) nanosheets by polymerizing aniline in the presence of ammonium persulfate (APS).\(^{106}\) Coral-like PANI nanofibers were grown between g-C\(_3\)N\(_4\) sheets as monomers were in situ polymerized on the surface of g-C\(_3\)N\(_4\) to form a hydrogel material (Figure 4a). Thus, a 3D hierarchical structure of the composite hydrogel was constructed with excellent contaminants degradation properties, 5.1-fold higher than that of pure g-C\(_3\)N\(_4\) (Figure 4b). In a similar way, Liu and coworkers fabricated PANI-g-C\(_3\)N\(_4\) composite photocatalysts by in situ oxidative polymerization of aniline onto g-C\(_3\)N\(_4\) powder in the presence of APS as initiator.\(^{107}\) There, g-C\(_3\)N\(_4\) was employed as a substrate and to serve as loci for monomer propagation and polymer chains propagated on the g-C\(_3\)N\(_4\) surface. Finally, improved photodegradation properties toward MB were found due to the enhanced electron-hole separation induced by the synergistic effect between PANI and g-C\(_3\)N\(_4\). Another hybrid material of PANI and g-C\(_3\)N\(_4\) was synthesized by Prakash and coworkers, who used sulfur and phosphorous co-doped g-C\(_3\)N\(_4\) (SP-g-C\(_3\)N\(_4\)) and covalently grafted PANI via oxidative polymerization. The SP-g-C\(_3\)N\(_4\)-grafted with PANI also featured a tuned band gap structure with extended light absorption. Hence, more active sites for photogeneration of charge carriers at the interfaces were formed. Moreover, PANI possesses unique electron and hole transport property and excellent chemical stability, which leads to an improved utilization of visible light. Therefore, the as-prepared metal-free nanocomposite showed an outstanding photocatalytic activity for the degradation of MB.\(^{108}\) Other water contamination can also be removed by g-C\(_3\)N\(_4\)/polymer composites. Qian and coworkers combined porous g-C\(_3\)N\(_4\) foams with acrylic resin for efficient oil and organic solvent capture.\(^{109}\) The g-C\(_3\)N\(_4\)/acrylic resin showed high adsorption capacity, fast capture rate and good recyclability toward removing oils and organic solvent from water.

A good way to improve efficiency of g-C\(_3\)N\(_4\)-based waste water remediation by improved transport engineering is the incorporation into fiber structures. The group of Chen fabricated visible light responsive electron nanofibers based on PAN dispersed g-C\(_3\)N\(_4\) via electrospinning, g-C\(_3\)N\(_4\) was dispersed and immobilized by PAN fiber structure.\(^{110}\) The g-C\(_3\)N\(_4\)/PAN hybrids demonstrated efficient photocatalytic properties of Rhodamine B (RhB) degradation over a wide pH range and were recycled in a simple way. Othman and coworkers incorporated g-C\(_3\)N\(_4\) into polyacrylonitrile nanofibers using electrospinning as well.\(^{111}\) A liquid-permeable self-supporting photocatalytic nanofiber was fabricated, demonstrating 85% degradation capability for purification of oil contaminated water under visible light irradiation. Liu and coworker utilized electrospun PAN nanofibers to immobilize a g-C\(_3\)N\(_4\)/BiO\(_x\) nanoheterojunction via a facile in situ synthesis strategy.\(^{112}\) The efficient separation of the...
electron–hole pairs and strong absorption in the visible region of PAN/g-C\textsubscript{3}N\textsubscript{4}/BiOI hybrids resulted in superior photocatalytic activity in the degradation of RhB and toxic Cr(VI) ions under visible-light. Moreover, the film-like and self-supporting nanostructure enabled the hybrids for floating photocatalyst application.

An issue of growing interest is the removal of antibiotic contaminations in water, which can be tackled via g-C\textsubscript{3}N\textsubscript{4} photocatalysis as well. For example, g-C\textsubscript{3}N\textsubscript{4}@poly(ethylene terephthalate) nanofibers was fabricated using poly(ethylene terephthalate) as a support and polyethylene glycol (PEG) as a porogen via electrospinning,\textsuperscript{113} which is beneficial for catalyst-substrate contact. This work demonstrated high photocatalytic activity for the degradation of antibiotics such as sulfamethazine and sulfadiazine under solar irradiation. Polyester fibers (from poly(ethylene terephthalate)) were utilized to support cellulose (CA) containing nanosheet g-C\textsubscript{3}N\textsubscript{4} in another work as well,\textsuperscript{114} aerogel g-C\textsubscript{3}N\textsubscript{4}@CA/poly(ethylene terephthalate) for enhanced photocatalytic activity towards the removal of hexavalent chromium and antibiotics, simultaneously. Chen and coworkers used poly(ethylene terephthalate) as support for g-C\textsubscript{3}N\textsubscript{4} via electrospinning and subsequently hydrothermal treatment, which enabled the exposure of g-C\textsubscript{3}N\textsubscript{4} on the poly(ethylene terephthalate) surface, avoided aggregation and improved recyclability.\textsuperscript{115} Low melting sheath-core composite polyester fibers were immobilized with g-C\textsubscript{3}N\textsubscript{4} to induce recyclability as well as enhanced photocatalytic degradation capability.\textsuperscript{116}

**g-C\textsubscript{3}N\textsubscript{4}/polymer hybrids as photocatalysts for sterilization**

The combination of polymers and g-C\textsubscript{3}N\textsubscript{4} for sterilization leads to improved antibacterial performance. In addition to the antibacterial properties of g-C\textsubscript{3}N\textsubscript{4},\textsuperscript{117} polymer fibers improve recyclability and antibacterial ability as well. Zhang and coworkers fabricated self-cleaning and antibacterial membranes via filtering g-C\textsubscript{3}N\textsubscript{4} nanosheets onto PAN porous substrates.\textsuperscript{118} The membrane showed high water permeability (11.7 L·m\textsuperscript{-2}·h\textsuperscript{-1}) and good antibacterial activity. Moreover, the g-C\textsubscript{3}N\textsubscript{4}/PAN membrane preserved its original permeability, e.g. rejecting dyes, and the surface was close to its initial color after three cycles via post treatment under visible light irradiation. A poly(ether sulfone) (PES) microfiltration membrane was combined with g-C\textsubscript{3}N\textsubscript{4} and Ag\textsubscript{3}PO\textsubscript{4} by Vatanpour and coworkers.\textsuperscript{119} Significant antifouling behavior was observed that was ascribed to the synergistic effects of photocatalytic activity, hydrophilicity and porosity.

