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A simple melamine-assisted exfoliation of polymeric graphitic carbon nitrides for highly efficient hydrogen production from water under visible light

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Polymeric graphitic carbon nitride with two-dimensional (2D) structure has intensively potential applications in hydrogen production from water splitting under visible light irradiation. Searching a efficient technology is a key to synthesize 2D materials from bulk powder. Here, a simple, high-efficient, large-scale and low-cost melamine-assisted exfoliation route is reported to obtain quasi-2D carbon nitrides under oil bath. Quasi 2D carbon nitride possesses high specific surface area (116.76 m²·g⁻¹), a larger bandgap (by 0.13 eV), enhanced electronic transport ability in the in-plane direction, prolonged photo-excited charge carriers lifetime, lowered recombination of photo-induced electrons and holes resulting from quantum confinement effect. Those make enormous contributions to photoactivity for hydrogen production under visible light. Therefore, melamine-assisted liquid exfoliation route can be applied to large-scale polymeric carbon nitride photocatalyst production and is envisaged to have a great promise for the exfoliation of other materials with layered structure.

Introduction

Exploiting and optimizing suitable semiconductor as highly efficient photocatalysts for a clean hydrogen energy production have attract tremendous attention due to the increasing global crisis of energy shortage and environmental issues. A superior photocatalyst should integrate an ability to split the water molecular, an appropriate bandgap to absorb visible light, great capacity of electronic transport to transfer charge carrier and superior stability in contact with water^{1, 2}. In addition, it should be non-toxic, abundant and cost-efficient. In past years, semiconductor-based photocatalyst including graphene-based semiconductor¹, MoS₂², ZnO³, CdS⁴, TiO₂⁵ and has been developed as catalyst for hydrogen evolution under visible light. It is regarded as economic, safe, clean and renewable technology⁶, but the hydrogen production rate is low. A new polymeric graphite carbon nitride (g-C₃N₄) has reported as visible-driven photocatalyst for hydrogen evolution from water splitting, because of visible-driven band gap, unique electronic structure and proper band edge that straddle the redox potential of water photocatalysis^{7, 8}. Bulk g-C₃N₄ as a polymeric photocatalyst can be utilized for visible-light photocatalytic water splitting in the presence of electron donor⁷. In order to enhance the reactive activity, fruitful efforts have been made in the field of g-C₃N₄ based photocatalyst including atomic-level doping^{10, 11}, molecular modification^{12, 13} and exfoliation^{14, 15}.

When bulk g-C₃N₄ materials are exfoliated to layered structure, it would exhibit a new physiochemical performance, due to the quantum confinement effect. As semiconductor-based photocatalyst, the layered materials affect the charge carriers due to its unique electronic structure with band edges straddling the water redox potentials^{16, 17}. Hence, layered structure materials possess unique superiority for promoting photocatalytic efficiency. For example, the higher surface area provides abundant reaction sites. The shorter bulk diffusion length lowers recombination of photo-induced electrons-holes.

More importantly, the larger bandgap produced by shifting conduction bands and valence bands in opposite directions strong the redox ability of charge carrier. The changed photo physical behaviour of charge carrier caused by quantum confinement effect prolongs the lifetime of photo-excited electrons. These characteristics make obvious contributions to highly photocatalytic efficacy.

Numbers ways have been used to synthesized two-dimension or quasi-two dimension structural materials. For example, Yang et al. exfoliate bulk g-C₃N₄ using continuous sonication-assisted liquid method¹⁸. Niu et al. synthesize g-C₃N₄ nanosheets utilizing thermal oxidation¹⁹. Li et al. prepare porous g-C₃N₄ by chemical oxidation²⁰. However, these strategies require long-time sonication (10-16h), high-temperature oxidation or strong oxidants. Encouraged by exfoliation of graphite into layered structure using solution method²¹, in this work, we synthesized quasi-2D polymeric carbon nitrides (quasi-2D-CN) by a simple and high-efficient melamine-assisted N, N-dimethylformamide (DMF) liquid exfoliation procedure. The route can be applied for large-scale production due to low-cost and high-efficiency. Remarkably, the quasi-2D-CN possess a larger surface area, unique electronic structure, elevated stoichiometric C/N ratio, prolonged lifetime of photo-excited electrons and enhanced electronic transport. As a consequence, the quasi-2D carbon nitrides exhibit superior photocatalytic performance for hydrogen production from water splitting under visible light.

Results and discussion

As is shown in Fig.1a, the mechanism of exfoliation procedure is that the DMF molecules enter into the stacking layer of bulk carbon nitrides (bulk-CN) through molecular adsorption, increasing the layer spacing and weakening the interlayer attraction. The melamine is an excellent intercalation agent²¹. Under condition of oil bath, the melamine molecules are favorable to minimize interlayer interaction, resulting in the formation of quasi-2D-CN materials. In detail, the bulk-CN is mixed with DMF solution in distilling flask under vigorous stirring and place it in oil bath at 80 °C for 2 hours allowing DMF molecules to intercalate into interlayer space of carbon nitrides. Then, addition melamine to above mixture to further

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enlarge the distance of interlayer of polymeric graphitic carbon nitrides, the quasi-2D structure materials are obtained after 4 hours in 80 °C oil bath.

The volume of the as-synthesized quasi-2D-CN photocatalyst with same weight is upgraded three times than that of bulk-CN (Fig.1b). It demonstrates that bulk-CN changes to fluffy state when it is exfoliated to quasi-2D structure. The morphology and microstructure of bulk-CN and quasi-2D-CN are carried out by scanning electron microscopy (SEM) and display in Fig.2. The bulk-CN accumulates by amounts of solid agglomerates with a size of several micrometers. The quasi-2D-CN is composed of many nanosheets with laminar morphology like vesicular structure. The high-magnification SEM further confirms that the basic cell the quasi-2D-CN is nanosheet with a lateral scale less 10 nm. Moreover, the basic cell of nanosheets tends to bend and the edge is rough. It could be attributed to the decrease of surface energy and the decomposition of polymeric melon unit during intercalation process.

In order to further certify the formation of 2D layered carbon nitride, the transmission electron microscopy (TEM) and atomic force microscopy (AFM) are carried out. The TEM

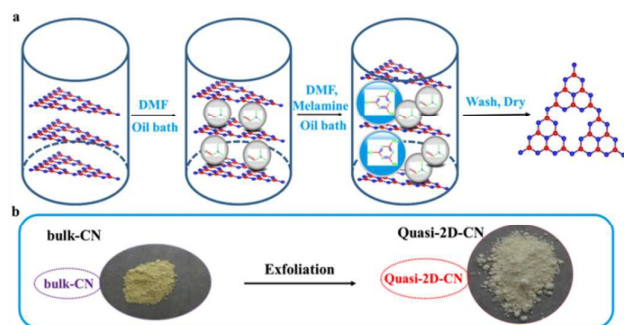


Fig.1 (a) Schematic illustration of the synthesis process about quasi-2D-CN materials, the carbon atoms are red and the nitrogen atoms are blue in atomic model. (b) Comparing the volume of bulk-CN (Left) and quasi-2D-CN (Right) with 30mg powder.

