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REVIEW
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2D/2D Graphitic Carbon Nitride ($g-C_3N_4$) Heterojunction Nanocomposites for Photocatalysis: Why Does Face-to-Face Interface Matter?

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In recent years, two-dimensional (2D) graphitic carbon nitride ($g-C_3N_4$) has elicited interdisciplinary research fascination among the scientific communities due to its attractive properties such as appropriate band structures, visible-light absorption, and high chemical and thermal stability. At present, research aiming at engineering 2D $g-C_3N_4$ photocatalysts at an atomic and molecular level in conquering the global energy demand and environmental pollution has been thriving. In this review, the cutting-edge research progress on the 2D/2D $g-C_3N_4$-based hybrid nanoarchitectures will be systematically highlighted with a specific emphasis on a multitude of photocatalytic applications, not only in waste degradation for pollution alleviation, but also in renewable energy production [e.g., water splitting and carbon dioxide (CO_2) reduction]. By reviewing the substantial developments on this hot research platform, it is envisioned that the review will shed light and pave a new prospect for constructing high photocatalytic performance of 2D/2D $g-C_3N_4$-based system, which could also be extended to other related energy fields, namely solar cells, supercapacitors, and electrocatalysis.

Keywords: graphitic carbon nitride ($g-C_3N_4$), photocatalysis, energy conversion, environmental remediation, 2D/2D heterojunction, face-to-face interface

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INTRODUCTION

Photocatalysis is emerged as one of the Holy Grails of sustainable and green technologies for solar energy conversion, energy storage, and environmental remediation, which has been intensively examined over the past few decades worldwide to search for novel photocatalysts (Inoue et al., 1979; Linsebigler et al., 1995; Ma et al., 2014; Ong et al., 2014a, 2016b; He and Que, 2016; Li et al., 2016a; Wenderich and Mul, 2016; Zhang et al., 2016a; Eftekhari, 2017; Liu et al., 2017; Osterloh, 2017; Roger et al., 2017). By harvesting solar energy as the source of renewable energy, photocatalysis will make significant impacts in the areas of (1) light-driven water splitting to hydrogen (H_2) and oxygen (O_2) (Chen et al., 2010; Bai et al., 2016; Wei et al., 2016; Putri et al., 2017; Yubin et al., 2017), (2) conversion of carbon dioxide (CO_2) to energy bearing fuels (Ong et al., 2013, 2014c; Tan et al., 2014, 2016, 2017; Gui et al., 2015; Guo et al., 2016a; Zhang et al., 2016c), (3) mineralization of waste and pollutants (Ong et al., 2014d,e; Fang et al., 2016; Liu et al., 2016c; Topcu et al., 2016; Zhao et al., 2016b), (4) selective organic transformations (Liu et al., 2014; Zhao et al., 2016a), and (5) disinfection of bacteria (Keane et al., 2014; Bing et al., 2015) (**Figure 1**). Very recently, two-dimensional (2D) semiconductor photocatalysts have triggered a renaissance of interest in the field of energy, and environmental-related applications thank to the high ratio of surface-to-volume and unprecedented electronic and optical characteristics (Ong et al., 2014b; Bai et al., 2015; Liang et al., 2015d; Fang et al., 2016; Kalantar-zadeh et al., 2016; She et al., 2017; Xueting et al., 2017). Among a large array of photocatalysts, research targeting at graphitic carbon nitride (g-C_3N_4) has been flourishing in recent years. Since the first exploratory study on the use of g-C_3N_4 in photocatalytic H_2 evolution in 2009 (Wang et al., 2009), there has been an exponential increase in the scientific research on the subject of g-C_3N_4-based materials with more than 800 publications in 2016 based on Web of Science.