**g-C\textsubscript{3}N\textsubscript{4}/polymer hybrid materials for biosensors**

Although the functionalization of g-C\textsubscript{3}N\textsubscript{4} hybrids has been widely investigated, the applications of g-C\textsubscript{3}N\textsubscript{4} in the field of sensing are still in the initial stage. Since the first report of the cathodic electrochemiluminescence (ECL) behaviors of g-C\textsubscript{3}N\textsubscript{4} nanosheets,\textsuperscript{120} it has attracted an increasing attention as a promising luminophore candidate for ELC biosensor systems. Especially as g-C\textsubscript{3}N\textsubscript{4} possesses many favorable advantages, such as non-toxicity, excellent biocompatibility, high thermal and chemical stability,\textsuperscript{53, 121} polymer functionalized g-C\textsubscript{3}N\textsubscript{4}s are investigated for improving the sensitivity and selectivity of ECL sensors. A combination of g-C\textsubscript{3}N\textsubscript{4} with phenoxy dextran (DexP) and bovine serum albumin was applied to obtain an ECL sensor for concanavalin A by Wei and coworkers.\textsuperscript{122} In this study, DexP and g-C\textsubscript{3}N\textsubscript{4} nanocomposites were fabricated via simple overnight stirring to induce physical adsorption via \pi–\pi stacking between g-C\textsubscript{3}N\textsubscript{4} and DexP. Later, biosensor performance was investigated, and it was shown that the DexP@g-C\textsubscript{3}N\textsubscript{4} composites not only serve as an excellent ECL signal probe, but also form specific carbohydrate-Con A interaction, which demonstrated a novel sandwich-type scheme with a signal-on ECL detection strategy. Chen and coworkers introduced PANI to the g-C\textsubscript{3}N\textsubscript{4} sheet structure by an in situ deposition oxidative polymerization using APS as initiator, then gold nanoparticles (AuNF) were in situ formed on the g-C\textsubscript{3}N\textsubscript{4}-PANI composite to achieve the AuNF@g-C\textsubscript{3}N\textsubscript{4}-PANI composite hydrogel.
The hybrid components were utilized for ECL biosensor construction, showing high sensitivity and low limit of detection for dopamine. Hence the sensors might be a potential material for determination of dopamine in the field of clinical disease diagnosis. Kim and coworkers attached cylindrical spongy shaped PPy onto protonated g-C₃N₄ (g-C₃N₄H⁺) in situ using oxidative polymerization. Cholesterol oxidase (ChOx) were immobilized on the as-prepared nanohybrids to construct cholesterol biosensor electrodes. Various features were demonstrated, e.g. long-term stability and good selectivity for cholesterol detection during electrochemical characterization. Wei and coworkers presented a CdS/PPy/g-C₃N₄ aptasensor for adenosine detection. Therefore, a SH-aptamer was adsorbed on CdS/PPy/g-C₃N₄ modified electrodes that formed bioaffinity complexes with adenosine. The readout of photocurrent changed according to adenosine concentration in a linear fashion in the range of 0.3 nmol L⁻¹ to 200 nmol L⁻¹.

**g-C₃N₄/polymer nanocomposites applied in electrochemical energy storage and solar cells**

Electrochemical energy storage and energy generation is one of the major current research areas. Hence, also g-C₃N₄ has found its way into materials for fuel cells, batteries and solar cells. Fuel cells are one of the main devices that can convert chemical into electrical energy. In particular, polymer electrolyte membrane fuel cells (PEMFCs) are of interest for electrochemistry and polymer chemistry. Commonly utilized polymers include poly(benzimidazole) (PBI),¹²⁶ poly(vinyl pyrrolidone) (PVP),¹²⁷ PVP-poly(vinyl alcohol) (PVP-PVA)¹²⁸ or PVP-PES.¹²⁹ However, PEMFC research faces several challenges. For example high cost, low durability and degradation of PEMFCs, which are due to the instability of membrane materials, seriously inhibit the widespread utilization of the technique.¹³⁰,¹³¹ Regarding these challenges, researchers introduced g-C₃N₄ nanosheets to the polymer matrix.¹³² One particular reason to employ a combination with g-C₃N₄ is its decent thermal stability with chemical bond energy of C-N and C=N of 305 KJ·mol⁻¹ and 615 KJ·mol⁻¹, respectively.¹³³ Another reason is that the amino (-NHₓ) and imino (-NH) groups of g-C₃N₄ can interact with acid groups in the polymer matrix, which leads to enhancement of the Grotthuss-mechanism proton transfer. For instance, Zhou and coworkers blended PVP-phosphonated-poly(2,6-dimethyl-1,4-phenylene oxide) (PVP/pPPO) with g-C₃N₄ nanosheets via a solution casting method,¹³⁴ by mixing a certain amount of g-C₃N₄ in 70% PVP/pPPO solution, then the solution was casted onto a glass plate to obtain the nanocomposite membranes. Improved proton conductivity and mechanical properties were realized due to the proton accepting sites provided by NH₂ and the interaction of g-C₃N₄ with polymer chains, thus leading to higher proton conductivity (74.4 mS·cm⁻¹) and power density (294 mW·cm⁻²) at 180 °C with a content of g-C₃N₄ nanosheets of 5 wt%.

To improve the proton conductivity of PA doped PES-PVP membrane material, Lu and coworkers introduced g-C₃N₄ nanosheets to the polymer composites matrix through a blending method (Figure 5).¹³⁵ The as-prepared nanocomposites have shown a significantly improved proton conductivity of 0.104 S·cm⁻¹ and power density of 512 mW·cm⁻² with 0.5% content of g-C₃N₄. Meanwhile, due to the physical reinforcement effect of 2D g-C₃N₄ nanosheets, the mechanical properties of the composite membranes were enhanced compared to PES-PVP without g-C₃N₄. Jiang and coworkers introduced g-C₃N₄ nanosheets to sulfonated poly(ether ether ketone) composites (SPEEK),¹³⁶ exhibiting a 68% increase of tensile strength of nanocomposite membranes with g-C₃N₄ content of 0.5 wt% due to the intrinsic mechanical stability of g-C₃N₄ nanosheets and favorable interfacial interactions of g-C₃N₄ nanosheets with the SPEEK matrix. The g-C₃N₄/SPEEK composites were applied to PEMFCs demonstrating a 39% increase in maximum powder density at a g-C₃N₄ content of 0.5 wt%.