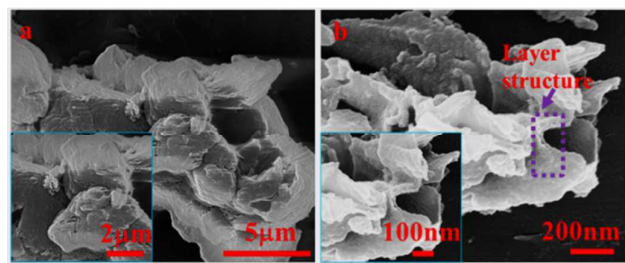


Fig.2 (a) SEM image of bulk-CN, low-, and (the insert) high-magnification (b) SEM image of quasi-2D-CN, low-, and (the insert) high-magnification image (Fig.3a and b) displays the very transparent features of carbon nitride and, indicating the formation of 2D layer carbon nitride. The quasi-2D-CN is composed of a fewer atomic layer carbon nitride. Fig.3c displays the typical atomic force microscopic (AFM) image of exfoliated quasi-2D-CN. The thickness analysis of the quasi-2D-CN by AFM indicates an average thickness of around 2-3 nm. It clearly demonstrates that bulk-CN has been successfully exfoliated into ultrathin quasi two dimension layered material.

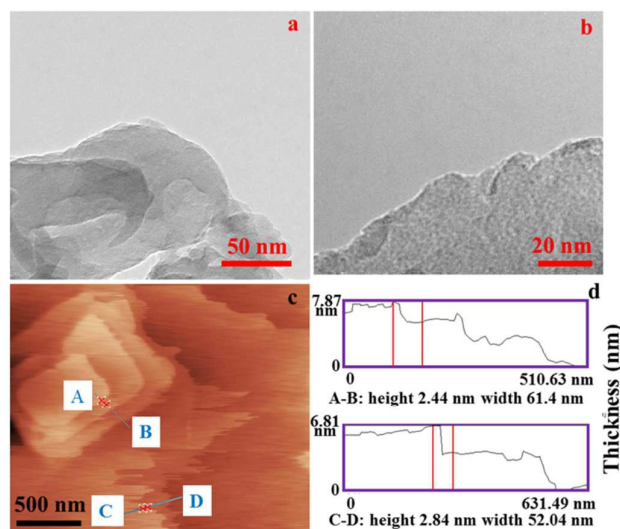


Fig.3 TEM images of (a) quasi-2D-CN and (b) the layer edge area. (c) AFM image of quasi-2D-CN deposited on the mica wafer substrate, (d) the height curve determined along the line between A-B and C-D.

The crystal structure of quasi-2D-CN and bulk-CN is characterized by X-ray diffraction (XRD) and is displayed in Fig.3a. Two characteristic peaks of quasi-2D-CN, is assigned to a typically graphitic polymeric carbon nitride. The peak (002) at 27.7° of 2 θ originates from the interlayer reflection of stacking structure, while the peak (100) at 13.1° of 2 θ is related to the in-plane structure of repeating motif of tri-s-thiazine²². Compared to the bulk-CN, the peaks originating from the periodic stacking of layer in quasi-2D-CN, shifts from 27.4° to 27.7°. It indicates that a decreased gallery distance between layered structures in quasi-2D-CN. The intercalation of DMF and melamine molecules leads to the generation of multilayer polymeric carbon nitride and the decrease of c-axis distance. The multilayer component in quasi-2D-CN is attributed to the (002) peak observed.

The chemical structure of C and N backbone element in quasi-2D-CN and bulk-CN is further studied by Fourier transform infrared spectroscopy (FT-IR). The bands of both are same and all of these observed in Fig.3b are assigned to typical graphitic polymeric carbon nitride. The sharp peak at 810 cm^{-1} is assigned to tri-s-thiazine ring. The skeletal vibrations at 1200–1600 cm^{-1} for aromatic C-N heterocycles are attributed to either trigonal C–N (–C) –C or bridging C–NH–C units²³. These bands become sharper owing to the more ordered packing of hydrogen-bond cohered long strands of polymeric melon units survived after liquid exfoliation in the layers of quasi-2D-CN, which promotes electronic transport. The broad band from 3000–3500 cm^{-1} corresponds to primary and secondary amines (–NH₂ or =NH groups) suggesting the partial hydro-generation of nitrogen atoms in 2D structure. These results are corresponds to graphitic polymeric carbon nitride materials fabricated by polycondensation²⁴.

The chemical component and oxidation state of the quasi-2D-CN are carried out by X-ray photo electron spectroscopy (XPS) (Fig.4). Comparing with bulk-CN, no evident change in the binding energy of carbon and nitride backbone in quasi-2D structure indicates that chemical state of both is same. High-resolution spectra of C 1s at 286.02 eV and N 1s at 398.60 eV are attributed to the sp² C=N bonds in the tri-s-thiazine. The peaks at 288.16 eV and 284.6 eV in the C 1s are contributed to electrons a sp² C atom attached to a –NH₂ group and to an

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aromatic C atom²⁵. The increase in the peak of intensity at 284.6 eV demonstrates that the graphitic carbon species (C (sp²)-C (sp²) bonds) originating from polymerization increases, during melamine-assisted DMF liquid exfoliation procedure. According to the percentage of carbon and nitride element conducted by XPS, the surface atomic ratio increases from 0.73 in bulk material to 0.82 in 2D structure. Melamine also is the raw of carbon nitrides, which runs defective polycondensation reaction during exfoliation process. In principle, graphitic carbon is favorable for optimizing aromatic π -conjugated system, resulting in the enhancement of electronic transport ability and the dissociation of exciton. The peaks at 400.66 eV and 404.28 eV in the N 1s are ascribed to tertiary nitrogen N-(C)₃ groups and amino functions carrying hydrogen (C-N-H), where N atoms are located at the heptazine ring²⁵. It is assigned to aromatic C N framework based on heptazine repeating motif.