By and large, g-C_3N_4 can be facilely prepared by nitrogen-rich precursors, namely urea, thiourea, melamine, and dicyandiamide (Han et al., 2015; Guo et al., 2016b; Zhou et al., 2016; Tong et al., 2017). Therefore, the development of g-C_3N_4-based photocatalysts is anticipated to surmount the issues of increasing concerns on fossil fuel depletion and environmental threats due to combustion of exhaustible fossil fuels. The metal-free g-C_3N_4 demonstrates distinctive attributes such as visible-light responsiveness with moderate band gap of *ca.* 2.7 eV, appealing band structures and electronic characteristic, its earth-abundant nature, non-toxicity, relative ease of synthesis, and excellent chemical stability (Lu et al., 2016; Ong et al., 2016b; Zhang et al., 2016b; Lee et al., 2017). Additionally, it has been proven that 2D semiconductor possessed improved mobility of charge carriers and reduced charge recombination as compared to the 0D and 1D nanomaterials (Meng et al., 2012; Ida and Ishihara, 2014). In spite of the fascinating properties possessed by 2D g-C_3N_4, pristine g-C_3N_4 demonstrated several shortfalls such as sluggish separation of electron–hole pairs, limited visible-light absorption beyond 460 nm, small specific surface area, and low electrical conductivity (Liang et al., 2015b; Hou et al., 2016; Shi et al., 2016; Zhang et al., 2016g; Li et al., 2017; Xia et al., 2017). To overcome these bottlenecks, modification of bare g-C_3N_4 such as nanostructure design (Niu et al., 2012; Liang et al., 2015c; Zheng et al., 2015), intercalation with Li^+ and Cl^- (Liang et al., 2015a), elemental doping (Hu et al., 2015; Huang et al., 2015; She et al., 2016), copolymerization (Fan et al., 2016; Rahman et al., 2016), coupling with metals or noble metals (Tonda et al., 2014; Ong et al., 2015b), incorporation with other semiconductors (Ong et al., 2016a; Putri et al., 2016a; Zhang et al., 2016g; Ye et al., 2017), hybridization with metal phosphides (Pan et al., 2017; Wen et al., 2017; Yi et al., 2017; Zhao et al., 2017a,b), and many more has been widely investigated to enhance the photocatalytic efficiency for practical benefits. To date, there are a number of excellent review articles highlighting on g-C_3N_4-based photocatalysts ranging from materials synthesis, functionalization, and hybridization to diversified applications (Cao et al., 2015; Dong and Cheng, 2015; Yin et al., 2015; Zhang et al., 2015a; Zhao et al., 2015; Liu et al., 2016a; Mamba and Mishra, 2016). This undoubtedly connotes the significance of this research field hitherto in the scientific community.

FIGURE 1 | Schematic of multifarious applications in photocatalysis research field.

Recently, the incorporation of 2D g-C_3N_4 photocatalyst with other 2D nanomaterials forming 2D/2D heterojunction hybrid nanocomposites has conceivably drawn increasing attention with practical importance (Hou et al., 2014; Xing et al., 2017). As a matter of fact, the layered heterojunction comprised dissimilar 2D nanomaterials is projected to give rise to positive impacts on charge transfer and separation as a result of built-in electric field at the atomically well-defined ultrathin interface (Hou et al., 2013b; Lu et al., 2016). Thus, the research on 2D/2D heterojunction with intimate face-to-face interface is of timely significance, which will elucidate us to deeply comprehend the photocatalytic reaction mechanism at the molecular level. Therefore, in this review, this leads to my immense interest to summarize the state-of-the-art research on 2D/2D g-C_3N_4 heterojunction nanohybrids to throw light on the future research horizon of g-C_3N_4 in artificial photosynthesis and environmental remediation.

DEVELOPMENT OF 2D/2D g-C_3N_4-BASED HETEROJUNCTION

It is well documented that 2D/2D nanocomposites bestow greater electron–hole mobility across the heterojunction interface, which will in turn reduce the distance and time of charge transport to impede the electron–hole recombination rate (Hou et al., 2013a; Cheng et al., 2015; Ong et al., 2015c). This is attributed to the larger 2D/2D face-to-face contact area compared with line-to-face contact in 1D/2D heterojunction and point-to-face contact in 0D/2D heterojunction as depicted in **Figure 2**.

