

Chapter 8

Carbon Nitride-Based Biosensors

Zhuang Wang, Wei Wei, Yanfei Shen, Songqin Liu, Yuanjian
Zhang*

Jiangsu Engineering Laboratory of Smart Carbon-Rich Materials
and Device, Jiangsu Province Hi-Tech Key Laboratory for Bio-
Medical Research, School of Chemistry and Chemical
Engineering, Medical School, Southeast University, Nanjing
211189, China.

*Yuanjian.Zhang@seu.edu.cn (Y Zhang)

Polymeric carbon nitride (CN), as a kind of promising two-dimensional conjugated matter exhibited outstanding photovoltaic effects. Recently, CN has also drawn increasing attention in constructing biosensors owing to its appealing properties such as responsive to visible light, facile synthesis from inexpensive raw materials with modulable electronic structures, remarkable thermal and physicochemical stability, abundant functional groups on the surface, and excellent photoelectrochemical features. This chapter introduces the synthesis as well as structure engineering of CN materials and further summarizes the advantages of CN in biosensing application. It is shown that plenty of efforts have been devoted to optimize the solubility, signal conversion efficiency, active surfaces/sites that interact with biomolecules of CN materials, making CN more attractive for biosensing application. As a metal-free semiconductor with a narrow band gap, CN owns outstanding optical properties (photoluminescence and chemiluminescence) and the photoelectric conversion ability (electrochemiluminescence and photoelectrochemistry), which contributes to multiple signal output modes and various biosensors designing. Interestingly, beyond the conventional configurations and sensing mechanisms, a few very recent examples taking advantage of unique properties of CN are introduced in the last part in order to further outlook the bright future of CN materials in biosensing application.

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1. Introduction

1.1 *History of Carbon Nitride*

Carbon nitride (CN), one of the oldest reported synthetic polymers was first found in 1834 by Berzelius and named by Liebig as “melon” afterwards.¹⁻³ As research continues, it was predicted that CN could be divided into five different phases: α -C₃N₄, β -C₃N₄, cubic C₃N₄, pseudocubic C₃N₄ and graphitic C₃N₄ (g-C₃N₄).⁴⁻⁵ Among all phases mentioned above, g-C₃N₄ with a layered structure analogous to graphite was proved to be the most stable allotrope under ambient conditions^{3, 6},

which accounts for tremendous attention on it. It was found that the aromatic planes constructed from triazine or tris-s-triazine units are stacked by weak van der Waals' forces. Nonetheless, instead of accurate C_3N_4 stoichiometry, most of real g- C_3N_4 is a defect-rich N-bridged "poly(tri-s-triazine)/poly(triazine)" due to the incomplete de-amination or polymerization of the nitrogen containing precursors.⁷ In the past few years, CN has experienced an explosion of interest due to its unique properties and facile structural manipulation in a diverse range of fields from photocatalysis to emerging biosensing, solar cells, nanoarchitecture processes and nonvolatile memory devices.⁸⁻¹⁴ Especially, both the semiconductor-driven properties and electron donating-driven property of CN materials arouse a variety of sensing applications which tend to be introduced in this chapter.

1.2 Appealing Properties of Carbon Nitride

As mentioned above, CN materials possess many outstanding properties. Initially, CN is a class of polymeric materials mainly composed of earth-abundant carbon and nitrogen elements, which means its inexpensive raw materials can be easily obtained. It also facilitates handling and disposal that CN does not contain any heavy metal ion. Moreover, the remarkable thermal and physicochemical stability of CN materials, especially g- C_3N_4 pave the way for practical applications. Specifically, the result of the thermal gravimetric analysis (TGA) demonstrated that g- C_3N_4 kept intact and non-volatile even at 600°C in the air. It eventually decomposed until the temperature reached 700°C.² In addition to its excellent thermal stability, g- C_3N_4 has also been proved to be stable under critical chemical conditions like acid, base or organic solvents.¹⁵ Moreover, g- C_3N_4 possess an appealing electronic structure to be a medium-bandgap semiconductor benefiting from its conjugated polymeric network.¹⁶ This feature hence made it widely applied in the fields related to sustainable energy such as photocatalysis and photoelectric conversion, as well as other important catalytic reactions.¹⁷⁻²¹ Afterwards, CN started to participate in constructing ingenious sensors owing to these semiconductor-driven properties including photoluminescence (PL), chemiluminescence (CL), electrochemiluminescence (ECL), and photoelectrochemistry (PEC) as

illustrated in Fig. 1.^{11, 22-27} As for the latter two mechanisms, the outstanding conversion capacity between light and electricity extremely enhance the sensitivity of g-C₃N₄ based sensors. Simultaneously, some colorimetric sensors has been successfully constructed on the basis of unique catalytic properties of g-C₃N₄.²⁸⁻³¹ Except for inherent properties above, the structure of CN is easy to be modulated at the molecular level for different optoelectronic properties by virtue of its moderate reactivity at the interface, together with the aromatic, π -conjugated framework and intralayer hydrogen bond. In principle, any desired molecules, elements and functional groups can be inserted into the final CN through reasonable designing strategy of molecular structures, thus intrinsically improving the fundamental properties of these CN materials aiming for task-specific applications.³² Owing to all these appealing properties, tremendous effort has been done to make full use of CN in various fields.

1.3 Opportunities for Biosensors by Using of Carbon Nitride

Recently, carbon nitride has gradually exhibited the enormous potential in biosensing, which is closely related to its outstanding properties. Firstly, the detection processes may be done in complicated environments. Hence, there is no doubt that the stability is a vital factor for an excellent biosensor. CN exactly possess the high thermal and chemical stability. The most stable allotrope of the CN family, g-C₃N₄ has been demonstrated to be unchanged even at 600°C in the air and some critical chemical conditions, which make it possible to construct fairly stable biosensors when facing practical and complex samples. And CN is mainly composed of earth abundant and inexpensive elements which also contribute to the low toxicity and biocompatibility. Furthermore, as a metal-free semiconductor with a narrow band gap, CN owns unique optical properties (photoluminescence, chemiluminescence) and the photoelectric conversion capacity (electrochemiluminescence and photoelectrochemistry), which can offer multifarious possibilities for biosensing designs. In particular, different from the traditional photoluminescence, both ECL and PEC can effectively avoid the disturbance from input signals by taking advantage of the conversion between electricity and light. It indeed boosted the sensitivity of

biosensors to adopt different forms of input and output signals. More importantly, one of the most attractive merits of CN is the facile modulation of molecular structures and optoelectronic properties due to its organic nature. Thus, the engineering of CN molecular structures not only optimizes the properties of CN according to specific requirements but also extremely enhances the flexibility of CN based biosensors.

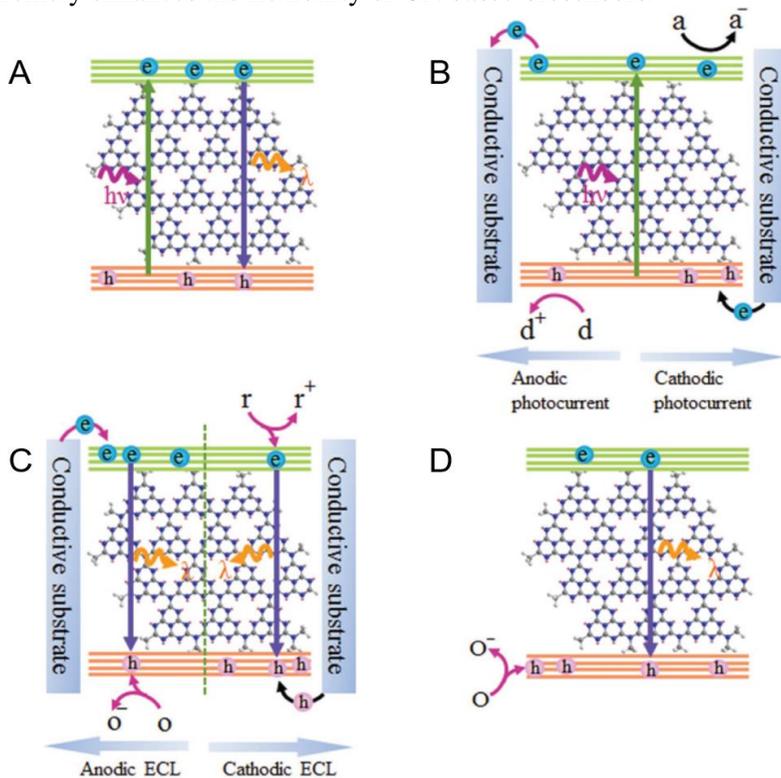


Figure 1. Sensing mechanisms using CN. A) Photoluminescent emission generated by rapid recombination of the photoinduced electrons and holes. B) Anodic or cathodic photocurrent produced by light illumination in the presence of solution-solubilized electron donors or acceptors, respectively. C) Anodic or cathodic electrochemiluminescence generated by electrochemical injection of electrons or holes in the presence of oxidative or reductive coreactants, respectively. D) Chemiluminescence produced upon injection of electrons or holes from chemical species.³³

2 Synthesis of Carbon Nitride

2.1 Engineering of Molecular Structures

2.1.1 Chemical Doping

Generally, inserting external impurities into semiconductors can effectively modulate their electronic structures for the manipulation of conductive, optical, luminescent, magnetic, or other physical properties, which refers to doping. As a metal-free polymeric semiconductor, CN can also be chemically doped to improve the properties. To date, a series of atoms including B³⁴⁻³⁵, C³⁶⁻³⁷, O³⁸⁻³⁹, F⁴⁰, P⁴¹⁻⁴², S⁴³, Br⁴⁴ and I⁴⁵ as well as some combinations⁴⁶⁻⁴⁷ between them have been successfully incorporated into the framework of CN (Fig. 2A). The introduction of heteroatoms can induce the change of the electronic structure of CN.