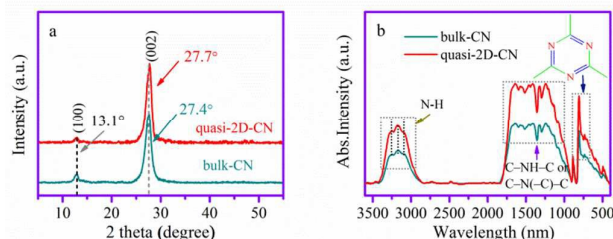


Fig.4 (a) XRD patterns and (b) FT-IR spectra of bulk-CN and quasi-2D-CN

The electronic structure of as-synthesized materials is investigated and the results are shown in Fig.5. UV-visible absorption (Fig.5a) demonstrates that the intrinsic absorption edge displays a remarkable blue shift upon quasi-2D-CN with respect to bulk structure. The larger bandgap by 0.13 eV of the quasi-2D structure is further confirmed by the blue shift of the fluorescence emission spectrum by 12 nm in Fig.7a. The bandgaps of bulk and quasi-2D carbon nitride are 2.62 eV and 2.75 eV respectively, indicating the enlarged bandgap (0.13 eV) of quasi-2D-CN. The result is ascribed to decrease of conjugation length and the strong quantum confinement effect by shifting conduction band edge and valence band in opposite orientation²⁶.

To confirm relative position of conduction band (CB) and valence band (VB), total densities state of VB and Motte-Schottky plots are carried out. From Fig.5b, compared to bulk-CN, quasi-2D-CN shows a VB maximum up-shift from 1.38 eV to 1.12 eV, as well as the VB being widened. Interestingly, the VB up-shift 0.26 eV doesn't couple with the 0.26 eV increase of bandgap (0.13 eV increase), indicating the up-shift of CB. The Motte-Schottky plots further confirm that CB minimum simultaneously, emerges up-shift from 1.24 eV to 1.63 eV as observed in Fig.5c. As illustrated in Fig 5d, a unique electronic structure characterizing an elevated CB minimum and widened VB. is established for quasi-2D-CN. The increase of VB width narrows the distance of potential between carbon nitrides and water, enhancing the redox ability of charge carries.

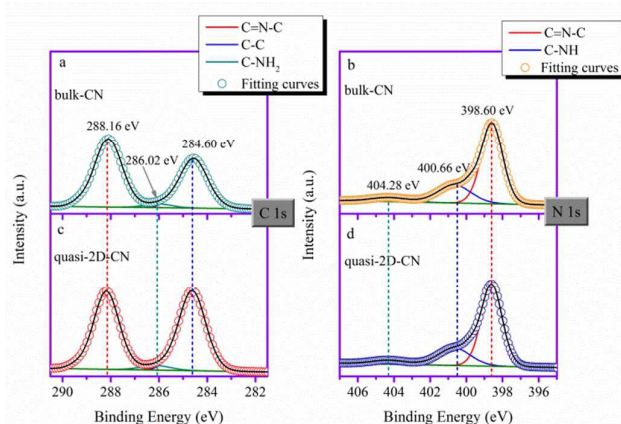


Fig.5 (a) Fig.4 (a) C 1s, (b) N 1s XPS of bulk-CN, (c) C 1s, (d) N 1s XPS of quasi-2D-CN.

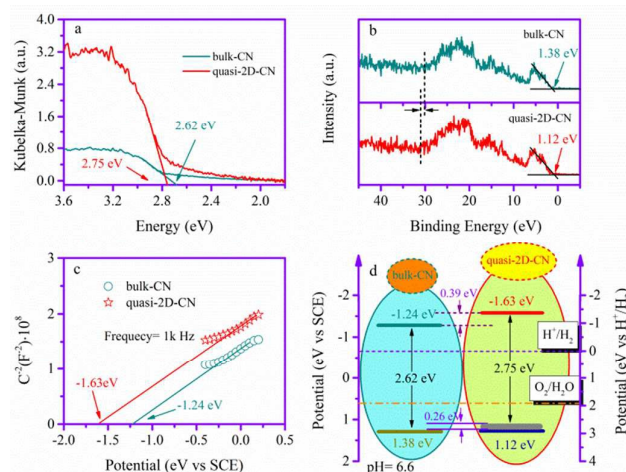


Fig.6 (a) UV-visible absorption spectra, (b) total densities of states of XPS valence band spectra, (c) electrochemical Motte-Schottky plots at frequency of 1k Hz and (d) schematic of electronic band structure of bulk-CN and quasi-2D-CN.

The electronic conduction behavior (Fig.6) of bulk-CN and quasi-2D-CN is studied through typical I - V curves. From Fig.6b, it can be seen that typical I - V curves is detected in bulk and quasi-2D structure, indicating a good semiconductor materials. In contrast to weaken current applied bias voltage -3V to 3V at bulk-CN electrode, the current density of quasi-2D-CN electrode shows 5 times enhancement, indicating the superior electronic transportation along in-plane direction in quasi-2D structure. Furthermore, the photocurrent density of 2D polymeric carbon nitride is upgraded to 5 times than that of bulk structure under visible light irradiation. From Fig.6 d, the change of photocurrent density between dark and visible-light at quasi-2D-CN is significant large than that of bulk-CN electrode. The 2D polymeric carbon nitride composed of abundant hydrogen-bond cohered strands of polymeric melon units survived after exfoliation could act as electronic transportation channel facilitating electron transfer and minimizing recombination of photo-excited electrons-holes¹⁹. However, the layer in bulk material is consisted of isolated small strands in various sizes, which will block charge carriers transport. The lack of charge carrier transport channel from bulk to surface in bulk materials leads to serious recombination of photo-induced electrons and holes, resulting in quantity of charge carrier not contributing to photocatalysis. To layered polymeric carbon nitride, under light irradiation, photo-induced

charge generates and efficiently, transfers to the materials edge, remarkably increasing the probability of photocatalysis reaction. Therefore, the quasi-2D-CN is favorable for obtaining superior photocatalytic efficiency.

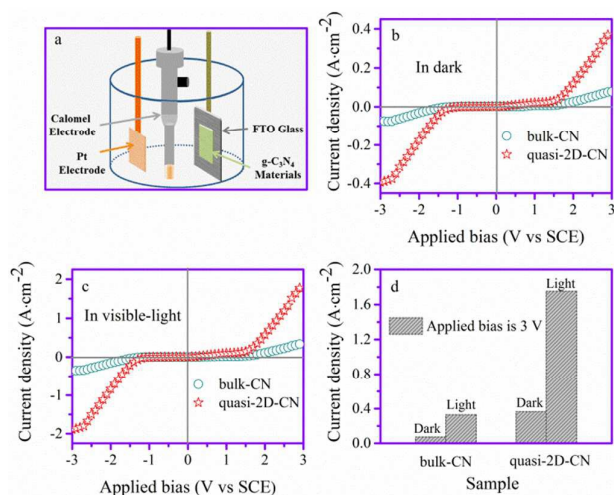


Fig.7 (a) Schematic of the test system of typical I - V curves. Typical I - V curves at (b) bulk-CN and quasi-2D-CN electrodes in dark, (c) in visible-light. (d) Compared with photocurrent density of bulk-CN and quasi-2D-CN electrode under 3V bias.