**Other energy storage devices such as vanadium redox flow battery (VRB), lithium metal batteries and supercapacitors**

Lithium metal batteries and supercapacitors were also combined with g-C₃N₄ for improved stability and battery efficiency. Particularly, for VRB, sulfonated aromatic polymers such as SPEEK,¹³⁶ sulfonated poly (sulfone) (SPSF)¹³⁷ or sulfonated polyimide (SPI)¹³⁸ are widely used for fabrication of membranes due to excellent proton conductivity and mechanical properties. However, improved proton conductivity and ion selectivity are still required. Incorporation of g-C₃N₄ regulates the interfacial interaction of the membrane materials, thus the ion selectivity, and vanadium ion permeation and structure stability could be effectively controlled.¹³⁹,¹⁴₀ Xiang and coworkers introduced g-C₃N₄ nanosheets into a Nafion matrix membrane to reduce vanadium ion crossover (Figure 6a).¹⁴² Crosslinking interaction between Nafion matrix and g-C₃N₄ nanosheets efficiently induced the shrinkage of the Nafion membrane (Figure 6b, c), resulting in a lamellar structure, thus the vanadium ion crossover is significantly reduced. An improved coulombic efficiency of 97% and energy efficiency of 85% at a current density of 80 mA cm⁻² was achieved (Figure 6d). Moreover, Li and coworkers proposed a lightweight polymer-reinforced electrolyte based on g-C₃N₄ mesoporous microspheres as electrolyte filler in lithium metal batteries.¹⁴³ Due to the high mechanical strength and nanosheet-built hierarchical structure of g-
C₃N₄, this electrolyte can effectively suppress lithium dendrite growth during cycling. The Li/Li symmetrical cell based on this electrolyte exhibited a long-term cycling of at least 120 cycles with a high capacity of 6 mAh/cm². Additionally, g-C₃N₄ was embedded onto conductive polymers as an efficient electrode material for supercapacitors to improve electrochemical and mechanical stability. Yang and coworkers prepared a novel electrode material for supercapacitors composed of poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrenesulfonate) (PSS) and g-C₃N₄ by the layer-by-layer assembly method. Compared with pure PEDOT, the PEDOT/ g-C₃N₄ composite demonstrated excellent electrochemical stability in neutral electrolyte and enhanced electrochemical performance of capacitance of 137 F·g⁻¹ in H₂SO₄ and 200 F·g⁻¹ in Na₂SO₄, respectively.

Additionally, several studies reported the combination of g-C₃N₄ with polymers for solar cell utilization. Yang and coworkers for the first time introduced g-C₃N₄ quantum dots (C₃N₄QDs) into the active layer of bulk-heterojunction (BHJ) polymer solar cells (PSCs). Solution-processable C₃N₄QDs were prepared by acid treatment of bulk g-C₃N₄, followed by a solvothermal treatment. Finally, they were doped to the active layers of the PSC with a doping ratio of 0.2 mg·mL⁻¹. The different active layers of the C₃N₄QDs doped BHJ-PSC device demonstrated an obvious enhancement of power conversion efficiencies of 17.5%, 11.6% and 11.8%, respectively, compared to that of Re-Nafion membranes. d) Single battery efficiency performance. Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) at current densities of 80–200 mA cm⁻² of the Vanadium redox flow battery (VRB) with the Re-Nafion membrane and the commercial Nafton 212 membrane [Reprinted with permission. Copyright 2018 Royal Society of Chemistry].

Figure 6. a) Proton and vanadium ion transport behaviors of the Re-N/CN(x) composite membrane. b) Tensile strength and c) swelling ratio of the composite Re-N/CN(x) membranes with various amounts of g-C₃N₄ nanosheets compared to that of Re-Nafion membranes. d) Single battery efficiency performance. Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) at current densities of 80–200 mA cm⁻² of the Vanadium redox flow battery (VRB) with the Re-Nafion membrane and the commercial Nafton 212 membrane [Reprinted with permission. Copyright 2018 Royal Society of Chemistry].
alginate (SA) nanocomposite films with different g-C$_3$N$_4$ loadings. This led to significant changes in surface hydrophilicity as shown via contact angle measurements after film formation.

Another work in our group fabricated a g-C$_3$N$_4$-based polymer thermosts coating, and thicker films were obtained via a prepolymer route, which is similar to already discussed g-C$_3$N$_4$-PDMA prepolymer. In this case, a prepolymer of PHEMA on g-C$_3$N$_4$ was formed in EG/water mixture, which led to the formation of a viscous precursor material composed of PHEMA grafted g-C$_3$N$_4$, EG and water. The viscosity of the precursor was tuned in a way that injectable material was obtained. As such, the precursor could be applied to various surfaces, including PS, wood and copper, with spatial control. After addition of citric acid and film formation on a glass slide, crosslinking was performed via heating. The so-formed thermosts formed smooth hydrophobic coatings that could be used for further processing. As the g-C$_3$N$_4$ in the coating retains its photoactivity, PDMA or PS could be modified to the surface via the “grafting from” method to tailor the surface polarity, as shown via contact angle measurements. Moreover, the photoactive surfaces could be used in dye degradation experiments as well as photoelectrochemistry.

g-C$_3$N$_4$/polymer nanoparticle composites
A very common and useful structure in polymer and materials science are latexes based on nanoparticles. Therefore, research regarding the introduction of g-C$_3$N$_4$ into or onto polymer particles is another major topic. As it was found that g-C$_3$N$_4$ can act as...
emulsifier to stabilize oil in water (o/w) emulsions,\textsuperscript{30, 158} one way to fabricate g-C\textsubscript{3}N\textsubscript{4}/polymer nanoparticles is to utilize g-C\textsubscript{3}N\textsubscript{4} as stabilizer in a Pickering emulsion polymerization.\textsuperscript{159} The approach was utilized by Li and coworkers to form g-C\textsubscript{3}N\textsubscript{4} based latexes.\textsuperscript{53} Pickering emulsion polymerization was conducted using g-C\textsubscript{3}N\textsubscript{4} as stabilizer and potassium persulfate (KPS) as initiator. Hence, monodisperse polystyrene (PS) microspheres with tunable size down to the 100 nm diameter region, surface charge and morphology were obtained. Herein, g-C\textsubscript{3}N\textsubscript{4} located in the continuous phase and adhered to the monomer droplet surface forming a network structure preventing the emulsion from coalescence. The as-prepared PS/g-C\textsubscript{3}N\textsubscript{4} possessed photoluminescence properties owing to the existence of g-C\textsubscript{3}N\textsubscript{4} sheets, and both g-C\textsubscript{3}N\textsubscript{4} and PS latex showed excellent biocompatibility during standard MTT assays. Nanoparticles were incubated with HeLa cells for 12 h and observed with confocal laser scanning microscopy, showing that the particles were internalized by HeLa cells, indicating that the fluorescent PS/g-C\textsubscript{3}N\textsubscript{4} hybrid particles are promising materials for bioimaging. Recently, sialic acid (SA) was introduced into the g-C\textsubscript{3}N\textsubscript{4} polymerization system, which is an important indicator of some certain cancers. The g-C\textsubscript{3}N\textsubscript{4} contained and SA-imprinted polymer nanoparticles exhibited good biocompatibility and excellent targeted image of DU 145 cells (SA-overexpressed surface).\textsuperscript{159}

Additionally, as discussed in Section 2, g-C\textsubscript{3}N\textsubscript{4} can effectively produce radical species under visible light irradiation, thus polymerization can be conducted on g-C\textsubscript{3}N\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4}/polymer nanocomposites can be obtained. For example, Weber and coworkers reported the formation of g-C\textsubscript{3}N\textsubscript{4}-based PBA composites via an aerosol polymerization process (Figure 8a).\textsuperscript{160} Spherical mesoporous g-C\textsubscript{3}N\textsubscript{4} (SMCN) was initially prepared with mesoporous silica nanoparticles as template (Figure 8b), then gas phase monomer was continuously added and polymerized in proximity of g-C\textsubscript{3}N\textsubscript{4} via photoinitiation under UV light irradiation. Later, spherical g-C\textsubscript{3}N\textsubscript{4}/polymer composite particles (Figure 8c) were obtained without solvent or surfactant. Such a strategy is suitable for fabrication of spherical nanocomposites with hydrophobic polymers. The as-prepared mesoporous CN acts not only as photoinitiator but also as filler and template.