Hybridization with 2D Transition Metal Chalcogenides

In recent years, the incorporation of 2D metal sulfides has underpinned enormous interests in photocatalysis (Liu et al., 2016b; Lu

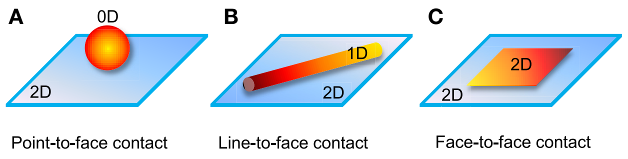

FIGURE 2 | **Diagram of (A) 0D/2D, (B) 1D/2D, and (C) 2D/2D heterointerfaces**.

et al., 2016; Yu and Sivula, 2016). In a work by Dong's research group, they reported a hierarchical sheet-on-sheet $ZnIn_2S_4$/g-C_3N_4 heterostructure by growing ultrathin $ZnIn_2S_4$ onto g-C_3N_4 nanosheets (Zhang et al., 2016e). As a result of intimate heterojunction interface formed between $ZnIn_2S_4$ and g-C_3N_4, the hybrid nanocomposites demonstrated walloping 17.6- and 3.9-folds enhancement of H_2 evolution compared to the single component g-C_3N_4 and $ZnIn_2S_4$, respectively. From the perspective of lifetime of charge carriers evidenced from time-resolved photoluminescence analysis, the average lifetime of the $ZnIn_2S_4$/g-C_3N_4 nanohybrids was reduced from 10.45 to 8.97 ns relative to that of pristine g-C_3N_4 nanosheets, which was attributed to rapid charge transfer and separation to hinder the electron–hole recombination. In addition to $ZnIn_2S_4$, MoS_2-decorated S-doped g-C_3N_4 heterojunction films were successfully developed by Chen and coworkers (**Figure 3A**) for enhanced photoelectrocatalysis (Ye et al., 2016). It is noted that the generation of anodic current by the MoS_2/S-doped g-C_3N_4 photoanode was markedly twice than that by the S-doped g-C_3N_4, highlighting the rational importance of a robust heterointerface with intact p–n junctions for effective charge migration (**Figure 3B**).

Till now, the theoretical understanding on the coupling interaction and transfer of charge carriers between 2D g-C_3N_4 and 2D MoS_2 has not been exhaustively investigated. Wang et al. (2014) elucidated the fundamental mechanism of photocatalytic improvements by systematically exploring the interface region between MoS_2 and g-C_3N_4. Based on the density functional theory (DFT) calculations, it was confirmed the presence of charge redistribution at the 2D/2D heterojunction interface of MoS_2/g-C_3N_4. It is worth mentioning that a type II heterojunction structure was successfully developed due to the well-matched band alignment as attested by the density of states results. As a result of efficient migration of charge carriers, a polarized field was formed at the contact heterointerface, prohibiting the electron–hole recombination. Therefore, this DFT finding provides new inroads into the importance of constructing 2D/2D nanocomposites for face-to-face interaction, which could certainly be extended to other binary or even ternary layered heterojunction for enhanced photochemistry applications.

Hybridization with 2D Metal Oxides

Apart from 2D transition metal chalcogenides, coupling g-C_3N_4 nanosheets with 2D metal oxides, such as TiO_2 (Gu et al., 2014), WO_3 (Li et al., 2016b), and $SnSb_2O_6$ (Zhang et al., 2016d), has become the recent research focus to improve the photocatalytic performance. For instance, Li et al. (2016b) employed a hydrothermal and deposition-heating technique to fabricate WO_3/g-C_3N_4 nanosheet arrays on the FTO substrates. The photoelectrochemical splitting of natural seawater using the WO_3/g-C_3N_4 nanostructures presented two times greater in the photocurrent density in reference to the pristine WO_3 nanosheet arrays under the simulated sunlight source. This was accredited to the well-matched band energy of WO_3 and g-C_3N_4 forming synergistic interfacial contacts for remarkably boosting the charge migration ability. In another work, Xing's group hybridized $AgIO_3$ with anisotropic g-C_3N_4 nanosheets to form a 2D/2D layered heterointerface toward increased photodegradation of Rhodamine B and methyl orange pollutants (Li et al., 2015). It is anticipated that these works will lay a pioneer groundwork and shed light for future directions in the interface engineering of 2D metal oxides and g-C_3N_4 for the advancement in solar energy conversion and environmental remediation toward practical applications.