Among these atoms, P, as a typical doping atom has been verified to effectively enhance and properly modulate the performance of CN in various applications including photoelectrochemistry⁴⁸, photocatalysis⁴² and bioimaging⁴⁹. For instance, it was firstly reported by our group that phosphorus atoms most probably replaced the corner or bay carbon in the structure to form P-N bonding in the doped CN framework.⁴⁸ The doped heteroatoms, P did remarkably change the electronic structure of CN, leading to a fairly broad light absorption covering almost full-range spectra. Therefore, P-doped CN showed not only a significant increase in electrical conductivity by up to 4 orders of magnitude, but also an improvement in photocurrent generation by a factor of up to 5. In fact, all of these outstanding features after doping made it possible for CN to construct more sensitive biosensors with intense signal feedback. Another typical doping heteroatom, S can also effectively modulate the properties of CN. For instance, our group has reported that the optical properties of CNNS can be facilely engineered by S atom doping, where the 2-aminothiophene-3-carbonitrile was used as a dopant in copolymerization with bulk CN to prepare the S-CNNS with a red-shift PL and ECL emission peak reaching 531nm.¹² Furthermore, to make full use of the adjustable emission wavelength of S-doped CN, our group continued to construct a wavelength-resolved ECL biosensor for the simultaneous detection of multiple biomarkers at a single-electrode interface.⁵⁰ By virtue of doping modulation, CNNS were explored as metal-free mono chromatic luminophores with different emission wavelengths but the same coregent and excitation potential, which could enrich the sorts of biocompatible monochromatic ECL luminophores for multiple biomarker detection.

Other than the altering of wavelength, Ma and co-workers has demonstrated that the S doping can effectively change the surface states of CNQDs and produced new element vacancy, which ultimately enhanced the ECL efficiency by 2.5 times and benefit for the sensitivity of the gene detection.⁵¹ In addition to heteroatom doping mentioned above, Zhang and co-workers found that carbon self-doping to substitute the bridging N atoms could form delocalized p bonds among the doped C atoms and aromatic heterocycles, which is beneficial for electron transfer and also results in decreasing the bandgap.³⁶ Thus, doping is serving as an effective and facile approach to improve and modulate the features of CN materials and broaden their application prospect in biosensing.

2.1.2. Defects

Defects modulation usually has great influence on the electronic structures of semiconductors. In general, the intrinsic nitrogen defects in CN might have a remarkable impact on its optoelectronic properties and band gap structure. The nitrogen defect engineering for CN materials has aroused tremendous interests in recent years to improve the desirable features in various applications. It was demonstrated that the introduction of N defects into CN networks would cause a change of local coordination environment, which could alter local electron distribution and extend the p-electron delocalization.⁵² Hence the introduction of N defects into the CN framework was also shown to significantly improve the performance of CN. For example, Zhang and co-workers described a novel route to prepare nitrogen defective CN via adding an alkali compound during the thermal polymerization of urea or other nitrogen-rich precursors (Fig. 2B). Two types of nitrogen defects, cyano groups in the bulk and surface N vacancies, were selectively introduced. Both experimental and theoretical results indicated that the introduction of nitrogen defects not only redshifted the CN absorption edge, but also separated photoexcited charge carries more efficiently. Therefore, the as-prepared CN displayed superior photoelectrochemical and photocatalytic hydrogen evolution performance.⁵³ There is no doubt that the participation of defects tends to enhance the sensitivity of CN based biosensors and improve the performance of CN in biosensing.

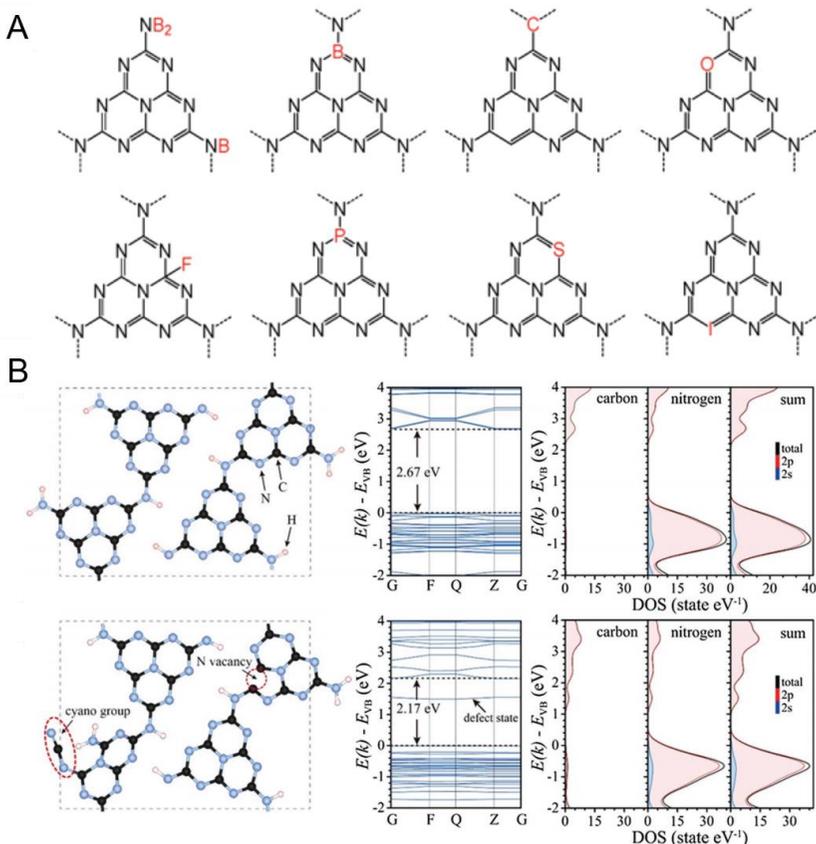


Figure 2. Engineering of CN molecular structures via doping and defects. A) Representative molecular motif of doped CN. Copied with permission³² B) Structure fragments of CN and CN with N defects as well as corresponding calculated band structures and partial density of states.⁵³

2.1.3 Topological Structure

In addition to the structural engineering by doping or defects introduction, it is also envisioned to engineer the physical/ chemical properties of CN by constructing unique topological structures that are closely relevant to molecular orbitals and electronic band structures. According to the different ratios of C and N atoms in the CN framework, a series of novel C_xN_y materials with different prosperous topologies and stoichiometries have been predicted and/or synthesized, which further triggers extensive

investigations of broad applications ranging from sustainable photocatalytic reactions and highly sensitive optoelectronic biosensing.⁵⁴ Hence, the modification in the molecular structure of most reported C_3N_4 has aroused tremendous attention. For instance, Kumar and co-workers have successfully synthesized a novel carbon nitride framework named C_3N_5 through the thermal deammoniation reaction. The monomer melem hydrazine obtained by the pre-reaction of the precursor melem and hydrazine, resulting in a new bridging azo linkage ($-C=C-$). It ultimately turned out to be that the overlap of tri-s-triazine heptazine cores and $-C=C-$ linkages increased the electron density, leading to the extended conjugation and the reduction of bandgap to 1.76 eV.⁵⁵ Another facile way to modifying CN is to change the repeating units. Vinu and co-workers have prepared a different topological C_3N_5 with the repeating unit with two six-membered ring triazines and one five-membered ring triazole, which is easy to synthesize through the self-assembly of the precursor, 5-amino-1*H*-tetrazole (5-ATTZ).⁵⁶ Compared with bulk g- C_3N_4 , the as-prepared C_3N_5 exhibited higher redox reaction activity and diffusion current density. What is more, C_4N_3 with the bridging groups changed from N atom to C atom was prepared by Zhou and co-workers.⁵⁷ It owned more dangling bonds and exhibited much improved optical absorption possibly on account of some unoccupied electrons in the bridging C atoms. Owing to the effective $n \rightarrow p^*$ transition in most C_xN_y materials, the relative energy level of the lone-pair electrons on N atoms is high. Thus, they are generally equipped with the capability of visible light absorption, which contribute to the sensitive in vivo biosensing. Meanwhile, the different repeating units, bridging groups and defect sites of these two kinds of C_xN_y allow them to effectively drive a diverse of promising applications that require specific electronic, interfacial and geometric properties.

Apart from the six-membered rings, our group has synthesized a five-membered aromatic ring-based C_3N_2 material by using the zeolite imidazole framework. The asymmetric five-membered rings and the rich dangling bonds in the condensed framework endow much lower first excitation energy of 0.8 eV, enabling the first successful PEC biosensing for the untransparent biological samples using near IR lights. More interestingly, by employing first-principles calculations, the structural, electronic and magnetic properties of various two-dimensional NC were

reported by Bafekry and co-workers. The different predicted CN gives rise to diverse electronic properties such as metals (C_3N_2), semimetals (C_4N and C_9N_4), half-metals (C_4N_3), ferromagnetic-metals (C_9N_7), semiconductors (C_2N , C_3N , C_3N_4 , C_6N_6 , and C_6N_8), spin-glass semiconductors ($C_{10}N_9$ and $C_{14}N_{12}$), and insulators (C_2N_2). A series of prosperous topological structures bring infinite possibilities, which can not only be applied to the PEC, ECL or PL, but also has a wide space in magnetic resonance imaging *in vivo*.