Very recently, our team attempted to utilize g-C\textsubscript{3}N\textsubscript{4} as emulsifier and photoinitiator at the same time to conduct emulsion photopolymerization.\textsuperscript{58} Herein, the emulsion photopolymerization of styrene was studied with non-functionalized g-C\textsubscript{3}N\textsubscript{4} latexes which lead to PS latexes with particle diameters around 170 nm. Nevertheless, no satisfying MMA latexes could be obtained that way albeit benzyl methacrylate (BMA) formed latexes with narrow particle sizes. Apparently, the monomer structure has a significant impact on the polymerization process, i.e. the interactions of monomer and g-C\textsubscript{3}N\textsubscript{4} seem to play a significant role to create the particle nucleation site. It is very likely that styrene and BMA feature enhanced interactions with g-C\textsubscript{3}N\textsubscript{4} due to π-π interactions, while MMA interacts to a lesser extent. Notably, the utilization of decene-functionalized g-C\textsubscript{3}N\textsubscript{4} enabled the formation of PMMA latexes, probably due to the improved interaction of the initiating stabilizer with the monomer. The formed latexes feature polymer particles that incorporated g-C\textsubscript{3}N\textsubscript{4} and were crosslinked directly. The specific location of g-C\textsubscript{3}N\textsubscript{4} was investigated, demonstrating that g-C\textsubscript{3}N\textsubscript{4} nanosheets ranging from 50-100 nm appeared to be inside of the latex with STEM tilt observation, and small pieces attached outside of latexes with a negative surface charge grants a stable emulsion latex/ g-C\textsubscript{3}N\textsubscript{4} composite. The combination of the traditional PS latex with the outstanding features of environmentally friendly g-C\textsubscript{3}N\textsubscript{4} provides novel polymer composites with multifunctional modern applications, e.g. in bioimaging or 3D printing.

Figure 8. a) Initiation mechanism of the photopolymerization using spherical mesoporous g-C\textsubscript{3}N\textsubscript{4} (SMCN) in the presence of the methyl diethanolamine (MDEA) as co-initiator. b) SEM image of SMCN replicas. c) SEM image of PBA-SMCN composites produced by aerosol-photopolymerization. (Reprinted with permission.\textsuperscript{160} Copyright 2016 American Chemical Society).

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Table 1. Polymer modified g-C\(_3\)N\(_4\) and their applications.

| Application area                      | Composition                              | Synthesis methods         | Enhanced properties                                                                 | Reference |
|----------------------------------------|------------------------------------------|----------------------------|-------------------------------------------------------------------------------------|-----------|
| Hydrogen evolution                     | PSSH/PU/g-C\(_3\)N\(_4\)/Au             | Self-assembly              | Efficient charge transfer, improved H\(_2\) evolution rate (320 µmol h\(^{-1}\))     | 140       |
| Hydrogen evolution                     | PP/g-C\(_3\)N\(_4\)                      | Ultrasonic                 | Efficient charge transfer, 50 times over g-C\(_3\)N\(_4\)                           | 96        |
| Hydrogen evolution                     | PANI/g-C\(_3\)N\(_4\)                    | Thermal condensation       | Efficient charge transfer, 37 µmol h\(^{-1}\) (H\(_2\) evolution rate), 3.8 times over g-C\(_3\)N\(_4\) | 96        |
| Hydrogen evolution                     | P3HT/g-C\(_3\)N\(_4\)                   | Physical absorption        | Efficient charge transfer, 300 times over g-C\(_3\)N\(_4\)                         | 96        |
| Degradation of MB                     | PANI/g-C\(_3\)N\(_4\)/EDD               | In-situ polymerization     | Efficient charge transfer, 3.6 and 3.2 times over pristine g-C\(_3\)N\(_4\)         | 90        |
| Degradation of MB                     | PANI/g-C\(_3\)N\(_4\)                   | In-situ polymerization     | Efficient charge transfer, 5.1 times over g-C\(_3\)N\(_4\)                         | 127       |
| Degradation of MB                     | PANI/SP-g-C\(_3\)N\(_4\)(sulfur and phosphorous doped g-C\(_3\)N\(_4\)) | In-situ polymerization     | Efficient charge transfer, synergistic effect, maximum degradation (99.9%)          | 108       |
| Degradation of RHB                    | PAN nanofibers/ g-C\(_3\)N\(_4\)         | Electrospinning            | Prevent agglomeraton of powder g-C\(_3\)N\(_4\)                                  | 110       |
| Oil and organic solvent capture       | Acrylic resin/g-C\(_3\)N\(_4\)           | In-situ polymerization     | Improved capillary and penetration interaction for oil absorption, -33.5 g g\(^{-1}\) (toluene), -20.6 g g\(^{-1}\) (DMSF), 15 wt% (MCHN) | 115       |
| CO\(_2\) reduction                    | 3H,1H,2H,2H perfluorodecanethiol/PGMA/g-C\(_3\)N\(_4\) | Photoinduced chemical reaction | Improved mass transfer of CO\(_2\) by 34 times                                     | 97        |
| CO\(_2\) reduction                    | Polymeric cobalt phthalocyanine/mpg/ C\(_3\)N\(_4\) | In-situ polymerization     | Efficient charge transfer                                                          | 96        |
| Eliminating antibiotics               | Poly(ethylene terephthalate) nanofoils/g-C\(_3\)N\(_4\) | Electrospinning            | Increased active sites, improved mass transfer and light absorption                | 113       |
| Eliminating hexavalent chromium and antibiotics | Cellulose aerogel/polyester fibers/g-C\(_3\)N\(_4\) | Blending                   | Improved mechanical strength and higher impact resistance                           | 114       |
| Degradation of tetracycline (TC) hydrochloride | Polyester fiber/g-C\(_3\)N\(_4\) | Hot-melt adhesive          | Improved contact to contaminants, recycling performance and structural stability    | 116       |
| Electrochemiluminescence biosensor    | Denv/g-C\(_3\)N\(_4\)                    | Blending                   | Wider linear response range (0.05 ng/mL to 100 ng/mL), lower detection limit (17 pg/mL) | 117       |
| Electrochemiluminescence biosensor    | AuNF@PANI/g-C\(_3\)N\(_4\)               | In-situ polymerization     | lower limit of detection (1.7 × 10\(^{-9}\) M)                                    | 122       |
| Electrochemiluminescence biosensor    | PPV/g-C\(_3\)N\(_4\)                    | In-situ polymerization     | Improved electro-conductive network, high sensitivity (645.7 µA·cm\(^{-2}\)) and lower detection limit (8.0 µM) | 124       |
| Fuel cell                             | Poly(arylene ether ketone)s/ g-C\(_3\)N\(_4\) | Blending                   | Improved anion exchange, ionic conductivity, alkaline resistance and methanol permeability | 144       |
| Proton exchange membrane for fuel cells | PVP-phosphonated poly(1,6-dimethyl-1,4-phenylene oxide)/g-C\(_3\)N\(_4\) | Solution casting          | Improved proton conductivity (74.4 mS·cm\(^{-1}\)) and mechanical properties        | 139       |
| Proton exchange membrane for fuel cells | PES-PVP/g-C\(_3\)N\(_4\)                 | Blending                   | Improved proton conductivity (0.104 S·cm\(^{-1}\)) and power density (512 mW·cm\(^{-2}\)) | 124       |
| Direct methanol fuel cells            | Nafion/g-C\(_3\)N\(_4\)                  | Blending                   | Enhances movement of hydronium ions                                               | 145       |
| Direct methanol fuel cells            | SPEEK/g-C\(_3\)N\(_4\)                   | Solution-casting           | Enhanced movement of hydronium ions                                               | 145       |
| Vanadium redox flow battery           | SPEEK/g-C\(_3\)N\(_4\)                   | Solution-casting           | Higher coulombic efficiency and improved cycling stability                          | 146       |
| Vanadium redox flow battery           | SPEEK/g-C\(_3\)N\(_4\)                   | Solution-casting           | Higher coulombic efficiency and improved structure stability over 300 charge-discharge cycles | 141       |
| Vanadium redox flow battery           | Nafion/g-C\(_3\)N\(_4\)                  | Blending                   | Higher coulombic efficiency and energy efficiency                                  | 142       |
| Lithium metal batteries               | Bis(trifluoromethanesulfonimide) lithium salt/di(ethylene glycol) dimethyl ether/g-C\(_3\)N\(_4\) | Blending                   | Improved mechanical strength, interfacial resistance and battery stability          | 142       |
| Supercapacitors                       | Camphor sulfonic acid/poly carbonate/g-C\(_3\)N\(_4\) | Chemical oxidative polymerization | Improved charge transfer and structure stability (over 1000 cycles)                | 144       |
| Supercapacitors                       | Cellulose/PPy/tubular g-C\(_3\)N\(_4\)   | Self-assembly              | Improved specific capacitance (158 F g\(^{-1}\))                                 | 145       |
| Supercapacitors                       | PANI/g-C\(_3\)N\(_4\)                   | In-situ polymerization     | Improved specific capacitance (797.8 F g\(^{-1}\)) and capacitance retention (84.4%) | 146       |
| Supercapacitors                       | PEDOT-PSS/g-C\(_3\)N\(_4\)               | Self-assembly              | Improved specific capacitance, 137 F g\(^{-1}\) (H\(_2\)SO\(_4\)) and 200 F g\(^{-1}\) (Na\(_2\)SO\(_4\)) Improved cycling stability | 142       |
| Solar Cells                           | Bulk-heterojunction polymer/g-C\(_3\)N\(_4\) | Blending                   | Enhanced power conversion efficiencies, improved active layer conductivity and charge transfer | 149       |
4.3 Improved properties of polymer materials via combination with g-C$_3$N$_4$