Most recently, perovskite-type nitrogen-doped $La_2Ti_2O_7$ (NLTO), comprising a 2D architecture with a thickness of 7 nm, was for the first time hybridized with 2 nm thick g-C_3N_4 nanosheets by means of a facile two-step hydrothermal method and a thermal treatment process (**Figure 4A**) (Cai et al., 2017). The hybrid layered nanomaterials showed excellent photocatalytic H_2 evolution with a high apparent quantum efficiency of 2.1% at 400 nm. The enhanced photoactivity was ascribed to the successful development of the large 2D/2D interface between NLTO and g-C_3N_4, resulting in long lifetime and favorable transfer of charge carriers *via* type II band alignment. Upon visible-light illumination, the photoexcited electrons were facilely migrated from g-C_3N_4 to NLTO, whereas the photogenerated holes were transported from NLTO to g-C_3N_4, hampering the charge recombination process (**Figure 4B**). Notably, this was arisen from the band bending formed at the heterointerface, which induced a built-in electric field for the flow of charge carriers.

Furthermore, 2D niobium phase-layered perovskite Dion–Jacobson compounds have become a hot focal field in materials science and engineering for clean energy production and environmental cleaning in the past few years (Maeda et al., 2014; Oshima et al., 2016). It is well known that the layered perovskite $Ca_2Nb_3O_{10}^-$ nanosheets, emerging from NbO_6 octahedra building blocks, are promising owing to their good chemical stability, high surface area, and relatively cost-effective (Sabio et al., 2010). Therefore, it is expected that by integrating the idea of $Ca_2Nb_3O_{10}^-$ nanosheets into 2D g-C_3N_4 photocatalysts from the viewpoint of materials design, the photocatalytic efficiency of the composite nanomaterials will be exhilaratingly elevated. In a very recent work published in 2017, Chen's group designed a visible-light-responsive 2D/2D $K^+Ca_2Nb_3O_{10}^-$ / g-C_3N_4 nanosheet heterojunction, which was fabricated by a hydrothermal process (**Figure 4C**), for photodegradation of tetracycline hydrochloride (Jiang et al., 2017). The hybrid photocatalyst manifested a strikingly high activity, which was 6.6 and 1.8 times greater compared with that of pure $K^+Ca_2Nb_3O_{10}^-$ and g-C_3N_4, respectively, due to the well-contacted heterointerfaces with strong interfacial coupling. Similarly, another group of researchers has synthesized the nanosheet composites by combining $Ca_2Nb_2TaO_{10}$ and g-C_3N_4 nanosheets through a simple solution exfoliation-reassembly

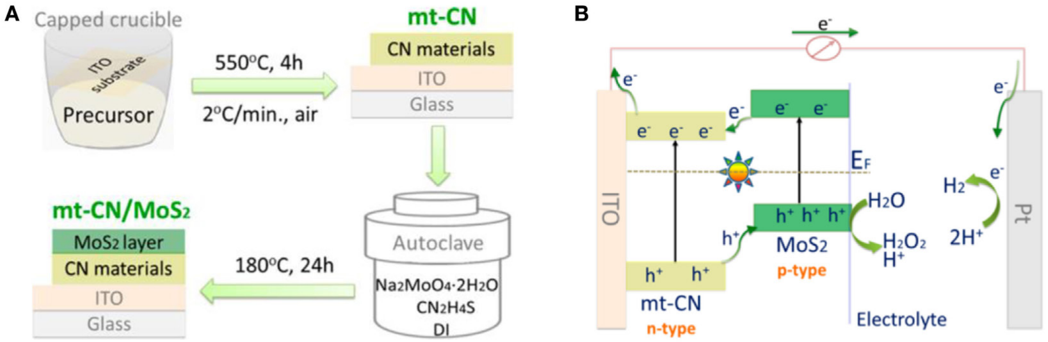

FIGURE 3 | **(A)** Synthesis route of MoS_2/S-doped g-C_3N_4 heterojunction film on ITO glass. **(B)** Charge transfer and separation of MoS_2/S-doped g-C_3N_4 photoanode *via* p–n heterojunctions for the improved H_2 generation. Reproduced from Ye et al. (2016) with permission from the American Chemical Society.