2.2 Engineering of Micro/Nanostructures

2.2.1 Nanosheets

Currently, the bulk CN can already be facily prepared at large scale and low cost. A variety of methods has been established for that such as solvothermal synthesis⁵⁸, solid-state reactions⁵⁹, electrodeposition⁶⁰ and thermal decomposition⁶¹, among which the thermal decomposition is most frequently used to synthesize bulk CN utilizing various precursors. Prepared by solid-state synthesis at high temperatures, pristine CN is a typical bulky material with low dispersity in most solvents and surface area. Nevertheless, sensitive biosensors with a fast kinetic response often desire large surface area, an abundance of active sites and high water dispersity.³³ And thus, pristine CN is not regarded as an ideal candidate for biosensing applications. To overcome these obstacles in practical applications, numerous approaches has emerged to tailor the bulk CN into various micro/nanostructures with high water dispersity and surface area as well as unique properties so as to improve its biosensing capabilities.

As the name suggests, graphitic C_3N_4 possesses the similar layer structure of graphite. Inspired by the success of graphene exfoliated from bulk graphite, it is thought to be possible to prepare CN nanosheets (CNNS) by exfoliating bulk g- C_3N_4 . several pioneering works have been reported to realize that in different ways including liquid exfoliation⁶² and thermal oxidation⁶³. The ultrathin two-dimensional CNNSs not only reserve the merits of bulk CN such as excellent stability and biocompatibility but also exhibit unique optoelectronic properties as well as better water solubility and higher surface area than bulk CN. Thus, a more intimate interaction

can be constructed between guest molecules and CN materials, which has drawn tremendous interests for biosensing.

However, the efficiency of thermal oxidation turned out to be relatively low, where the hydrogen bonds among layers were destroyed through oxidizing by air. Similarly, a typical liquid exfoliation cost a long sonication time up to ~ 16 h to obtain CNNS with a low concentration of ~ 0.15 mg/mL (Fig. 3A).⁶² To solve this issue, Qiao and co-workers prepared CNNS by virtue of the sonication-exfoliation of bulk g-C₃N₄ under an acid condition, which reduced the exfoliation time to 2 hours and altered the negatively charged g-C₃N₄ to be positive by protonating the bulk g-C₃N₄ surface with HCl.⁶⁴ Other than the low efficiency, the poor dispersion of CN in most solvents makes it hard to tailor. Also, it is fairly difficulty to form a robust linkage between guest molecules and the chemically inert pristine CNNS. For this reason, our group have developed a facile approach to simultaneously modify and exfoliate bulk CN with aromatic molecules via the facile mechanical grinding as illustrated in Fig. 3B. The obtained CNNSs not only retained the pristine optoelectronic properties of bulk CN but also enriched a friendly interface for further coupling biomolecules.⁶⁵ Obviously, the appearance of CNNS inherits unique properties but simultaneously remedies some disadvantages of bulk CN, which broaden the application range of CN materials in biosensing.

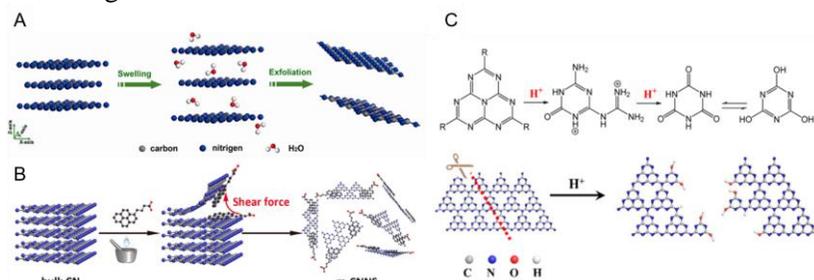


Figure 3. Engineering of CN nanostructures. A) Liquid-exfoliation process from bulk CN to ultrathin nanosheets.⁶² B) Mechanical grinding simultaneous exfoliation and modification process of bulk CN into nanosheets.⁶⁵ C) Chemical tailoring of CN into quantum dots in acidic aqueous solution.¹¹

2.2.2 Dots

Fluorescent semiconductor quantum dots (QDs) with unique tunable optical and electronic properties as well as good stability have been applied in various fields including biomedicine, solar cells, optical devices, sensing and so on. And various types of semiconductor QDs with different photoluminescence emission were already developed, for instance: CdS/Se, PbS/Se, ZnS/Se, AgS/Se, etc.⁶⁶ Although these metal-based QDs indeed overcome some inadequacies of traditional organic dyes such as low photo stability and high photobleaching, their applications in biosensing are still hindered by some shortcomings including complicated synthesis pathways, high preparation cost, poor solubility in water and especially high toxicity to the organism. As a kind of metal-free quantum dots, carbon-based QDs have drawn increasing attention and been regarded as promising candidates for biosensing owing to their outstanding features. Compared with metal-based QDs, carbon-based QDs remain the excellent optical properties and meanwhile manifest facile synthesis, nontoxicity and good biocompatibility.⁶⁷ As mentioned above, CN materials has exhibit enormous potential in biosensing. Nevertheless, the practical applications of CN were actually confined due to the poor dispersibility and broad size distribution. Hence, great efforts have been made to prepare homogeneous carbon nitride quantum dots (CNQDs) which are more appropriate for biosensing. Generally, the synthesis approaches of CNQDs can be divided into two categories: top-down synthesis and bottom-up synthesis. As for the top-down strategy, bulk CN should be initially prepared and subsequently cut into nanosized CNQDs by means of various manipulations including chemical oxidation⁶⁸, ultrasonication⁶⁹, chemical tailoring (Fig. 3C)¹¹, hydrothermal treatment⁷⁰, electrochemical oxidation³¹ and hot-tailoring⁷¹. Different from the top-down strategy with multiple processes, the bottom-up synthesis aims to prepare CNQDs through self-assembly and polymerization of small nitrogen-rich organic molecules just in one step. Typical bottom-up methods include hydrothermal method^{23, 72}, solvothermal method⁷³ and solid-phase method⁷⁴. Although different synthesis methods lead to CNQDs with different features, CNQDs generally show some common merits such as small size distribution, excellent water solubility, nontoxicity and good biocompatibility, which are more beneficial to biosensing applications than bulk CN. CNQDs also remain the outstanding stability in critical

chemical and physical conditions by virtue of the tri-s-triazine structural unit. Moreover, superior to carbon-based QDs, CNQDs exhibit expanded emission spectral range, high quantum yield and explicit mechanism.⁶⁶ Given all of excellent features of CNQDs above, it has been regarded as a promising optical probes for optical biosensing.

3. Signal Conversion of Carbon Nitride

3.1 Photoluminescence

Serving as a metal-free semiconductor, CN materials can output various signals in biosensing via producing electron–hole pairs in conduction band (CB) and valence band (VB) respectively through some external excitation and subsequently modulating their fluxion and recombination rate. Initially, bulk CN materials have exhibited unique photoluminescence properties as most typical semiconductors did. Generally, once illuminated by photons with sufficient high energy, electrons of CN tend to rise from the VB to the CB, leading to an equal number of holes. After the rapid recombination of these electron–hole pairs, the luminescence with specific wavelength can be emitted.

Based on the flexible and adjustable molecular structure and nanostructure of CN materials, the PL features of CN can be facilely modulated through the degree of polymerization, morphology modification or the construction of nanocomposites. It has been demonstrated that the degree of polymerization during the condensation of precursors could obviously distinctly alter the emission wavelengths. Specifically, the pure melem gives a PL peak around 366 nm. Once condensed to bulk CN materials at 450 °C for 1 hour, the PL peak was red-shift to about 435nm.⁷¹ When the condensation temperature rise to 550 °C for 4 h leading to a higher degree of condensation, the PL peak would further red-shift to 480nm due to the transition from a lone pair of nitrogen atoms to a π^* conduction band. However, the PL peak was blue-shifted when precursors was heated at 600 °C, which was likely to alter the electronic coupling between the layers.²

As mentioned in the second part, bulk CN materials are often tailored to nanosized structures in the practical biosensing applications for the sake

of improving water solubility, surface area and other desired properties. Compared with bulk CN, CNNS generally exhibit a stable and blue-shifted PL emission ($\lambda_{\text{max}} \sim 440\text{nm}$) and higher PL quantum yield (19.6 %) (Fig. 4A and 4B).⁷⁵ Due to the quantum size effect, the wider band gap of CNNS account for the blue-shifted PL. And the enhanced PL intensity of CNNS is reduced by defects and termination sites in the nanoscaled CN, which promotes the delocalization of electrons and thus contribute to the recombination of photogenerated electron-hole pairs.⁶³ Moreover, CNNS were reported to exhibit excellent two-photon PL emission at 438nm when irradiated by near-infrared light ($\lambda_{\text{ex}} = 760\text{nm}$) with a large two-photon absorption cross section and extremely weak photo-bleaching (Fig. 4C).⁷⁶ It was verified that CNQDs could also emit bright green PL emission via simultaneously absorbing two near-infrared photons.⁶⁹ By taking advantages of two-photon PL emission, nanosized structures of CN can be further implied in in-depth imaging and in vivo biosensing due to the excellent permeability of near-infrared excitation and good biocompatibility. As for CNQDs, another vital nanostructure of CN has emerged as outstanding fluorescent tags due to their unique optical features such as high PL quantum yield and unambiguous PL emission mechanism. Similar to the CNNSs, CNQDs generally showed a blue-shifted PL on account of the quantum size effect. Nonetheless, our group reported a sort of CNQDs with an abnormal redshifted PL emission by means of a facile hot-tailoring top-down fabrication method as shown in Fig. 4D.⁷¹ This phenomenon could be explained by the improved C/N ratio and functionalized oxygen-containing groups in the liquid-collection stage. The tunable PL emission tends to further broaden the biosensing applications of CNQDs.