It is reported that hybridizing g-C$_3$N$_4$ and polymers on one side significantly improves surface and photocatalytic properties of g-C$_3$N$_4$, on the other side also enhances the thermal and mechanical properties of polymers as well as surface properties.\textsuperscript{162-164} Few studies reported that the introduction of g-C$_3$N$_4$ to mechanical properties of polymers.\textsuperscript{165} Myllymaa and coworkers deposited Si-doped CN (CN-Si) on poly(propylene) (PP) disc samples via pulsed laser deposition.\textsuperscript{166} The coating of CN-Si can significantly converted the PP surface from being hydrophobic to hydrophilic, leading to enhanced adherence of Saos-cells on PP. Hu and coworkers reported a mix of PP-grafted maleic anhydride (PP-g-MA) with g-C$_3$N$_4$ by refluxing the mixture for 4 hours in xylene.\textsuperscript{167} It was reported that the incorporation of g-C$_3$N$_4$ with PP-g-MA significantly improved the storage modulus, i.e. 2445 MPa for neat PP-g-MA and 2784 MPa for pp-g-MA/ g-C$_3$N$_4$, respectively. Moreover, optical results showed that the hybrid materials possessed fascinating UV absorption. Cai and coworker introduced g-C$_3$N$_4$ as reinforcing filler for wood plastic compositions (WPCs), pp-g-MA was added as a coupling agent to increase the interaction between different components.\textsuperscript{168} The tensile modulus indicating an increase of 143\% with g-C$_3$N$_4$ contents of 5\% and, the thermal tests demonstrated that the degradation temperature shifted to higher values after g-C$_3$N$_4$ addition. Lin and coworker fabricated g-C$_3$N$_4$/poly(vinyl alcohol) (PVA) nanocomposites by solution casting using water as solvent, demonstrating that the g-C$_3$N$_4$ could be well dispersed in PVA matrix.\textsuperscript{169} The introduction of g-C$_3$N$_4$ nanosheets increased the glass transition temperature and crystallinity of the nanocomposites, leading to improved mechanical performance with ~71\% enhancement of tensile strength.\textsuperscript{169} Very recently, Guo and coworker synthesized g-C$_3$N$_4$ on carbon fiber surfaces in-situ in order to enhance interfacial properties of carbon fiber reinforced epoxy resin composites.\textsuperscript{170} The g-C$_3$N$_4$ on the carbon fiber surface greatly increased the roughness, the content of polar functional groups and wettability of carbon fibers. Thus, significant enhancement of interfacial properties of the composites was obtained.

5. Carbon Nitride-based Hydrogels

Hydrogels constitute an important class of polymeric materials due to their unique features such as swelling properties, soft character while being shape persistent.\textsuperscript{171} Consisting of a crosslinked hydrophilic network, hydrogels contain significant amounts of water. Their similarity to natural tissues is another important point for the frequent investigation of hydrogels, especially when biomedical applications like tissue-engineering or drug-delivery are targeted.\textsuperscript{172, 173} Other discussed applications comprise actuators,\textsuperscript{174} self-healing,\textsuperscript{175} absorption of contaminants\textsuperscript{176} or shape-memory materials.\textsuperscript{177} Commonly, hydrogels possess rather weak mechanical properties but research has introduced reinforced hydrogels with partly extraordinary properties. For that, several methods are utilized, e.g. double network hydrogels,\textsuperscript{178, 179} topological (slide-ring) gels,\textsuperscript{180, 181} nanofiber reinforced hydrogels\textsuperscript{182} or the introduction of charged supports.\textsuperscript{183-185} Especially, the introduction of particles as reinforcing provides increased stress dissipation, in some cases charge–charge repulsion between the single filler particles or sheets leads to an additional stabilization especially against compression.\textsuperscript{20} One common example are clay nanosheets that combine ionic interaction and hydrogen bonding with polymeric chains acting as additional crosslinking points.\textsuperscript{186-188}
based hydrogels retain the photocatalytic properties of g-C$_3$N$_4$, which allows utilization in contaminant degradation or H$_2$ evolution (Section 5.2). Besides the formation of hydrogels via covalent bonds, g-C$_3$N$_4$ can be utilized in supramolecular hydrogels as well as blended into hydrogel scaffolds to improved mechanical properties for instance, which is discussed in Section 5.3.