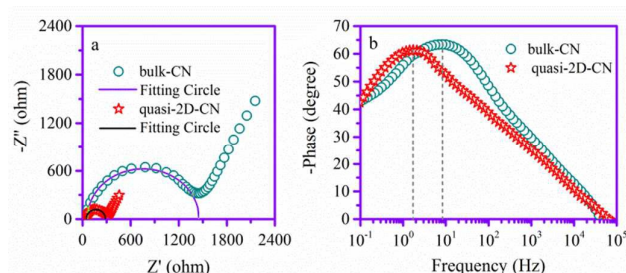


Fig.8 (a) EIS Nyquist plots and (b) Bode phase plots of bulk-CN and quasi-2D-CN, investigated by applying a sine wave current at frequency from 1M Hz to 0.01 Hz in dark.

The internal resistances and electronic transport kinetics of bulk-CN and quasi-2D-CN are investigated by the electrochemical impedance spectra (EIS), and the results are shown in Fig.7. There are two well-fitting semicircles in high frequency region and middle-frequency region. The quasi-2D-CN displays a smaller impedance circle than that of bulk-CN, indicating a decrease of resistance and enhancement of electronic transportation in interface of quasi-2D-CN electrode (Fig.7a). The layered quasi-2D-CN materials significantly accelerate the electron transfer process, which in turn improves the separation efficiency of photo-induced electrons and holes²⁷. Fig.10b showing a plot of phase versus characteristic frequency elucidates the electron transfer ability, electron lifetime and recombination²⁸. The characteristic frequency peak of quasi-2D-CN shifts to lower frequency compared to that of bulk-CN, indicating a more rapid electron transport process, prolonged electron lifetime or recombination time²⁹. The frequency (f) ranging from 1 Hz to 10^3 Hz, is related to the inverse of electron lifetime (τ) as follows²⁹:

$$\tau = 1 / (2\pi \cdot f) \quad (1)$$

With respect to bulk-CN electrode electron lifetime (19.3 ms), quasi-2D-CN materials display a higher electron lifetime (92.2 ms). The opportunity that photo-excited electrons and holes can be captured in photocatalytic procedure increases because of prolonged lifetime, which enhances photo-redox functions.

Photoluminescence (PL) emission spectrum originating from the recombination of charge carriers and instant photocurrent curves are usually used to reflect charge carriers transfer and separation. A strong PL emission peak for bulk-CN observed in Fig.8a ascribes radiative recombination of charge carriers²⁸. The quenching photoluminescence behavior and the remarkable enhanced photocurrent density (the density at bulk-CN electrode is $16 \mu\text{A}\cdot\text{cm}^{-2}$, the quasi-2D-CN is $78 \mu\text{A}\cdot\text{cm}^{-2}$) in Fig.8b are attributed to suppressed recombination of photo-induced electrons and holes, and great electronic transportation ability in quasi-2D-CN without significant grain boundaries. Hence, the quasi-layered polymeric carbon nitride is beneficial for photocatalyst.

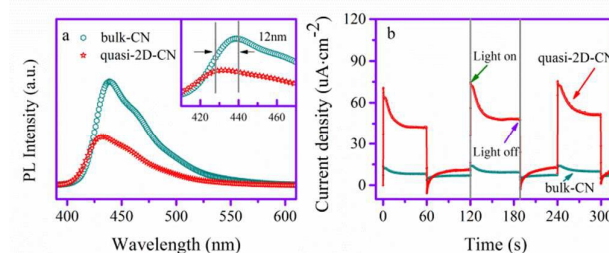


Fig.9 (a) Fluorescence emission spectra recorded at 298K and (b) periodic on/off photocurrent response under visible-light irradiation at bulk-CN and quasi-2D-CN electrodes in 0.5M Na_2SO_4 solution without ant bias potential.

The time-resolved fluorescence decay spectra (Fig.9) of bulk-CN and quasi-2D-CN, is recorded to investigate the photo-physical behavior of photo-induced charge carrier. The fluorescent intensities of both materials decay exponentially. However, the quasi-2D-CN displays slow decay kinetics. In detail, the shortest lifetime of 0.09 ns in the bulk-CN increases to 0.42 ns in the quasi-2D-CN and its percentage increases from 12.94% to 16.06%. The medium lifetime and percentage of charge carrier increase from 3.06 ns for 51.01% in bulk-CN to 4.94 ns for 55.90% in quasi-2D-CN. The longest lifetime of quasi-2D-CN is up to 12.74 ns, about 1.5 ns longer than bulk-CN (11.20 ns) through its percentage decreases from 36.05% to 28.04%. The prolonged lifetime is related to the enhanced electron transport and/or electronic band structure changes induced by quantum confinement effect. Moreover, the prolonged lifetime increases the probability of photo-induced electrons and holes that are captured by reactive materials and able to run photo-redox functions. The results are consistent with electrochemical impedance spectra.

Nitrogen gas absorption-desorption isotherms are measured to investigate specific surface area and pore volume distribution (Fig.10). The Brunauer-Emmett-Teller (BET) specific surface area and pore volume obtained for bulk-CN and quasi-2D-CN are $9.38 \text{ cm}^3\cdot\text{g}^{-1}$ and $116.76 \text{ cm}^3\cdot\text{g}^{-1}$, respectively. It can be seen from pore volume distribution curves that the pore volume of quasi-2D-CN is far larger than that of bulk-CN and quasi-2D-CN materials show more small pores, which is in favor of bsorption of molecular. Based on Niu at el. work reported¹⁹, photocatalytic activity is significantly related to the quantity of

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•OH radicals under both UV-visible and visible light irradiation¹⁷. The quasi-2D-CN possessing stronger absorption with bulk-CN, quasi-2D-CN possessing high surface area and the abundant active sites must be favorable for photocatalysis.