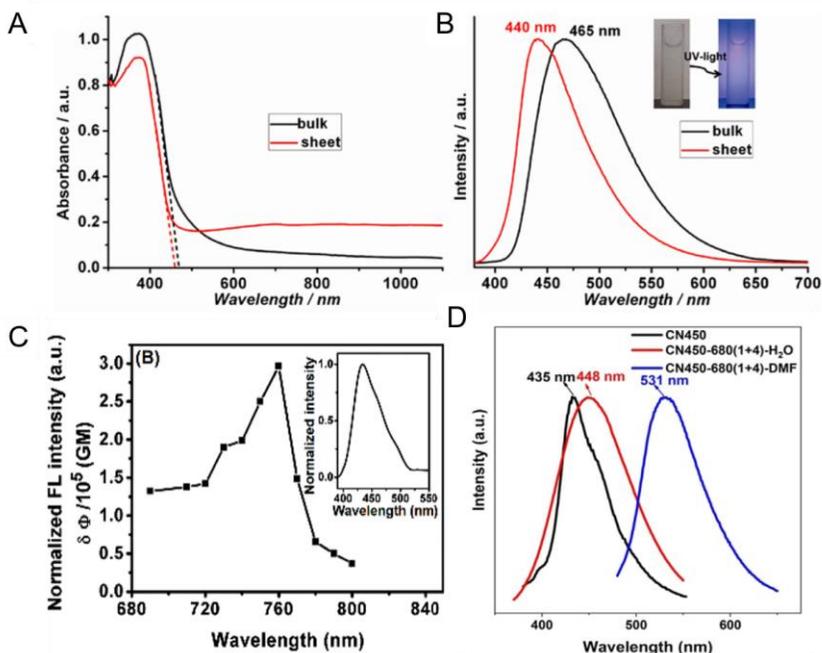


Figure 4. Photoluminescent properties of CN in various forms. A) UV-visible absorption spectra. B) Normalized photoluminescence spectra of bulk g-C₃N₄ and CN nanosheets.⁶² C) Two-photon photoluminescence emission of CN nanosheets.⁷⁶ D) Red-shifted photoluminescence spectra of hot-tailoring CN quantum dots.⁷¹

3.2 Photoelectrochemistry

With the development of innovative semiconductor-based photoactive materials, photoelectrochemistry (PEC) has aroused increasing interests in biosensing, as it simultaneously couples the merits of optical and electrochemical techniques. The signal conversion from light to electricity endows PEC biosensing with low undesired background and high sensitivity. As a kind of typical metal-free semi-conductor, CN with a highly delocalized π -conjugated system has emerged as a promising and novel transducer for PEC biosensing. In early studies, our group investigated the fundamental PEC properties of CN (Fig. 5A).⁷⁷⁻⁷⁸ Generally, CN serves as a semiconductor electrode immersing in the electrolyte containing electron donors or acceptors. Upon the illumination of light, charges separation and transfer occur in CN and consequently an

electrical signal is generated. In details, the transfer of electrons from the CB of CN to the electrode gives rise to an anodic photocurrent when the holes on the VB are consumed by electron donors solubilized in electrolyte. Conversely, a cathodic photocurrent arises due to the transfer of photo-induced electrons on the CB of CN to electron acceptors in electrolyte. Hence, sensing applications can be realized when various targets in the electrolyte modulate the separation and flow of photo-induced electrons and holes in the whole electro-circuit through redox to consequently affect the electrical signals.

Nonetheless, pristine CN materials exhibit a quite rapid recombination rate of its photo-induced electron-hole pairs, which suppresses photocurrent output to some extent. Moreover, pristine CN merely responds to UV and fairly limited visible light of wavelength shorter than 460 nm.³² It limits the application of CN in biosensing, as the short-wavelength light cannot penetrate tissues for effective in-depth biosensing and also tends to generate reactive oxygen-containing species harmful for DNA, protein and cells.⁷⁹ Thus, tremendous efforts have been made to enhance the carrier separation and charge migration, facilitate charge rectification as well as modulate CN optoelectronic properties, which thus improve the performance of CN-based PEC biosensing. It was proved that constructing composites of CN and multiple interacted substances with can effectively promote the photocurrent. Materials with high conductivity (noble metal nanoparticles and conducting polymers) are able to reserve electrons from the CB of CN, improve the interfacial electron transfer and thus enhance the photocurrent. Also, if semiconductors with a large band gap are deposited on CN nanostructures, CN can serve as an electron donor to transfer photoinduced electrons from its CB to these semiconductors, improving the charge separation as well as PEC signals.^{27, 80} CN can also accept photoinduced electrons from the CB of semiconductors with a narrow band gap, which similarly enhances the photocurrent.^{26, 81} Besides, the composition of appropriate dyes on CN can not only promote the photocurrent in the same way as typical semiconductors do, but also possibly modulate the wavelength of responsive light via D-A coupling.⁷⁹ In addition to the construction of heterojunction, another vital factor influencing the photocurrent is the contact state between CN materials and the conductive substrate. The homogenous and dense CN film with an

intimate contact with electrodes as well as less boundary defects generally results in high photocurrent density and stable performances. To date, extensive efforts have been made to fabricate high-qualified CN film.⁸²⁻⁸⁴ Recently, our group developed several effective methods to enhance the photocurrent signal such as modifying CN with P doping to increase visible light irradiation⁴⁸, coupling a hole/electron-transfer layer and redox shutter species to increase the charge separation efficiency⁷⁸, controlling the morphology to enlarge the surface area and improving crystallinity to suppress unwanted charge recombination⁸⁵. Moreover, Our group proposed a versatile microwave-assisted method for preparing a high-quality CN photoelectrode, which resulted in a strongly adhesive CN layer on the electrode with gradient carbon-rich texture, suppressed grain boundaries as well as excellent electron mobility, leading to the improved PEC response (Fig. 5B).⁸³ As a polymetric semiconductor, CN exhibit enormous potential in PEC biosensing on account of its excellent photon-harvesting ability and unique optoelectronic properties.

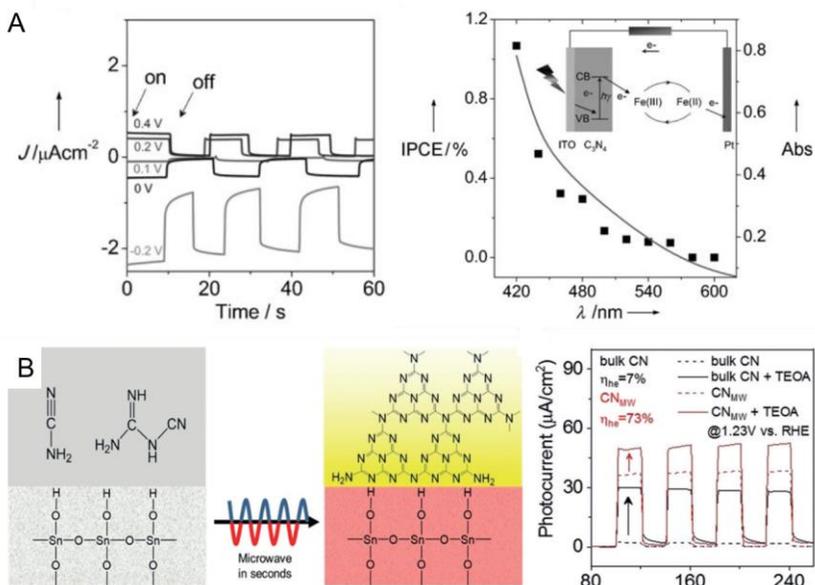


Figure 5. Photoelectrochemical properties of CN materials. A) Transient current response of ITO/rpg- C_3N_4 at different voltages.⁷⁸ B) Microwave-assisted synthetic illustration of the CN photoelectrode and enhanced transient photocurrent of microwave-assisted CN compared with bulk CN before and after adding TEOA.⁸³

3.3 Electrochemiluminescence

As the reverse process of PEC, electrochemiluminescence (ECL) has been equally regarded as an important approach for biosensing on account of its outstanding feature, including flexible design, low background emission, low cost, excellent controllability, and high sensitivity. Except for the illumination, electron-hole pairs can also be created in CN through the electrochemical injection. In general, the processes for generating ECL signals can be divided into two distinct categories. One is the annihilation ECL, where both the oxidation and reduction states of ECL-reagent are generated at single electrode with the subsequent annihilation between these two states to generate the excited state of ECL-reagent and the final ECL signal. Nonetheless, ECL of mere CN is not observed during the alternative pulsing of potential to inject holes or electrons to generate the oxidized $\text{CN}^{\bullet+}$ and reduced $\text{CN}^{\bullet-}$ respectively, which attributes to the poor stability of the $\text{CN}^{\bullet+}$ in solutions. The other method is the coreactant ECL, where a coreactant was adopted to assist the generation of the excited state of ECL-reagent via the redox reaction. CN has exhibited tremendous potential ECL properties in such a coreactant way (Fig. 6A). Upon the electrochemical injection of electrons or holes into CN materials attached to the working electrode, the electron-hole annihilation via electron transfer between g-CN and redox-active coreactants results in visible light. Hence, redox-active coreactants are frequently required for the CN-based ECL measurements. As for the reduction, coreactants including dissolved O_2 , H_2O_2 , and $\text{S}_2\text{O}_8^{2-}$ can serve as hole donors and react with the reduced $\text{CN}^{\bullet-}$ to produce the cathodic ECL.^{24, 86} Besides, coreactants with strong reducibility like tripropylamine can also serve as electron donors and react with oxidized $\text{CN}^{\bullet+}$ to generate the anodic ECL (Fig. 6B)^{87, 87}