5.1 Hydrogels with tailored mechanical properties

It was already stated that the photoactive properties of g-C$_3$N$_4$ enable the formation of radicals in aqueous dispersion.\textsuperscript{190} Thus, after addition of monomer and crosslinker, hydrogels can be formed with greatest ease via visible light irradiation (Scheme 5a). For example, water-soluble acrylamide-derivatives can be utilized, which feature fast gelation rates and a broad spectrum of functionalities. g-C$_3$N$_4$ then indeed does not only act as photoinitiator but also as reinforcer. The reinforcement effect is due to the lateral extension of the g-C$_3$N$_4$ sheets that dissipate mechanical stress throughout the network and thus improve mechanical properties, very similar as the previously mentioned clay nano sheets.

As a first example our group employed DMA and N,N’-methylene bisacrylamide (MBA) with a dispersion of 0.6 wt.% CM in water for hydrogel formation.\textsuperscript{191} Hydrogels were obtained after several hours of visible light irradiation. Notably, the hydrogels retained the photocatalytic properties of g-C$_3$N$_4$. In addition, remarkable mechanical properties were observed, such as super-stretchability or being very hard and flexible at the same time. Such behavior opens up a completely new field of applications. In the next step the mechanical properties and origin of gel formation were studied in more detail (Figure 9).\textsuperscript{54} To investigate the role of g-C$_3$N$_4$ in the network formation, control reactions were performed, i.e. hydrogel formation with a common photoinitiator without g-C$_3$N$_4$ (Figure 9a), which lead to very weak hydrogels. Furthermore, hydrogelation employing g-C$_3$N$_4$ without external crosslinker and non-nitrogen containing monomers was investigated as well. Indeed, hydrogelation took place even without addition of external crosslinker, which indicates the incorporation of g-C$_3$N$_4$ into the network. Moreover, hydrogels could be formed from non-nitrogen containing monomers and crosslinkers, which indicates that the reaction is not dependent on radical transfer from g-C$_3$N$_4$ to amines as instrumentalized in various other reactions.\textsuperscript{56, 57} Moreover, remarkable mechanical properties were obtained ($G'$ up to 8.3 kPa at solid contents of 11 wt.%) (Figure 9c). One reason is the particular structure of g-C$_3$N$_4$ that acts as colloidal filler via formation of a secondary network of inorganic sheets inside of the hydrogel providing additional structure to the structure. In addition, g-C$_3$N$_4$ introduces additional crosslinking points, which strengthens the hydrogel further. This effect could be analyzed via a control experiment of hydrogel formation in g-C$_3$N$_4$ dispersion but with redox initiation in the absence of light (Figure 9b). Compared to a reference sample without g-C$_3$N$_4$, improved mechanical properties were found albeit the mechanical properties from visible light g-C$_3$N$_4$ mediated hydrogels were not reached. Thus, both reinforcement via inorganic secondary network as well as via additional crosslinking points are important. The fabricated hydrogels showed a significant shear thinning effect. Such an effect is common to reinforced hydrogels as shear leads to alignment of the polymer network as well as g-C$_3$N$_4$ particles, and such ordering is weakening the g-C$_3$N$_4$-g-C$_3$N$_4$ interactions.
Liu and coworkers showed the formation of a g-C₃N₄/NIPAM hydrogel. A hydrogel was formed via visible light mediated photopolymerization albeit no external crosslinker was added. The NIPAM-based hydrogels showed thermostressive properties. For example, the viscosity, storage and loss modulus of the obtained hydrogels decreased until the lower critical solution temperature (LCST) of PNIPAM and increased again above the LCST. Moreover, the authors could form the hydrogels in specific patterns that changed transparency reversibly according to temperature (Figure 9d). Farzaneh and coworkers physically incorporated g-C₃N₄ into acrylamide hydrogels for gel electrophoresis via a redox polymerization of AAm and MBA. Due to the thermal conductivity of g-C₃N₄, Joule heating in the hydrogels was reduced and band broadening in the electrophoresis was lowered. Moreover, the presence of g-C₃N₄ allowed to refrain from utilization of tetramethyl ethylenediamine as polymerization catalyst, which can be a disadvantage for some analytes.

As g-C₃N₄ provides the opportunity to modify the surface charge (zeta potential), surface area and light absorption via variation in the precursor composition, effects of the precursor composition on mechanical properties were investigated as well. Notably, the zeta potential had a profound effect on storage modulus. It was found that stronger negative zeta potential g-C₃N₄ compounds led to stronger hydrogels. Such an effect can be explained by g-C₃N₄ sheet repulsion that increases with more negative zeta potentials. A similar effect was already described in the literature for other reinforcing particles. The effect of surface charge was further investigated by our group employing AHPA-modified g-C₃N₄, which features significantly lower zeta potentials and high dispersibilities due to the sulfonic acid group. A mixture of AAm, DMA and MBA were used as monomers together with CM-AHPA as initiator. The hydrogels obtained were rather soft with G’ in the range of 100-200 Pa and contained solid contents below 10 wt.%. However, the hydrogels featured remarkable compression properties, e.g. withstand loads above 12 MPa (Figure 10) and resisted multiple hits with a hammer. Probably, the extreme compressibility is due to the fact that the gels contained highly negatively charged g-C₃N₄, which shows significant repulsion of the g-C₃N₄ sheets in compression. In addition, the gels were soft and could dissipate the compressive force over the whole structure by electrostatic coupling. Compression led to a complete flattening of the structure and a return to the initial shape after release of the force. In order to get further insights into the origin of the remarkable compression properties, hydrogels were formed from the individual monomers with MBA. It was found that the DMA-based hydrogels were stronger but less compression resistant, while the AAm-based hydrogels were weaker but more resistant to compression. Swelling the AAm/DMA hydrogels with salt solution (NaCl or CaCl₂) showed increased strength but less compressibility, which might be due to the screening of the negative charges on the g-C₃N₄ surface. Hence, the surface charge of g-C₃N₄ is certainly the main reason for the enhanced compressibility, while the monomer mixture supports compressibility due to enhanced elasticity, which leads to improved distribution of the stress in the network.