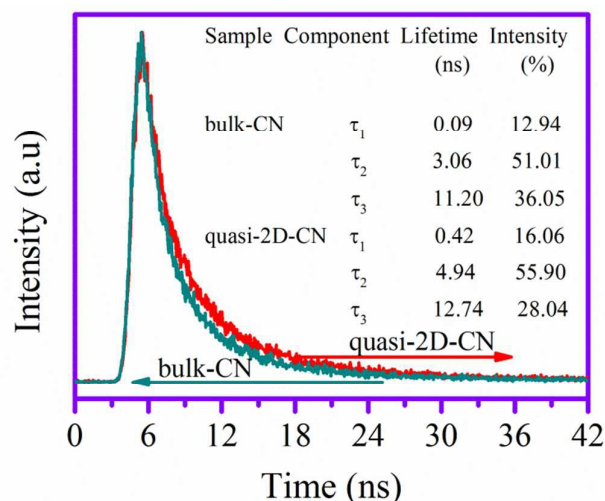


Fig.10 Time-resolved fluorescence decay spectra of bulk-CN and quasi-2D-CN monitored at 460 nm by time-correlated single-photon counting. The products are excited by the incident light of 380 nm from a picosecond pulsed light-emitting diode at room-temperature. The insert is the radiative fluorescence lifetimes and their relative percentages of photo-induced charge carriers in the bulk-CN and quasi-2D-CN.

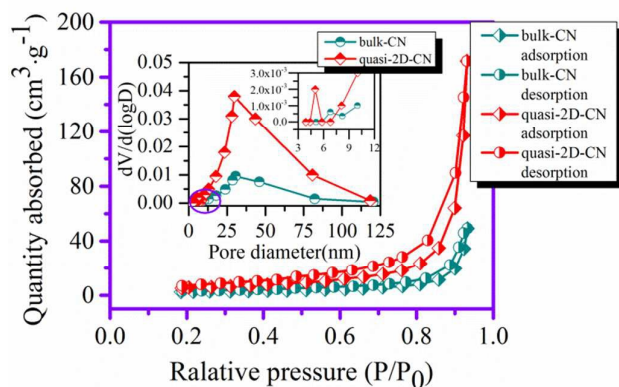


Fig.11 Nitrogen gas adsorption-desorption isotherm and (the insert) corresponding pore size distribution of bulk-CN and quasi-2D-CN materials.

The photocatalytic hydrogen production from water splitting of bulk-CN and quasi-2D-CN is evaluated by using triethanolamine as electron donor and deposited-Pt as co-catalyst. The bulk-CN gives only an average hydrogen production activity of $16.31 \mu\text{mol}\cdot\text{h}^{-1}$ in 8 hours of visible light irradiation due to its limited visible light responsible ability and higher recombination of photo-induced charge carriers. After exfoliation with melamine-assisted DMF, the photoactivity of carbon nitride dramatically enhances to $89.82 \mu\text{mol}\cdot\text{h}^{-1}$ (Fig.11). Even under UV-visible light, the photoactivity of quasi-2D materials is upgraded to five times than that of bulk-CN. The Long-term stability of as-synthesized photocatalyst is assessed in Fig.11b. After first photocatalytic reaction cycle, the reaction mixture is placed in air for one month and the second circle is

capacity can adsorb abundant •OH radicals as redox species, resulting in remarkable redox ability. Meanwhile, compared carried out to examine the stability of this photocatalyst in contact with water and dissolved oxygen. It can be seen that as-synthesized photocatalysts display excellent stability for hydrogen evolution, which shows only a deterioration of 0.28% after three cycle reaction. As shown in Fig.12, the photocatalyst of quasi-2D-CN collected after three cycles photocatalytic hydrogen evolution reaction, shows a same crystal structure as before photocatalytic reaction. The results indicate the excellent recycling performance of the polymeric carbon nitride catalyst. To confirm that the photo-induced charge carrier originating from polymeric carbon nitride dominate the enhancement of photoactivity, the wavelength dependence of photocurrent based on hydrogen production is shown in the inset of Fig.11d. The variation tendency of photocurrent of bulk-CN and quasi-2D-CN is exactly similar to their respective optical absorption spectra. The photocurrent of quasi-2D-CN is significantly higher than that of bulk-CN in the range from 300 nm to 550 nm light irradiation is largely governed by photo-induced charge carrier. The wavelength dependence of hydrogen evolution of quasi-2D carbon nitrides (Fig.11d) is consistent with its optical absorption, indicating that the hydrogen evolution reaction is indeed induced by the photo excitation of carbon nitrides. Meanwhile, an overall enhanced photocurrent performance is observed on as-synthesized product across the whole of its absorption spectrum, similar to the enhancement of hydrogen evolution. The wavelength-independent enhancement indicates the band offsets of the product support visible light photocatalysis²⁸. Finally, the comparison with other reported carbon nitrides for hydrogen production shows in Table.1. Photocatalytic activity of carbon nitrides is significantly superior to those previously reported, and in fact, the malmine-assisted liquid exfoliation can drastically improve photocatalytic performance. Importantly, this method is simple and cost-efficient and can be applied to large-scale production.

Based on above discussion, the probable photocatalytic mechanism of polymeric carbon nitride for hydrogen evolution

Table.1 Hydrogen evolution of quasi-2D-CN and comparison with other reported carbon nitrides

Materials	method	H ₂ evolution ($\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$)	Light (nm)	Sacrificial reagent	Ref
Quasi-2D-CN	Liquid exfoliation	898.2	$\lambda > 400$	10% TEOA	This work
Monolayer-C ₃ N ₄	Sonication-assisted chemical exfoliation	252	$\lambda > 400$	10% TEOA	15
g-C ₃ N ₄ nanosheet	Thermal oxidation	780	$\lambda > 420$	10% TEOA	19
g-C ₃ N ₄ nanosheet	Sonication-assisted Liquid exfoliation	900	$\lambda > 420$	10% TEOA	21
S-doped bulk-C ₃ N ₄	S doping	380	$\lambda > 420$	10% TEOA	31
N-doped bulk-C ₃ N ₄	N-self doping	560	$\lambda > 400$	10% TEOA	33
Defected g-C ₃ N ₄	Hydrogen treatment	230	$\lambda > 420$	20% TEOA	34
TiO ₂ -In ₂ O ₃ @ g-C ₃ N ₄	Surface modification	160	$\lambda > 400$	25% methanol	35