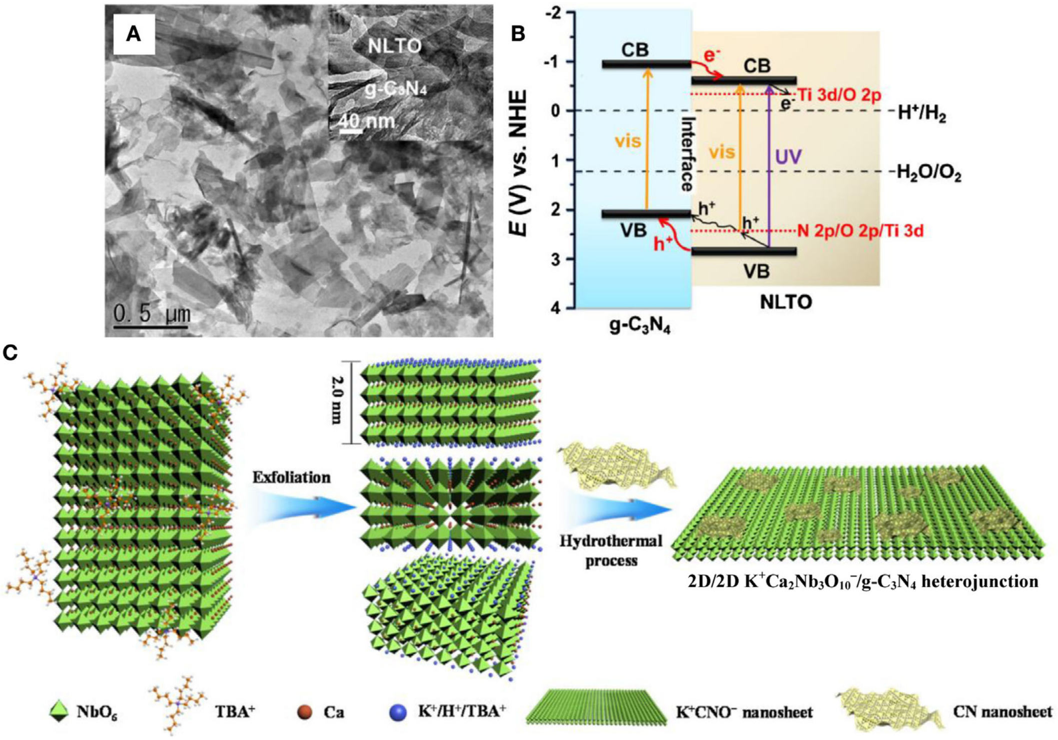

FIGURE 4 | **(A)** Transmission electron microscopy image of NLTO/g-C_3N_4 hybrid photocatalysts. **(B)** Schematic of effective transfer of photogenerated electrons and holes across the heterojunction interface of NLTO/g-C_3N_4 through a type II band alignment. Reproduced from Cai et al. (2017) with permission from Elsevier. **(C)** Synthesis procedure of 2D/2D $K^+Ca_2Nb_3O_{10}^-$/g-C_3N_4-layered nanohybrids. Reproduced from Jiang et al. (2017) with permission from Elsevier.

technique for solar H_2 production (Thaweesak et al., 2017). As such, it is believed that this research will cast new opportunities for engineering 2D/2D perovskite-based nanosheets coupled with g-C_3N_4 heterojunction interface for multitudinous light-driven applications.