Regarding the mechanical properties of the hydrogels, not only the charge on the g-C₃N₄ matters but also the amount of incorporated g-C₃N₄. Therefore, EG/water mixtures were used to increase the amount of non-functionalized g-C₃N₄ during hydrogel formation. Incorporating g-C₃N₄ contents up to 4 wt.% led to hydrogels with G’ of 88 kPa for 2 wt.%, 430 kPa for 3 wt.% and 729 kPa for 4 wt.% of g-C₃N₄ at 0.1% strain, which is a remarkable increase of two orders of magnitude compared to the first hydrogels with 0.6 wt.% g-C₃N₄. In addition to enhanced mechanical performance, hydrogelation was much faster with higher g-C₃N₄ content which proves g-C₃N₄ acts as photoinitiator. As the hydrogel formation is photoinitiated, patterning was investigated as well. For that, parts of the reaction mixture were covered with a photomask to obtain an inversely pattered hydrogel. The success of such experiments also proves that there is no significant radical transfer to dark area (solution) and the polymerization takes place only in the illuminated area via g-C₃N₄ initiation. In order to enable the fabrication of hydrogels with a broader range of monomers our group utilized g-C₃N₄-PDMA prepolymer formed in EG/water mixture without crosslinker as charged monomers could not be employed. With prepolymer, hydrogels from 3-sulfopropyl methacrylate potassium salt (SPMA) and DMA could be obtained. The SPMA monomer introduces negative charges into the hydrogel structure, which is a useful feature for low friction surfaces. Hence, hydrogels with both very low friction coefficients (around
0.03) and remarkable compression properties due to g-C₃N₄ incorporation were obtained. This combination of properties is rather uncommon and challenging to achieve but of particular interest for applications, e.g. in artificial cartilage.

Figure 11. Spatially controlled photopolymerization for gel formation: a) formation of a self-standing half-circle, b) self-standing club shape and c) photopatterning of stripes on a glass slide (Licensed under CC-BY).

5.2 Utilization of photophysical properties

The incorporation of g-C₃N₄ into hydrogels occurs under retention of its photophysical properties in the dispersed state inside of the network. As such, various properties are accessible, e.g. photocatalysis or water contaminant degradation. Dong and coworkers obtained acrylamide-based hydrogels for "light filtering" applications. AAm was utilized as monomer in a visible light induced polymerization. Due to the hydrogen bonding interactions between g-C₃N₄ and PAAm in the hydrogel self-healing was observed after cutting the hydrogel. Similar mechanical properties (compression and tensile) were observed before and after healing. The hydrogels featured high photostability and could be utilized for UV shielding due to the broad absorption of g-C₃N₄ in the gel. For example, for UV-A, UV-B and UV-C a transmittance of 0 to 28% was observed, while at 550 nm a transmittance of 89% was measured.

Thus, these gels might be used as sun-light blockers. Shalom and coworkers formed g-C₃N₄-based hydrogels for photocatalytic applications (Figure 12a). For example dye degradation reactions could be performed easily. Several dyes were probed as reference compounds for other impurities in water waste. Depending on the type, absorption in the gel proceed with different efficiency, which was mainly attributed to ionic interactions. In addition, hydrogen evolution could be performed after addition of platinum cocatalyst (Figure 12b). In addition, the catalytic hydrogel could be recycled easily (Figure 12c). Another hydrogel for water waste treatment was described by Yao and coworkers. In this case, bentonite, g-C₃N₄, AAm and MBA were combined to form hydrogel monoliths via thermal polymerization. Finally, the monoliths were cut into small cubes, and adsorption of tetracycline was tested. The incorporation of bentonite led to enhanced adsorption of the organic contamination. In the next step, tetracycline was degraded via visible light irradiation. Furthermore, adsorption and degradation were studied in the flow process that showed a high removal efficiency and cycling stability.

Another photocatalytic process employing g-C₃N₄-based hydrogels was presented by Lamkah and Randorn. A PAAm hydrogel was formed via photopolymerization of AAm and MBA under UV light. Finally, the hydrogel was utilized for the photocatalytic reduction of Cr(VI) to Cr(III). Cui and coworkers described a hydrogel formed from g-C₃N₄, graphene and PPy. Improvement was the photocatalytic properties were obtained via graphene as electron transporter and PPy as hole transporter. The obtained hydrogels were utilized for photodegradation of phenol and reduction/adsorption of Cr(VI). Tu and coworkers introduced another application of g-C₃N₄ based hydrogels. An AAm/acrylic acid-based hydrogel was formed via thermal initiation that could be utilized as sensor for Ag⁺ ions. Due to the acidic acid incorporation, the hydrogels were pH sensitive, i.e. the swelling state changed according to pH. Moreover, the hydrogels showed fluorescent behavior because of the g-C₃N₄ incorporation. The fluorescence could in turn be utilized for sensing. The change in fluorescence after addition of various metal ions was tested, and in the case of Ag⁺ down to concentrations of 6.31 µM a significant quenching effect was observed. Notably, the detection of Ag⁺ was still possible when other contaminant ions were present.
5.3 Blending and supramolecular hydrogels

In addition to covalent hydrogels formed via polymerization, g-C$_3$N$_4$ was incorporated into hydrogels via blending or supramolecular interactions as well (Scheme 5c). For example, Park and coworkers presented the combination of g-C$_3$N$_4$ and peptide materials. In those experiments, Fmoc-diphenylalanine (FMOC-DPA) was utilized to undergo self-assembly in the presence of g-C$_3$N$_4$ yielding hydrogel. The formed hydrogel was utilized to reduce NAD$^+$ to NADH. Moreover, the incorporation of an enzyme facilitated the combination of photo and enzymatic catalysis. A remarkable hydrogel was described by Fan and coworkers, who combined g-C$_3$N$_4$ with the Ca$^{2+}$/alginate supramolecular hydrogel and 3D printing (Figure 13a). Hence, 3D hydrogel scaffolds were obtained that could be utilized for photocatalytic tasks. A carbon nitride nanosheet/sodium alginate (CNNS-SA)-based ink was printed and crosslinked in CaCl$_2$/glycerol solution (Figure 13b, c). Inclusion of gold nanopyramids in such 3D scaffolds boosted the photocatalytic activity for solar wastewater remediation. Thus, the gel architecture could be utilized to tailor the catalysis effectiveness via enhanced substrate transport. Ayajan and coworkers presented a gel from g-C$_3$N$_4$ and ionic liquids (IL) forming an amphiphilic network that was utilized as H$_2$S gas sensor at ambient temperature. IL served as exfoliating agent for g-C$_3$N$_4$ sheets at high temperatures, and gel formation was observed at 200 °C after 24h, where exfoliated g-C$_3$N$_4$ nanosheets assembled in the IL matrix.
Figure 13. a) Schematic illustration of the 3D fabrication process: A highly concentrated homogeneous CNNS–SA (g-C₃N₄ nano sheet-sodium alginate) ink was extruded and directly printed onto a glass substrate covered with a layer of Vaseline (Route 1), into a reservoir composed of a CaCl₂/glycerol solution (Route 2) or Pluronic F127 (Route 3). Subsequently, the printed lattices were submerged in a CaCl₂ aqueous solution overnight to cross-link the SA. b) Optical image of a woodpile structure (mass ratio CN:SA = 1:2) printed via Pluronic F127 (Route 3) and c) a cross-sectional SEM image (Reprinted with permission. Copyright 2018 John Wiley and Sons).