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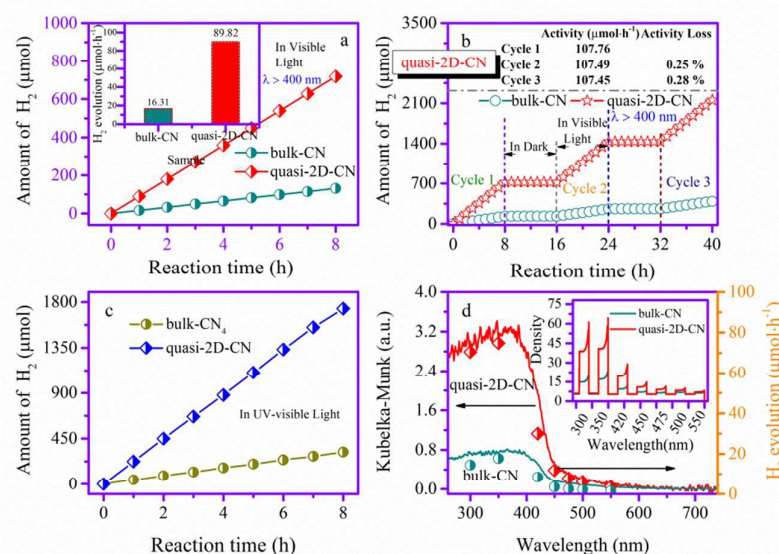


Fig.12 Photoactivity for H₂ production from water splitting containing 10 vol % triethanolamine scavenger, the insert is H₂ evolution rate per hour (b) long-time stability test over bulk-CN and quasi-2D-CN under visible-light irradiation (λ > 400nm). (c) Time vs H₂ production curves under UV-visible irradiation, (d) wavelength dependence of H₂ evolution by bulk-CN and quasi-2D-CN. For comparison, UV-visible absorption spectrum of quasi-2D-CN is also given. The insert is wavelength dependence of photocurrent density at bulk-CN and quasi-2D-CN electrodes in 0.5M Na₂SO₄ solution without any bias potential.

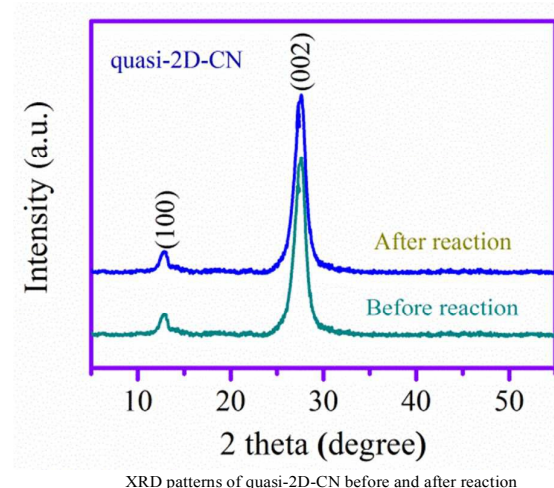


Fig.13

from water splitting with triethanolamine (TEOA) as electron donor and deposited-Pt as co-photocatalyst under visible-light is illustrated in Fig.13. Under the excitation of visible light, the electrons originating from polymeric carbon nitride jump from VB to CB. The photo-induced electrons transfer to the surface of photocatalyst, and couple with Pt particles. The hydrogen ions accept coupled-Pt electron to product hydrogen, while the holes react with TEOA through oxidation. The synergistic effects of larger surface area, enhanced electronic transport, enlarged absorption bandgap, prolonged electron lifetime and lowered recombination of photo-excited charge carrier, is beneficial for the remarkable hydrogen production. Compared to bulk-CN, the quasi-2D-CN composed of thickness nanosheets possesses larger surface area providing abundant photoactivity site for reactant molecular and enhances electronic transport resulting in substantially low bulk recombination of charge carrier. Importantly, as quantum confinement effects, the increasing intrinsic bandgap and width

of valence improve the redox ability of charge carrier. The prolonged lifetime has a significant contribution to promoting photoactivity under visible-light or UV-visible light.

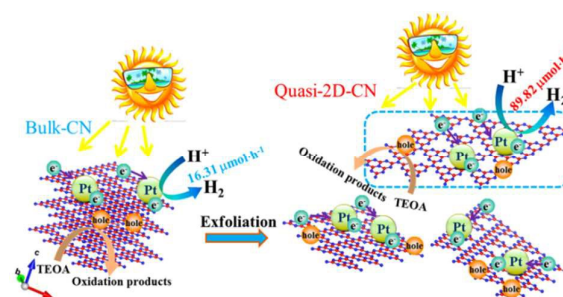


Fig.14 Schematic illustration of the visible-light photocatalytic performance of Pt-deposited bulk-CN and quasi-2D-CN, TEOA is triethanolamine.

Conclusions

In conclusion, the quasi two-dimension polymeric carbon nitride is synthesized by a simple and high-efficient melamine-assisted DMF liquid exfoliation procedure. This method can be applied to actual production, due to the merit of easy scale-up, high-efficiency, low-cost and environmental friendly. The quasi-2D-CN material is demonstrated to enhance electronic transport ability and lower recombination of photo-induced electrons and holes, which arises from electronic transport along with in-plane direction. On account of quantum confinement effect, the bandgap of quasi-2D-CN increases and the lifetime of it prolongs, compared to bulk structure. These characteristics make obvious contribution to a significant improvement in photocatalytic activity for hydrogen evolution from water splitting. The 2D materials offer good opportunities to convert sustainable sunlight to green energy, to resolve the

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problem of energy crisis. These polymeric carbon nitride materials can also be envisaged to be useful in organic photosynthesis and photovoltaic devices.

Experiments

Materials Synthesis Procedure

Chemicals: dicyandiamide ($C_2H_4N_4$), melamine ($C_3N_3(NH_2)_3$), 2-Hydroxyethyl ($C_6H_{15}NO_3$), N, N-Dimethylformamide (DMF, C_3H_7NO), chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were analytical pure and used without further purification.

Synthesis of bulk-CN: Bulk g- C_3N_4 was synthesized according previous work. 10.0g dicyandiamide was heated at 520 °C for 4 h in air at ramp rate 6.7 °C/min. The resultant solid was milled into powder in mortar and bulk-CN was obtained.

Synthesis of quasi-2D-CN: Open quasi-layer-structured g- C_3N_4 was synthesized by adding 50 mg bulk-CN powder into 200 mL DMF under vigorously stirring and heated in the oil bath at 80 °C for 2 hours. Then 10mg melamine was added to above mixture solution. After that, the precipitate was collected by filtration and washed three times with distilling water and ethanol, respectively. Finally, the quasi-2D-CN photocatalyst was obtained by drying at 80 °C under vacuum conditions.