Tremendous efforts have been made to effectively improve the ECL efficiency of CN materials, which plays a vital role in improving the sensitivity of the biosensor. Initially, modifications of CN itself by introducing an vacancy into CN could enhance the ECL efficiency.⁵¹ For instance, Wang and co-workers has introduced an vacancy into the Eu-doped CN, in which the O vacancy accelerated the energy transport between the catalyst and ECL reagents.⁸⁸ Moreover, to construct composites of CN and other conductive materials is regarded as an effective approach for the enhancement of ECL efficiency of CN. On the

one hand, it can promote the electrode interfacial electron transfer and weaken the CN passivation induced by electrons with high energy. A variety of materials has been reported to enhance the ECL in this way such as: gold nanoparticles (Fig. 6C)⁸⁹⁻⁹⁰, platinum⁹¹, Galinstan liquid metal²⁵, titanium carbide MXene (Fig. 6D)⁹² and so on. On the other hand, the assembly of CN onto other materials with high surface area can realize more load of CN and thus enhance the ECL signal.⁹²⁻⁹³ In addition to the modification of ECL reagents, the participation of catalytic materials in the substrates or composites can also promote the ECL efficiency by virtue of accelerating the whole ECL reaction⁸⁸ or generating more coreactants⁹³. And the substrates can likewise modulate the ECL efficiency, which could enhance the electroconductivity catalyze the generation of coreactants or increase the load of ECL reagents.⁹⁴ Notably, apart from the heterogeneous composites, the ECL efficiency is also intimately related to the quality of CN materials prepared on the electrodes. For instance, the high-quality CN photoelectrode made by the microwave-assisted method which was reported by our group realized a record-level cathodic efficiency of ECL.⁸³

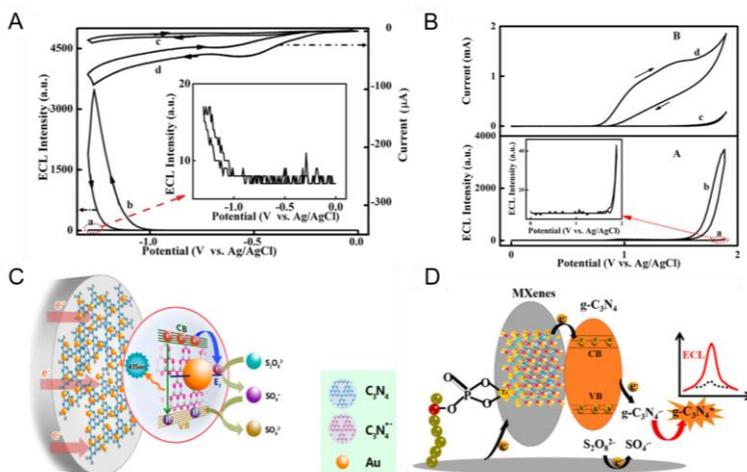


Figure 6. Electrochemiluminescent properties of CN materials. A) Cathodic electrogenerated chemiluminescence of CN⁹⁵ B) Anodic electrogenerated chemiluminescence of CN.⁸⁷ C) Schematic illustration of the ECL emission mechanism of the Au-CN nanocomposite with coreactant.⁸⁹ D) Enhanced ECL signals of MXene-CN nanocomposites with coreactant.⁹²

4. Interface Optimization with Biomolecules

As for an integrated biosensor, the conjugation of recognition elements or analytes themselves to CN materials is the cornerstone for subsequent designs of various signal modes and sensing mechanisms. The facile and stable interaction between biomolecules and CN materials without intense interference to their intrinsic properties makes significant sense to the sensitivity, selectivity as well as stability of biosensors. Hence, numerous efforts have been made to engineer the interface between CN and a variety of biomolecules and analytes. Initially, CN materials can themselves directly serve as recognition units by virtue of the inherent ligands such as amino groups, imino groups and nitrogen atoms. A series of metal ions have been successfully detected via CN-based sensors such as Ag^+ ,⁹⁶ Cu^{2+} ,^{22, 70} Fe^{3+} ,^{11, 70} where their chelation with multiple function groups on the surface of CN enhanced the selectivity and stability effectively. For the sake of more recognition sites, CN can be cut down to various nanostructures to get enormous surface area as mention before. For example, Chen and co-workers has demonstrated that Ag^+ can interact with the four-edge nitride atoms at each cavity site of CNNS and thus realized the PL sensing of Ag^+ .⁹⁷ Besides, CNQDs have also been reported to chelate with Fe^{3+} via hydroxyl groups and nitrogen by our groups.¹¹ In addition to the chelation of metal ions, amino-terminated biomolecules can be facilely conjugated to carboxylated CN nanostructures via the EDC/NHS activation.^{51, 98} For instance, Wei and co-workers have reported the covalent modification of the antibody on CNNS with carboxyl groups, which realized the typical sandwich-type biosensing for the carcinoembryonic antigen by virtue of the specific binding between the antigen and antibody.⁹⁴ Besides the intrinsic functional groups of CN, the construction of nanocomposites endows CN more chances to bind with biomolecules. Gold nanoparticles (AuNPs) have been most commonly deposited onto CN, which could be anchored to abundant N atoms in the framework of CN. Interesting, AuNPs can not only improve the conductivity of CN in PEC and ECL sensing, but also enhance the bioconjugation reliability of multiple biomolecules such as the single-strand DNA⁹⁹, DNA hairpin probes^{24, 100}, DNA tetrahedron nanostructures¹⁰¹, antibodies^{50, 89}, peptides¹⁰² and so on. Another kind of

noble metal, platinum (Pt) can also assist CN materials to covalently conjugate with amino-terminated biomolecules via the Pt-N bond.^{91, 93} In addition to metal nanoparticles, some semiconductors can also be employed for immobilization of biomolecules. For example, titanium dioxide (TiO₂) was demonstrated to conjugate both phosphate groups of peptide¹⁰³ and carboxyl groups of DNA¹⁰⁴ in the complex of TiO₂ and CN materials. And CdS quantum dots were also used to modified CNNS to realize the binding with DNA probes.¹⁰⁵ Various substances with abundant recognition sites such as β -cyclodextrin¹⁰⁶⁻¹⁰⁷ and polyethylenimine¹⁰⁸ have also been used to functionalize CN materials, offering intense and specific interaction with biomolecules. Apart from the covalent combinations, the non-covalent conjugation of CN materials has also been practiced through electrostatic interactions^{76, 109}, hydrophobic interactions⁷⁶, hydrogen bonding interactions¹⁰⁹ and π - π stacking^{80, 110}. For instance, Ju and co-workers have constructed a versatile PL sensing platform by virtue of the affinity between the single-stranded DNA and CNNSs as illustrated in Fig. 7A. Meanwhile, the affinity order of different bases was demonstrated as : Poly A > Poly C \approx Poly T due to the stronger π - π interaction of adenine with CNNS¹¹¹. However, the affinity of double-stranded DNA was fairly weak, which can be utilized to construct a variety of biosensors based on DNA aptamers. By means of electrostatic interactions, CN can be facilely conjugated to targets themselves like negatively charged heparin or dopamine^{64, 79} for the direct biosensing or other substances⁷⁶ for the indirect biosensing. Our group also developed a facile approach for modifying the interface of CNNS with aromatic molecules via mechanical grinding, which made the interface of CNNS more friendly for efficient conjugation of various biomolecules through the coupling between carboxyl groups and amino groups.⁶⁵ This kind of covalent modification was stable and specific, resulting in the better sensitivity than traditional biosensors constructed by physical adsorption of DNA (Fig. 7B).

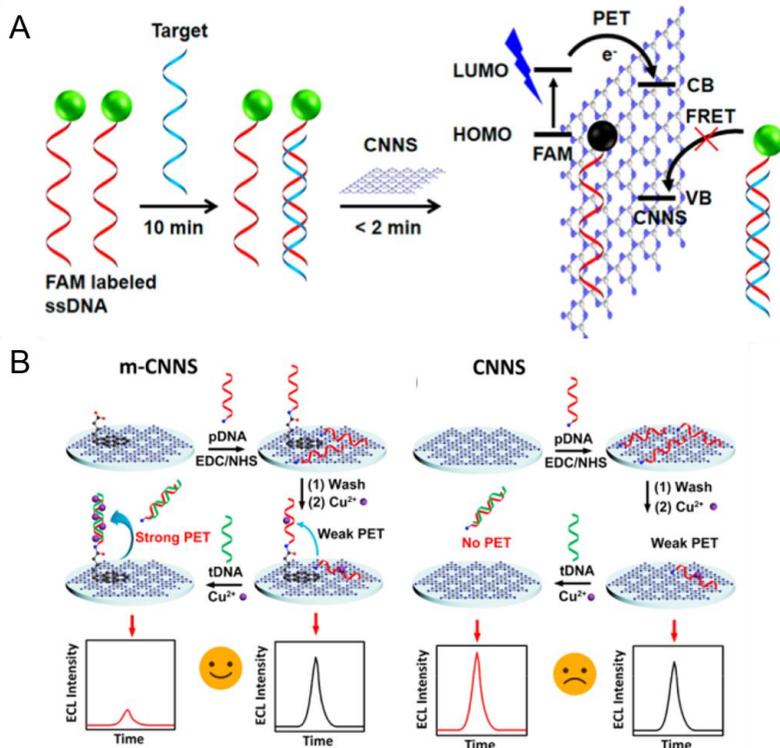


Figure 7. Interactions of CNNS with biomolecules A) Interaction of DNA with CNNS via π - π stacking.¹¹¹ B) Covalent binding of DNA with CNNS modified by aromatic molecules.⁶⁵