A hydrogel solely formed from g-C₃N₄ was investigated by Zhang and coworkers. Here, g-C₃N₄ was partially hydrolyzed in sodium hydroxide solution. The obtained material formed reversible hydrogel structures via bubbling with CO₂ or N₂ that could be utilized for selective dye absorption. In the presence of agar, heating-cooling polymerization yielded hydrogels including g-C₃N₄. The agar-based hydrogels were further utilized for effective photocatalytic degradation due to enhanced adsorption capacity. In a similar way, Zhu and coworkers utilized a g-C₃N₄/agar hydrogel for photocatalytic tasks. Therefore, g-C₃N₄ and agar were dispersed in water and heated. After cooling a hydrogel was obtained that was used for the photodegradation of MB and phenol. A significant activity was obtained due to the adsorptive behaviour of the hydrogel.

Table 2. Hydrogels based on g-C₃N₄ and their properties.

| Synthesis method                        | Monomers/gelators | Properties/applications                          | Reference |
|-----------------------------------------|-------------------|-------------------------------------------------|-----------|
| Photopolymerization                     | DMA/MBA           | Photocatalytic dye degradation and H₂ evolution | 191       |
| Photopolymerization                     | DMA/MBA           | High G’ (up to 8.3 kPa), salt and pH response   | 64        |
| Photopolymerization                     | NIPAM/MBA         | Thermoresponse                                  | 190       |
| Photopolymerization                     | AAm/DMA/MBA       | High compressibility                            | 193       |
| Photopolymerization in water/EG         | DMA/MBA           | High G’ (up to 729 kPa)                         | 196       |
| Photopolymerization with g-C₃N₄ prepolymer | DMA/SPMA/MBA     | Low friction                                    | 197       |
| Photopolymerization                     | AAm/MBA           | Tetracycline degradation                         | 200       |
| Photopolymerization                     | AAm/MBA           | Photooxidation of Cr(VI)                         | 201       |
| Redox polymerization                    | AAm/MBA           | Gel electrophoresis                             | 192       |
6. Conclusion and Outlook

Combining exfoliated g-C\textsubscript{3}N\textsubscript{4} nanosheets with polymers is a recent hotspot of materials research, thus enabling many advanced functionalities and hybrid materials with unusual properties extending the previous range of the possible. The combination was mainly driven by typical g-C\textsubscript{3}N\textsubscript{4} properties, such as photoinitiation, photocatalysis, or photoluminescence. However, it turned out that these properties are significantly improved or optimized in the polymer hybrids, which is due to improved delamination, but also due to synergies of the two sides. Introducing for instance conducting polymers to g-C\textsubscript{3}N\textsubscript{4} enables us to overcome the drawback of low electron conductivity of g-C\textsubscript{3}N\textsubscript{4}, and hence the photocatalytic or H\textsubscript{2} evolution properties of g-C\textsubscript{3}N\textsubscript{4} were promoted.

In biosensor systems, polymer functionalized g-C\textsubscript{3}N\textsubscript{4} has shown an improved sensitivity and selectivity, which we attribute to improved dispersion and access to the sensing sites. Polymer modified g-C\textsubscript{3}N\textsubscript{4} showed enhanced dispersibility and processability, and for instance can be employed in film formation.

On the other hand, g-C\textsubscript{3}N\textsubscript{4} with its multiple properties brings advantages to polymer materials as well. For example, doping the polymer matrix with g-C\textsubscript{3}N\textsubscript{4} enhances the performance of electrode materials in energy storage and improves stability and efficiency compared to the pure polymer matrix. Photoinitiation with g-C\textsubscript{3}N\textsubscript{4} facilitates polymerization in solution and on g-C\textsubscript{3}N\textsubscript{4} to obtain g-C\textsubscript{3}N\textsubscript{4}/polymer nanocomposites with inherent photoluminescence that can be applied for various applications. In addition, combination of g-C\textsubscript{3}N\textsubscript{4} with polymers enhances the thermal and mechanical properties of polymers. In the realm of bulk soft materials, g-C\textsubscript{3}N\textsubscript{4} is particularly useful as reinforcing in hydrogels and g-C\textsubscript{3}N\textsubscript{4}/hydrogel hybrids can be obtained. Overall, the plethora of monomer combinations and g-C\textsubscript{3}N\textsubscript{4} types allows the fabrication of tailored hydrogel materials with very unusual and most useful properties, e.g. ultralow friction, being thermo-responsive, or tough but compressible. Indeed, the storage modulus of hydrogels could be varied over a broad range (approximately 7 kPa to 700 kPa) via g-C\textsubscript{3}N\textsubscript{4} content and type, only, while the toughness of the material could be adjusted by monomer mixtures, e.g. AAm and DMA. By inherent photopolymerization, reinforced hydrogels can be obtained also in a spatially controlled way and directions of additive manufacturing are certainly a promising approach a toolbox is needed for.\textsuperscript{210, 211}

Polymers might pave the way for novel applications for g-C\textsubscript{3}N\textsubscript{4}, however some main issues still need to be addressed. Although some promising results were reported so far, the research for g-C\textsubscript{3}N\textsubscript{4}/polymer hybrids are still in the infant stage, and further investigations and developments are still needed. To date, there are a number of issues, which need to be resolved for improved combination of g-C\textsubscript{3}N\textsubscript{4} and polymer. For example, most of the
research reported utilizes the simple blending method of fabrication, thus interaction between polymer and g-C$_3$N$_4$ is enabled by physical interaction, only, which may cause restrictions for the future commercial application. Moreover, the synthesis process mainly depends on organic solvents, which is not environment friendly when expanded to commercial scale, thus solvent-free, mechanochemical and green routes should be developed in the future research. In oxygen evolution and organic synthesis, g-C$_3$N$_4$ is also of great significance as a photocatalyst. Nevertheless, g-C$_3$N$_4$/polymer hybrids are rarely applied in these areas so far. As such, one can expect significant outcomes in the future in organic synthesis and oxygen evolution. Overall, g-C$_3$N$_4$ has a promising future especially in energy conversion and storage, and enhancing surface area of g-C$_3$N$_4$ by polymers might become key for utilization of g-C$_3$N$_4$ in batteries, supercapacitors and other high-efficiency energy conversion devices.

Polymers have opened up new doors for g-C$_3$N$_4$ which could not be imagined seven years ago. Previously, dispersibility and processability issues were the main problems for integration of g-C$_3$N$_4$ materials, however with the current ideas dispersibility becomes less of an issue. Ultimately, g-C$_3$N$_4$ is a sustainable and cheap alternative for other semiconductors, and we believe that with precise tailoring of both g-C$_3$N$_4$ properties and design of a surrounding polymer helper team, g-C$_3$N$_4$ will play an increasingly important role both in academia and in the industry of the future.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

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Carbon Nitride and Polymers for Advanced Properties
Graphitic Carbon Nitride and Polymers: A Mutual Combination for Advanced Properties

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The present review highlights the combination of carbon nitride and polymers for materials with outstanding properties.