Characterization

The crystal structure was analyzed by powder X-ray diffraction with Cu K α irradiation ranging from 5 degree to 60 degree in steps of 0.02 degree (XRD; X'pert, Philips, Eindhoven, The Netherlands). Their surface morphology was determined by field emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL, Tokyo, Japan) and high resolution transmission electron microscopy (HR-TEM, JEM-3010, JEOL, Tokyo, Japan) operated at an accelerating voltage of 200 kV. The formation of 2D materials was analyzed by atomic force microscopy (AFM; SPM-9600, Shimadzu, Tokyo, Japan) in air. The chemical structure was investigated with Fourier Transform Infrared spectra (FT-IR; TENSOR27, Bruker, Billerica, MA, USA) with a resolution of 1 cm⁻¹ between 4000 and 600 cm⁻¹ at room temperature under air atmosphere. In experiment, all as-synthesized products were 0.1g and all products were measured at same condition. Chemical compositions and valence band spectra of samples were analyzed using X-ray photoelectron spectroscopy (XPS, VGESCALAB220i-XL, Thermo Scientific, Waltham, MA, USA) with Al K α source (E = 1486.6 eV). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption-desorption isotherm measurements (V-Sorb 2800 P, Gold APP Corp., Beijing, China) at 77 K. The optical absorbance spectra of as-synthesized products were performed in a UV-visible spectrophotometer (UV-vis DRS; Cary 5000, Agilent, Santa Clara, CA, USA). Time-resolved fluorescence decay spectra were recorded at room temperature with a fluorescence spectrophotometer (FLS980, Edinburgh Instruments, Edinburgh, Britain) at room temperature. Fluorescence emission spectrum was recorded with a fluorescence spectrophotometer (F-4600, Hitachi Corp, Tokyo, Japan) at room temperature, excited by incident light of 380 nm. The *I-V* curves and electrochemical impedance spectrometer (EIS) were determined by using electrochemical workstation (CHI660E, Chenhua, Shanghai, China).

All electrochemical tests were carried out using three electrodes cell that platinum electrode and mercurous chloride electrode (3 mol/L KCl) act as counter electrode and reference electrode, respectively. The work electrodes were prepared by screen-printed method, based on previous work³⁰. The as-synthesized products scattering particles were fabricated by the process reported³¹. The prepared scattering particles were screen-printed (area: 10 mm×10 mm) on fluorine-doped tin oxide (FTO) glass substrates (TEC8, 8 Ω per square, Xiangnan, China). Each screen-printed g- C_3N_4 layer was placed a room temperature for 10 min and then dried at 60 °C for 30 min, and annealed at 350 °C for 1 hour to improve its adhesion. In test, the g- C_3N_4 electrode was immersed in 0.5 M Na₂SO₄ solution and irradiation light source was 150 W the Xenon lamp.

Photoactivity Measurement

Water splitting reactions were carried out in a lateral irradiation reaction vessel connected with gas chromatograph (GC98908; Linghua, Shanghai, China). 300 W Xenon lamp (MAX-302; Asahi Spectra, Torrance, CA, USA) with different UV cut-off filters were used as irradiation source, which could provide different wavelength light source. 100 mg photocatalyst powder was dispersed in 100 mL aqueous solution containing 10mL triethanolamine in volume (10 vol. %) as electron donor. The decomposition of 0.6% Pt co-catalyst is conducted by injecting 300 μ L 0.2 g/L H₂PtCl₆ solution into above solution. The reaction temperature was maintained at 5 °C. The amount of produced H₂ was determined by gas chromatograph equipped with thermal conductor detector, where nitrogen was afforded as carrier gas.

Acknowledgements

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Fig.1

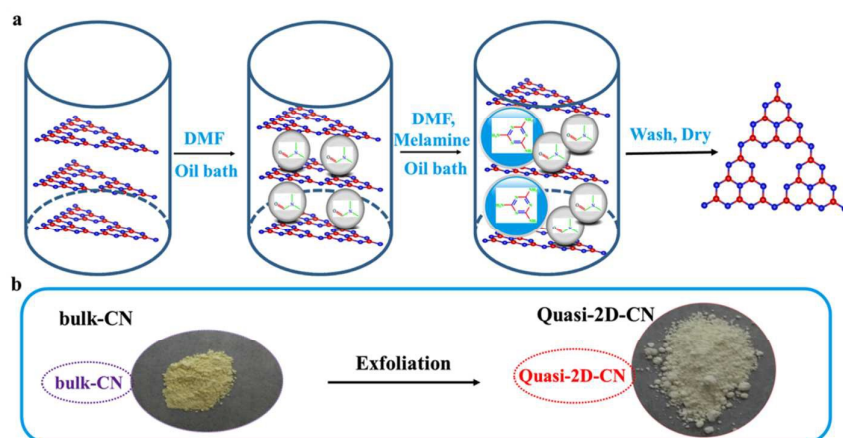


Fig.1 (a) Schematic illustration of the synthesis process about quasi-2D-CN materials, the carbon atoms are red and the nitrogen atoms are blue in atomic model. (b) Comparing the volume of bulk-CN (Left) and quasi-2D-CN (Right) with 30mg powder.

Fig.2

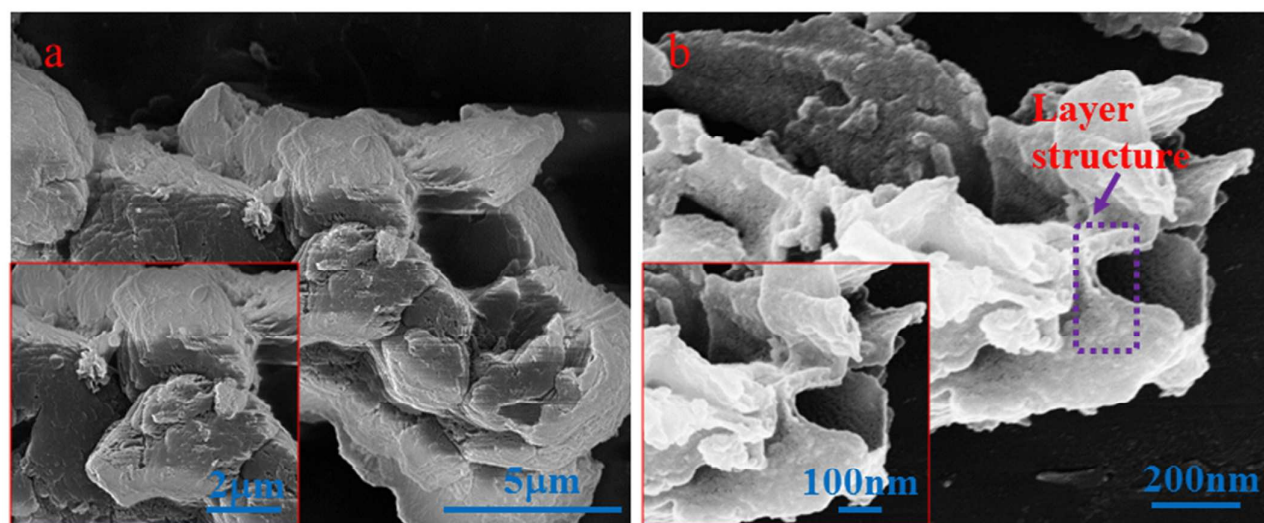


Fig.2 (a) SEM image of bulk-CN, low-, and (the insert) high-magnification (b) SEM image of quasi-2D-CN, low-, and (the insert) high-magnification