Hybridization with 2D Graphene

At present, π-conjugated carbonaceous nanomaterials, including carbon nanotubes, grapheme, and carbon nanodots has emerged as one of the most fascinating and exciting research directions in the past 10 years especially in the arena of environmental remediation, energy conversion, and energy storage (Tan et al., 2013; Cazorla-Amorós, 2014; Li et al., 2014; Cao and Wei, 2015; Fan, 2015; Ali Tahir et al., 2016; Carmona et al., 2016; Kotal et al., 2016; Xu et al., 2016). These carbon nanostructures have been commonly utilized as excellent reduction cocatalysts by incorporating with semiconductor photocatalysts to prolong the lifetime of charge carriers to diminish the recombination of electron–hole pairs (Xu et al., 2013; Himaja et al., 2015; Liu et al., 2015; Tan et al., 2015a; Hu, 2016; Zhang et al., 2016f; Ong et al., 2017). It is discernable that the 2D graphene has directed a worldwide trend in the materials research stemming from its large surface area, remarkable electronic, optical and mechanical features, and high chemical stability (Putri et al., 2015, 2016b; Voon et al., 2016; Xiang et al., 2016). Up to now, a plethora of literature reports has been devoted to fabricate 2D/2D graphene/g-C_3N_4 nanohybrids for photoredox catalysis in H_2 evolution, pollutant degradation, and CO_2 reduction (Xiang et al., 2011; Li et al., 2013; Xu et al., 2015; Wan et al., 2016). In a work by Ong et al. (2015a), sandwich-like graphene/g-C_3N_4 nanocomposites were prepared *via* a one-step impregnation-thermal reduction process by employing graphene oxide and urea as the precursors (**Figure 5A**). Interestingly, the absorption band edge of the nanohybrids was slightly red shifted toward a longer wavelength, resulting in a reduction in the band gap energy. This phenomenon was contributed by the covalent cross linker (C–O–C) formed between g-C_3N_4 and graphene as a result of thermal heating at the high temperature. For the first time, the metal-free graphene/g-C_3N_4 photocatalyst played a prominent role in the reduction of CO_2 to CH_4 under visible light, which was 2.3 times higher than pristine g-C_3N_4. In this sense, this study incontrovertibly focuses the spotlight on the innovative design of metal-free layered photocatalysts as a new class of light-active materials for a cornucopia of catalytic applications.

In another closely related work by the similar research group, the novel 2D/2D-reduced graphene oxide (rGO)-hybridized protonated g-C_3N_4 (rGO/pCN) was rationally constructed by π–π stacking and electrostatic self-assembly between the positively charged pCN and the negatively charged rGO (**Figure 5B**) (Ong et al., 2015c). In the rGO/pCN hybrid nanoarchitectures, a well-dispersed sheet-on-sheet structure of rGO and pCN confirmed the well-intact interfacial contact (**Figures 5C,D**) as compared to the rGO/g-C_3N_4, which employed the unmodified g-C_3N_4 with a negatively charged surface. Essentially, the rGO/pCN heterojunction nanosheets endowed pronounced 5.4 and 1.7 times enhancement in the photoconversion of CO_2 to CH_4 with respect to the pCN and rGO/g-C_3N_4, respectively. Thus, this distinctly underlines the fundamental and technological importance of surface charge modification between two dissimilar 2D nanomaterials for robust interfacial interactions in unraveling the charge dynamics for enhanced photocatalysis. Benefiting from the predominant role of graphene as the electron reservoir (Zhang et al., 2012, 2015b; Tan et al., 2015b; Mateo et al., 2016; Varadwaj and Nyamori, 2016), the photoinduced electrons were transferred from pCN to rGO across the interface to overwhelmingly suppress the charge recombination rate (**Figure 5E**). All in all, the smart 2D/2D interface engineering design of graphene/g-C_3N_4 developed thus far is considered as an auspicious means, which