5. Typical Examples of Carbon Nitride-Based Biosensors

5.1 Photoluminescent Biosensing

As a result of the outstanding photoluminescent properties of CN, plentiful studies have successfully applied CN in biosensing to construct unique and sensitive sensors. Generally, the sensing mechanisms includes “on-off”, “on-off-on” and ratiometric strategies. As for the “on-off” sensing process, CN with unique optical features and excellent biocompatibility can serve as the luminophore which intimately interacts with targets leading to the quenched photoluminescence via multiple mechanisms. First of all, the photoinduced electron transfer (PET) between nanosized CN and targets

in the corporate nanocomposites can effectively realize the quenching of CN materials. If the redox potential of the linking targets is exactly situated between the VB and CB of CN, the PL signal of nanosized CN can drop obviously due to the electrons transferring from CB of CN to the neighboring targets. Under the certain conditions, the decrease of PL of CN is closely related to the concentration of corresponding targets and hence reflects their levels. Lee and co-workers have constructed a “on-off” PL sensor for Cu^{2+} by virtue of the cubic mesoporous graphitic (mpg)-CN for the first time, in which the synthesized cubic (mpg)-CN with high surface area could effectively bind to metal ions but exhibited highly selective and sensitive PL response only to Cu^{2+} without any interference by any other metal ion.²² This phenomenon was interpreted as the PET process from the cubic (mpg)-CN to Cu^{2+} after the coordination of Cu^{2+} to the inherent ligands. Similarly, a variety of metal ions have been sensitively detected based on CN in multiple nanostructures but the same PET mechanism. For example, Chen and co-workers has realized the detection of Ag^+ using acetaldehyde-modified CNNS as the luminophore whose photoluminescent signal can be effectively and selectively quenched by Ag^+ .⁹⁷ Also, Chen and co-workers have constructed a CNNS nanofilm based sensor for the detection of Ag^+ and Cu^{2+} in cooperation with the glutathione to distinguish these two kinds of metal ions.¹¹² It was demonstrated that abundant functional groups on the surface of CN exhibited high adsorption capacity to metal ions, especially to Ag^+ and Cu^{2+} . More importantly, the redox potentials of these two metal ions exactly lie in the range between the VB and CB of CNNS. These two advantages made it possible to realize the PET process. In addition to CNNS, CNQDs with high PL quantum yield were also applied into the PET sensing process. Our group reported that CNQDs prepared by the chemical cleavage exhibited excellent optical properties. The PL of CNQDs distinctly declined in the presence of Fe^{3+} due to the PET process, which thus realized the selective detection of Fe^{3+} with a lower detection limit of $1\mu\text{M}$ than C-dots.¹¹ Not merely for the detection of metal ions coordinating with CN, the PET sensing can also involve various analytes facilely attached to the surface of CN. Interestingly, Li and co-workers has introduced a sensor for tetracycline based on CN nanoseaweeds with high

selectivity.¹¹³ The photoinduced electron of CN nanoseaweeds could be trapped by the surface-interaction of tetracycline.

In general, the PET sensing of CN highly depends on two vital factors: the intimate contact of targets and nanosized CN materials and the appropriated redox potentials. The inner filter effect (IFE), as another important approach for “turn-off” sensors has also been utilized in CN-based sensing applications. For instance, our group proposed a solid-state sensor for polycyclic aromatic hydrocarbons (PAHs) based on homogeneous CNNSs distributed in the polymethyl acrylic acid.¹⁰⁷ Due to the IFE process, the intense PL signal of CNNSs could be quenched by PAHs specifically recognized by the β -cyclodextrin. Moreover, the 2,4,6-trinitrophenol (TNP) has also been demonstrated to be detected when attached to CNNSs via the IFE process in a typical “on-off” model.¹⁰⁹ The intense interaction between the TNP and CNNSs including electrostatic, π - π , and hydrogen bonding interactions improved the IFE and thus enhanced the sensitivity of this sensor. Moreover, CN materials are not restricted to electron donors in the PET process. They can also serve as electron acceptors to quench the PL of other fluorophores. Ju and co-workers constructed a versatile sensing platform for DNA and Hg^+ by virtue of the PET process from the excited fluorophores to the conductive band of CNNSs.¹¹¹ In addition to the PET and IFE, the aggregation of CN nanostructures can also induce the PL quenching. Qiao and co-workers reported the PL detection of heparin by virtue of its electrostatic interaction with CNNSs (Fig. 8A).⁶⁴ The binding of heparin with CNNSs not only induced the aggregation of CNNSs, leading to self-quenching and collisional quenching but also changed the electronic distribution in the CNNSs planar framework.

In order to further improve the sensitivity of CN-based sensors, a “on-off-on” strategy has emerged to avoid fake signals produced by interference in the detection environment. In general, the PL of CN can be effectively quenched by various substances initially to change the “always-on” state of CN nanostructures. Afterwards, the PL signal merely tend to recover in the presence of targets and hence realize the detection of targets. For instance, Lv and co-workers has reported that CNNSs with persistent luminescence could be utilized to construct a sensitive sensing method for the detection of biothiols using Ag^+ as the quencher as shown

in Fig. 8B.⁹⁶ The PL of CNNSs was first quenched by Ag^+ via the PET and turned on due to the interruption of biothiols, which obviously impressed the effects of impurities and thus enhance the sensitivity. It has been realized to detect multiple substances like ascorbic acid¹¹⁴, hyaluronidase⁷⁶, alkaline phosphatase¹¹⁵, and cyanide¹¹⁶ using a “on-off-on” strategy by means of the PET between metal ions and CN nanostructures. Apart from metal ions, MnO_2 has also been reported by Yang and co-workers to quench the PL of CNNSs, which could be eliminated in the presence of glutathione due to the reduction of MnO_2 to Mn^{2+} and thus monitored the content of glutathione.¹¹⁷

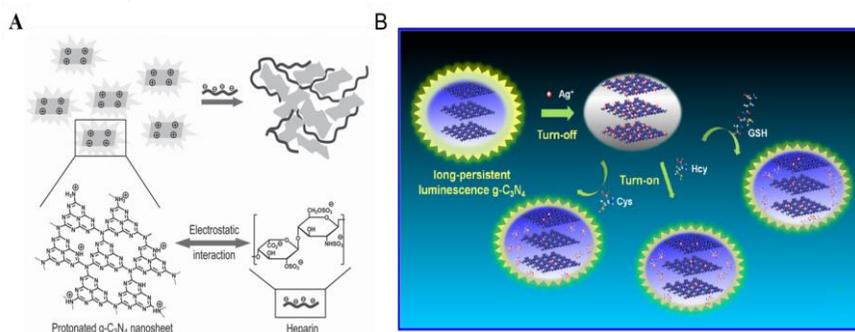


Figure. 8. Photoluminescent sensing application of CN. A) Scheme of turn-off photoluminescent sensing of heparin by CNNS.⁶⁴ B) Scheme of on-off-on photoluminescent sensing of biothiols by CNNS.⁹⁶

For further enhancement of the sensitivity of CN-based sensors, the ratiometric PL strategy with dual-output signals was presented so as to normalize the variation from environmental changes and realize more accurate sensing. For example, Yin and co-workers have constructed a ratiometric PL probe composed of gold nanoclusters (AuNCs) and CNQDs to capture and detection of circulating tumor cells (CTCs).¹¹⁸ AuNCs and CNQDs served as two fluorophores respectively. The former kept unchanged but the later recovered in the presence of CTCs due to the decline of CNQDs aggregation.

5.2 Photoelectrochemical Biosensing

As mentioned above, PEC is a switching process from light to electricity, which mainly comprises the separation of electrons and holes under the irradiation, the conduction of electrons and holes from photoactive materials to the working electrode and electrolyte respectively as well as the oxidation of soluble substances by holes to complete the current circuit in the PEC cell. Certainly, it is possible for photo-induced electrons and holes transfer in the reverse direction. Thus, any variation in these several step in the PEC process may result in changes of photocurrent signals, which contributes to flexible and multiple possible biosensing designs. The fundamental mechanisms can be mainly divided into two pathways. One is to directly consume the photo-induced electrons or holes by the redox of targets dissolved in the electrolyte to hinder the recombination of electron-hole pairs and consequently generated enhanced PEC signals.

A series of “turn-on” PEC biosensors have been constructed via the direct consumption of holes on the VB of CN materials, which generally require the appropriate redox potential of targets.¹¹⁹⁻¹²⁰ For example, Zhang and co-workers presented a PEC sensor for the detection of tetracycline which could be oxidized after capturing by the aptamer and encountering the holes of CN-CdS nanocomposites.⁸⁰ Besides, Yuan and co-workers constructed a PEC biosensor coupling with a DNA walker for the detection of microRNA, where the photoinduced current obviously rose after the approach of Dox to the g-C₃N₄ substrate as illustrated in Fig. 9A.²⁶ Similarly, targets can also be detected by means of accepting the electrons on the CB of CN materials, resulting in improved PEC signals. Dai and co-workers have realized the PEC sensing of human interleukin-6 by virtue of nanocomposites of CN and AgI with enhanced PEC signals, which could be further improved due to the decreasing photoinduced electrons scavenged by the product of biocatalytic precipitation reaction.¹⁰⁸ The other strategy is to indirectly affect the concentrations of electron donors or acceptors via interactions or reactions with targets and hence to vary the PEC signals, which can be further classified into two types according to the enhancement or suppression of photocurrents. As for the increased PEC signal, Yin and co-workers has constructed a CN-TiO₂ based PEC biosensor for the detection of PKA which could catalyze

the *L*-ascorbic acid 2-phosphate trisodium salt (AAP) to produce electron donor of ascorbic acid (AA), resulting in the enhanced photocurrent.¹⁰³ Moreover, materials with catalase-like activity to generate the electrons donors or acceptors have also been applied in the CN-based PEC sensors. Dai and co-workers have realized the monitoring of H₂O₂ by capturing G-quadruplex/hemin/Pt nanoparticles on CNNSs through the base complementary, which could catalyze the decomposition of H₂O₂ into oxygen and consequently consume the photoinduced electrons of CN and boost the photocurrent (Fig. 9B).¹⁰⁵ Differently, Tang and co-workers designed a CN-based “turn-off” PEC biosensor for the detection of prostate-specific antigen (PSA), where the Cu²⁺ generated by the oxidation of DNA-templated copper nanoclusters could effectively suppress the photocurrent via grabbing the electrons from CB of CN.¹²¹ This kind of indirect approach can fairly enrich the species of targets in CN-based PEC sensors. Apart from these two typical biosensing designs, as a kind of photoactive materials, CN can serve as a PEC tag which tends to access the working electrodes in the presence of targets to generate the photocurrent intimately related to the concentrations of targets.²⁷ Besides, given the insulation of biomacromolecules, the PEC biosensing can also be realized through the binding of targets with low conductivity on the surface of CN, reducing the photocurrent. Wu and co-workers have constructed a “turn-off” PEC sensor for thrombin which could block the electron transfer from the electron donor to the CN and TiO₂ composite.¹⁰⁴ Multiple steps in the PEC process contribute to various mechanisms of CN-based PEC biosensors towards abundant targets.