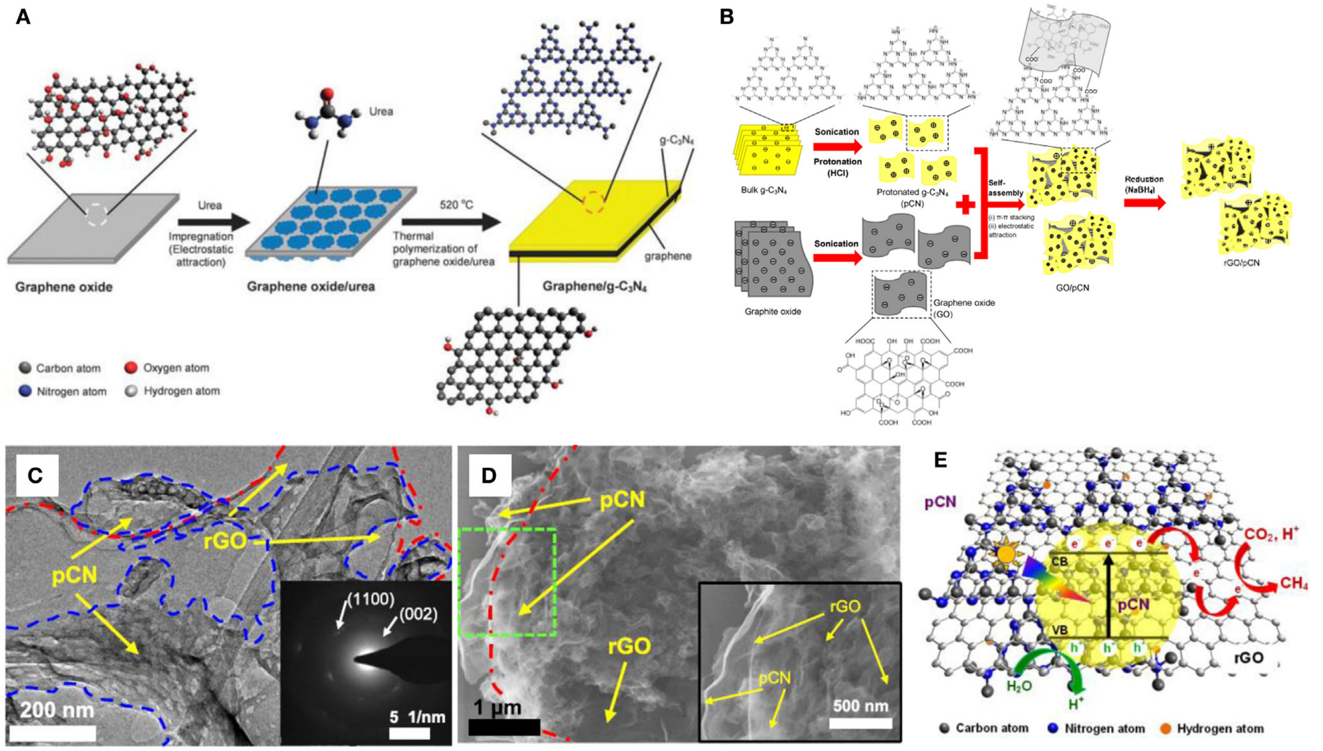

FIGURE 5 | (A) Fabrication of graphene/g-C_3N_4 photocatalysts by means of a facile impregnation-thermal reduction process. Reproduced from Ong et al. (2015a) with permission from Royal Society of Chemistry. **(B)** Schematic of reduced graphene oxide (rGO)/pCN samples developed by a sonication-aided electrostatic attraction and π–π interaction process. **(C)** Transmission electron microscopy and **(D)** scanning electron microscopy images of rGO/pCN samples. Inset of panel **(C)** is the selected area electron diffraction of rGO/pCN. **(E)** Reaction mechanism of photoreduction of CO_2 with H_2O over rGO/pCN samples. Reproduced from Ong et al. (2015c) with permission from Elsevier.

could be eminently extended to heteroatom-doping graphene-hybridized g-C_3N_4 for targeting superior photochemistry applications for real-life applications.