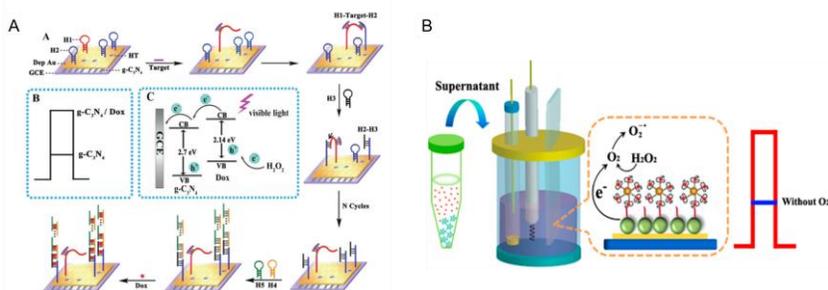


Figure 9. Photoelectrochemical sensing application of CN. A) Schematic illustration of photoelectrochemical sensing of micro-DNA via the combination of CN and Dox with an improved PEC signal.²⁶ B) Schematic illustration of photoelectrochemical sensing of H₂O₂ by CNNS and PbS quantum dots.¹⁰⁵

5.3 Electrochemiluminescent Biosensing

As the reverse process of PEC, ECL that is driven by the electrochemical generation of excited states mostly with the assistance of coreactants, has drawn increasing attention for biosensors because of its attractive merits such as the avoidance of photoexcitation background and the principally high signal-to-noise ratio. Based on multiple steps of the ECL process involving the conversion between electrons and photons, the ECL sensing mechanisms can be flexible and various. Firstly, some analytes can accept the electrons from the CB of CN materials in the excited state to quench the ECL signal, which has been widely used to construct reliable sensors especially for metal ions. Choi and co-workers constructed the “turn-off” ECL sensor to detect the copper ions for the first time, in which copper ions coordinated with the inherent ligands of CN could quench the ECL due to the electrons transfer from CN.⁹⁵ Our groups realized the detection of Cu^{2+} via CNNS prepared by liquid-exfoliation of bulk g-CN with different degrees of polymerization.¹² It is worth noting that the selectivity of copper can be attributed to the redox potential of Cu^{2+}/Cu lying between the CB and VB of CN materials. Not merely for sensing metal ions, our group has realized the detection of the target DNA by means of the ability of Cu^{2+} to bind with the N7 position of DNA bases and quench the ECL of CNNS.⁶⁵ An alternative way to quench the ECL signal of CN is thought to be the ECL resonance energy transfer (ECL-RET) in which the energy of excited CN can be efficiently transferred to some neighboring substances to realize the “turn-off” biosensing.¹⁰⁶ For example, Xiao and co-workers has presented an ECL sensor for rutin since its oxidation product could effectively quench the anodic ECL of CN due to the energy transfer.⁸⁷ To further enhance the sensitivity, a series of ratiometric assays have been constructed based on the ECL-RET process, which could effectively normalize for environmental changes through the ratio of double signals. Usually, CN can serve as the donor whose signal is declined in the presence of targets and consequently generate another signal through the energy transfer to other substances such as dimethylthiodiaminoterephthalate,¹⁰¹ $\text{Ru}(\text{dcbpy})_3^{2+}$ nanocomposites⁹⁰ and so on. Chen and co-workers realized the dual-wavelength ratiometric detection of microRNA by means of the RET from the AuNPs

functionalized CN to $\text{Ru}(\text{dcbpy})_3^{2+}$ (Fig. 10A).¹²² Moreover, CN nanostructures can be directly utilized as ECL tags in the biosensing to realize the “turn-on” detection when reaching the surface of electrodes due to the recognition interaction of biomolecules.^{25, 92, 94} For instance, Yuan and co-workers reported an ECL sensor for cardiac troponin I using the antigen-antibody interaction to capture CNNSs whose ECL signals was improved by MIL(Fe).⁹³ Our group developed a sandwich-assembled ECL biosensor for the detection of DNA methyltransferase via the affinity of single-stranded DNA and CNNSs, where multifunctional CNNSs served as both the analyte reporter and the self-test reporter to enhance the reliability.⁹⁹ Given the necessity of coreactants in CN-based ECL biosensing, ECL signals can be indirectly disturbed through the changes in the concentration of coreactants neighboring CN materials induced by various recognition interactions of targets. For example, Ju and co-workers has ever constructed a DNA ECL biosensor by virtue of the DNA strands labeled by hemin which could consume the dissolved oxygen and thus inhibited the generation of H_2O_2 , the endogenous coreactant for CNNSs.¹²³ In addition to chemical reactions, the steric hindrance of biomolecules with high molecular weights can also been taken as effective approach for modulating the diffusion of coreactants or electrons to the surface of CN materials. A variety of proteins have been successfully detected by limiting the concentration of coreactants or electrons at the surface of CN modified electrodes.^{50, 89} Notably, Kim and co-workers has built Boolean logic gates OR and AND for simultaneously sensing proteases and nucleases by virtue of the steric hindrance of polymers.¹²⁴ Lastly but not the least, the multiple-mechanism-driven ECL biosensing has emerged to boost the sensitivity and broaden the detection range. Our group developed a biomimetic ECL biosensor for 8-hydroxy-2'-deoxyguanosine based on two competitive mechanisms involving catalysis and steric hindrance, resulting in inherently improved sensitivity compared with those of single-mechanism-driven biosensors as illustrated in Fig. 10B.²⁴

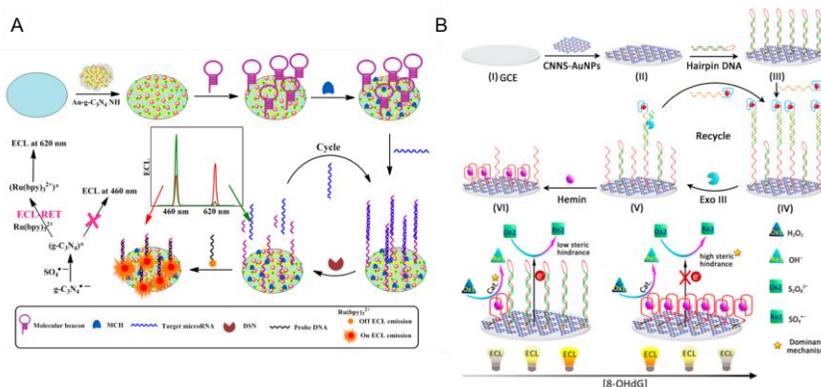


Figure 10. Electrochemiluminescent sensing application of CN. A) Scheme of the dual-wavelength ratiometric ECL-RET sensing of micro-RNA by CNNS and Ru(bpy)₃²⁺.¹²² B) Scheme of the dual-mechanism-driven electrochemiluminescent sensing of 8-OHdG with different reactions occurring at the biosensor at (left) low and (right) high concentrations of 8-OHdG.²⁴

6. Outlook

It should be noted that as a metal-free semiconductor most investigations of CN are focusing on its optoelectronic properties, which have already demonstrated its great potential to be an emerging probe to address the challenges in more demanding biosensing applications. Nonetheless, new mechanism and more insights of kinetics for carbon nitride in biosensing are still significantly lacking, which deserves a future comprehensive study.

Moreover, beyond the wide studied semiconducting properties, other interesting features, e.g., that originate from its unique molecular structures also show new lights of advancing functions of CN for biosensing. For example, CN materials own an intense electron donating nature by virtue of the high nitrogen content, which also endow CN with unique catalytic properties. In addition to their photocatalytic activity, CN materials also exhibit a peroxidase-like activity to catalyze the decomposition reaction of H₂O₂ to generate reactive hydroxyl radicals, which has been frequently applied in colorimetric sensing coupled with the 3,3',5,5'- tetramethylbenzidine (TMB). For instance, Qu and co-workers have constructed a facile proteins sensing array using CNNSs as

the single sensing receptor with multiple readout signals owing to the different interactions between CNNS and proteins.²⁹ The intense interaction could severely affect the accessibility of substrates to the active sites on the surface of g-C₃N₄ nanosheets, suppressing the catalytic efficiency of CNNSs. However, Jiang and co-workers have found that single-stranded DNA adsorbed on g-C₃N₄ nanosheets could obviously improve the peroxidase-like catalytic activity of CNNSs and realized the sensitive colorimetric detection of exosomes in the solution of H₂O₂ and TMB (Fig. 11A).³⁰ Such activity enhancement could be attributed to the strong interaction between TMB and ssDNA mediated by electrostatic attraction and aromatic stacking. Moreover, some CN-based nanozymes can also catalyze the conversion of o-phenylenediamine (OPD) to fluorescent 2,3-diaminophenazine (DAP) in the presence of H₂O₂. Given the fluorescent property and quenching effect of the product DAP, ratiometric fluorescence sensors were established to directly detect hydrogen peroxide or indirectly detect the glucose with the assistance of glucose oxidase.¹²⁵⁻¹²⁶ Interestingly, it was demonstrated by Zhang and co-workers that the intense electron donating feature also endowed CNQDs with the reducibility for the reduction of Ag⁺ to Ag nanoparticles with a unique absorption peak, which could be utilized for colorimetric biosensing of biothiols.³¹ Besides, CN-based nanocomposites have also been found to possess the electrocatalytic activity. Wang and co-workers have realized the electrochemical sensing for the hydrogen peroxide due to the unique catalytic performance of the synthesized copper oxide-CN nanocomposites.¹²⁷

In another interesting work, by virtue of the strong affinity for Lewis acid, the mesoporous carbon nitride (MCN) was applied in volatile organic compounds sensors with the assistance of the quartz crystal microbalance (QCM) technique (Fig. 11C).¹²⁸ It has been demonstrated that the presence of 3D structures with large specific surface area as well as tremendous active Lewis basic sites (-NH₂, -NH) of MCN could offer widely opened spaces and access to more number of interaction sites for the targets absorption. Our group found the CN nanofibers could be obtained by means of hydrolyzing bulk CN in sodium hydroxide solution, the surface of which were modified with abundant functional groups such as -NH_x and -OH.¹²⁹ Interestingly, the as-obtained CN nanofibers could transform into

a 3D hydrogel network once contacted with CO₂ which formed a delicate complexation with functional -NH_x groups. The reverse transformation process could be easily realized by bubbling N₂ to remove CO₂. More importantly, this kind of CN hydrogel exhibited excellent ability to highly selectively extract specific dyes as well as reversibly release them by virtue of the collaborative electrostatic and π - π interactions. Such feature could significantly contribute to the sample preconcentration and release with high selectivity and efficiency for biosensing.

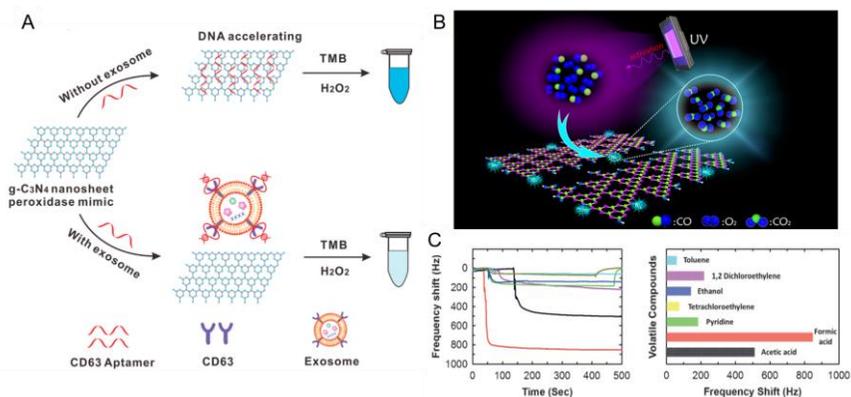


Figure 11. Multiple novel sensing mechanisms of CN materials. A) Scheme of DNA aptamer accelerating the intrinsic peroxidase-like activity of CNNS for the detection of exosomes.³⁰ B) Scheme of the UV-assisted cataluminescence sensor for gaseous CO based on CN.¹³⁰ C) Response of quartz crystal microbalance sensor coated by mesoporous CN on different organic vapors.¹²⁸

Various unique chemiluminescence (CL) phenomena dependent on CN-based materials have been discovered recently, and it would also be developed as a future research field. As for these systems, CN served as luminophores. For example, Lv and co-workers found that prepared CNQDs exhibited a strong chemiluminescence emission in the presence of NaClO and thus realized the direct CL sensing for the free chlorine.²³ Moreover, a UV-assisted cataluminescence (CTL) sensor for the detection of gaseous CO was successfully developed by means of CN, where CO molecules activated by the UV irradiation were combined with the

functional carboxyl groups on CN and catalyzed to emit strong luminescence (Fig. 11B).¹³⁰

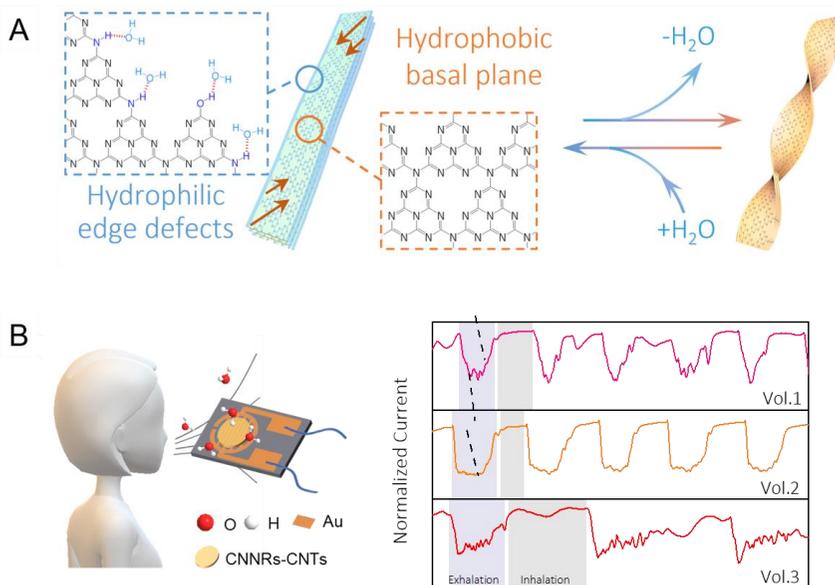


Figure 12. CN-based mechanical deformation sensor for breathing. A) H_2O -induced deformation of CN nanoribbons with an anisotropic intraplanar and interplanar molecular arrangement. B) Scheme of breath management using the proposed contactless CNNRs–CNTs humidity sensor in an open environment and graphic waveforms of breathing from different volunteers detected by the CNNRs–CNTs humidity sensor.¹³¹

CN materials can also be utilized to construct effective sensing platforms through the mechanical deformation due to the interaction between their nanostructures and small molecules. For instance, our group proposed a humidity sensor with high selectivity and sensitivity based on the anisotropic deformation of CN nanoribbons (CNNR) upon interaction with water molecules, which derived from the reversible formation of a hydrogen-bonded H_2O adsorption layer as illustrated in Fig. 12A.¹³¹ Such mechanical deformation could be facilely converted into measurable electrical readouts after coupling with carbon nanotubes (CNTs) via π – π interaction. The excellent reversibility of as-obtained sensor was attributed to the competitive wettability between the hydrophilic edge and

hydrophobic basal plane of CNNR. Taking advantage of the ultrafast response speed (50 ms), the CNNR-based humidity sensor was successfully applied to real-time respiratory monitoring in a contactless and open-environment mode (Fig. 12B). Interestingly, the as-obtained real-time breathing graphic waveforms exhibited much higher sensitivity than that by the clinic pulmonary function testing station in a sealed mode.

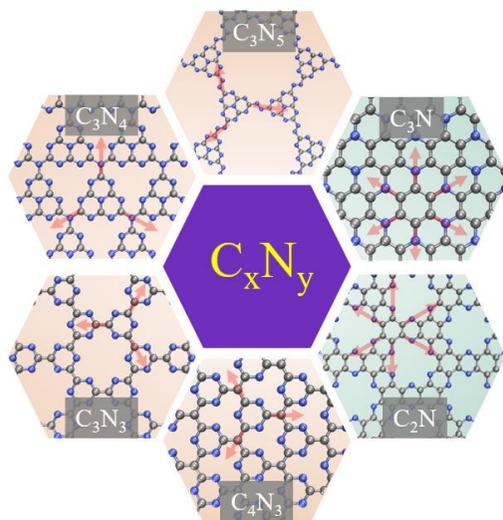


Figure 13. Carbon nitrides with different stoichiometric C/N ratio. C atoms are colored in gray, while N atoms are colored in blue. The red arrows highlight the bond directions in each topological structure. The three- and six-bond-extending framework in different C_xN_y materials are classified by using orange and green background, respectively.⁵⁴

Despite the rapid development of CN-based sensors, the sensing application of CN materials just takes the initial step. As a kind of metal-free polymeric semiconductor, CN with flexible structures and various C and N stoichiometric ratios can be facily designed and prepared for further improved properties and performance in construction of sensors (Fig. 13).⁵⁴ Moreover, the excellent dispersibility in wet media and intense interaction as well as recognition with target molecules contribute to highly selective and sensitive sensing, which demands for novel approaches for preparing CN nanostructures and effective modification of

abundant functional groups on the surface. Furthermore, the low electronic conductivity of CN itself and poor charge transfer between CN and substrates still hinder the sensing application of CN materials, especially for ECL and PEC with the photoelectric transformation. Hence, it makes sense to improve the electronic conductivity of CN by doping with proper atoms, constructing nanocomposites with other highly conductive materials and so on. Besides, outstanding preparation techniques of CN electrodes are supposed to be discovered to realize the intimate contact and effective charge transfer between CN materials and substrates and further enhance the sensing performance.

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