CONCLUSION AND OUTLOOK

In short, the burgeoning developments of nanoscale architecturing of g-C_3N_4-based hybrid structures over the past 8 years have witnessed a wealth of knowledge and information for the intelligent design and myriads of applications in sustainable energy conversion and environmental purification. The applications, which encompass water splitting, H_2 generation, O_2 evolution, CO_2 fixation, and pollutant degradation, have readily made full use of the intriguing features of g-C_3N_4, namely metal-free 2D nanomaterials, earth-abundant nature of the elements, visible-light optical absorption, high redox power, and excellent chemical stability. Since the advent of g-C_3N_4 photocatalysts by Wang et al. (2009) for H_2 generation, there is a rocket rise of research works on the modification of bare g-C_3N_4 to conspicuously increase the specific surface area, introduce porosity by textural modifications, extend visible-light absorption to longer wavelengths (even up to near infra-red) for the utilization of whole solar spectrum, decrease the band gap energy and bolster the charge migration and separation.

In this mini-review, a systematic discussion on the most updated advancements of engineering 2D/2D g-C_3N_4 heterojunction layered nanoarchitectures with boosted photoactivity has been reviewed. It is worth mentioning that albeit there is a large library of recent research discoveries on the 2D/2D g-C_3N_4-based photocatalysts, there exist numerous open issues, limitations, questions, and complexities of materials science, chemistry, physics, and environmental science, which require extensive research now and future. Among all, the actual mechanisms of enhanced catalytic efficiency toward the water splitting and CO_2 reduction followed by their respective reaction pathways are still up in the air yet until now. It is envisaged that the pertinent mechanism underlying the photocatalytic performance should be deeply explored by joining the experimental findings and theoretical computational simulations for the future research. In this manner, the rationale behind the profound photocatalytic enhancement especially on the rate determining steps of the reaction in the 2D/2D nanohybrids can be entirely comprehended. Apart from that, the charge carrier dynamics and transfer pathway for the Z-scheme system, p–n heterojunction, n–n heterojunction, Schottky junction, homojunction, and facet junction in the 2D/2D g-C_3N_4-based system will be facilely understood. Benefiting from both experimental results and first-principles DFT calculations, this will in turn provide us a rational outline to advance the state of the research on photocatalysis for the next breakthrough in the field of energy conversion.

Moreover, the coupling interaction between 2D g-C_3N_4 nanosheet and another 2D semiconductor is of utmost importance for developing intact heterojunction interfaces for efficient electron–hole shuttling to prolong the lifetime of charge carriers to accelerate the photocatalytic efficiency. In-depth studies in engineering, the intimate heterointerfaces of the 2D/2D nanohybrids at a molecular level will give rise to captivating results for tuning the existing molecular structure of bare g-C_3N_4, thereby enhancing mobility of electron–hole pairs and subsequently improving the photocatalytic redox ability. Additionally, it is crucial to attain a facile and low-cost metal-free 2D/2D g-C_3N_4-based photocatalyst system without comprising metal-containing semiconductors for practical benefits. Thus, continuous efforts in exploring non-metal semiconductors to couple with g-C_3N_4 will be advantageous for industrialization and commercialization in the long run to combat the cost concern for the large-scale processes.

To cut a long story short, it is apparent that the research progress has been tremendously impressive at this juncture by viewing at the relatively short period of time and history of g-C_3N_4-based photocatalysis. Undeniably, the incessant research efforts on the 2D/2D-layered nanocomposites will open new vistas and lay a strong foundation for advanced light-driven catalysis and electrocatalysis, which undeniably warrant continuous research along this direction. Without any doubts, this will act as a new paradigm for the next generation smart artificial photocatalytic systems for practical and commercial benefits in order to bridge the gap between lab-scale research and large-scale industrial applications. All in all, with the ceaseless cooperative work from all segments and disciplines in the world, the targets of building a cleaner, greener, sustainable, and zero-energy environment will be systematically accomplished in years to come. Last but not least, it is genuinely hoped that this mini-review will paint a much clearer image to direct us for the upcoming research horizons in 2D/2D photocatalysis for momentous breakthroughs in attaining highly effective, efficient, and economical g-C_3N_4-based system in future.

AUTHOR CONTRIBUTIONS

W-JO carefully outlined the contents of the review and wrote the entire manuscript.

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