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Fig.3

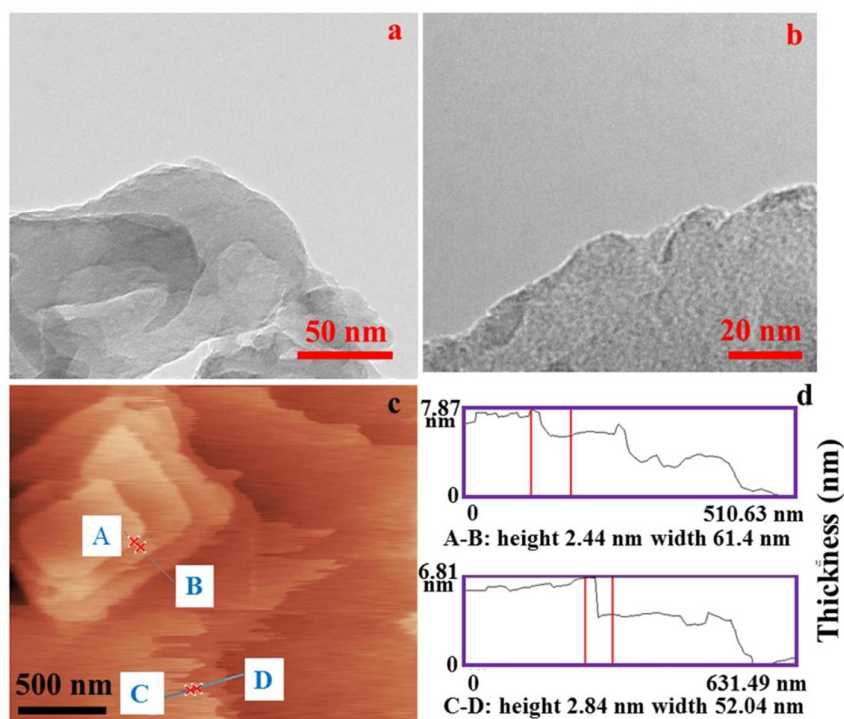
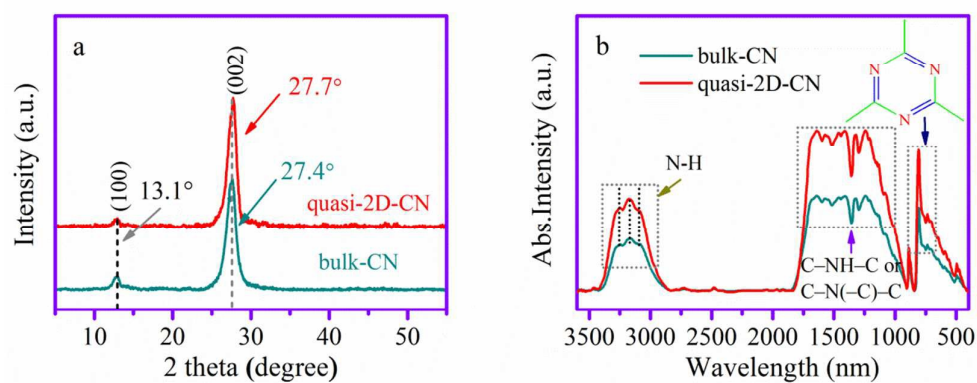


Fig.3 TEM images of (a) quasi-2D-CN and (b) the layer edge area. (c) AFM image of quasi-2D-CN deposited on the mica wafer substrate, (d) the height curve determined along the line between A-B and C-D.

Fig.4

**Fig.4** (a) XRD patterns and (b) FT-IR spectra of bulk-CN and quasi-2D-CN

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Fig.5

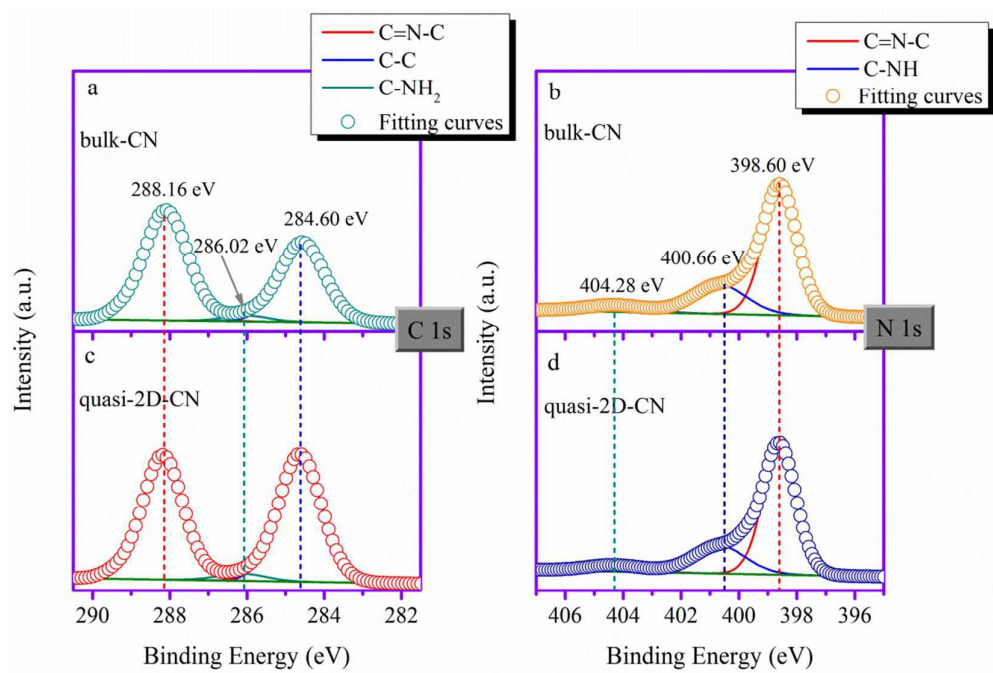


Fig.5 (a) C 1s, (b) N 1s XPS of bulk-CN, (c) C 1s, (d) N 1s XPS of quasi-2D-CN.

Fig.6

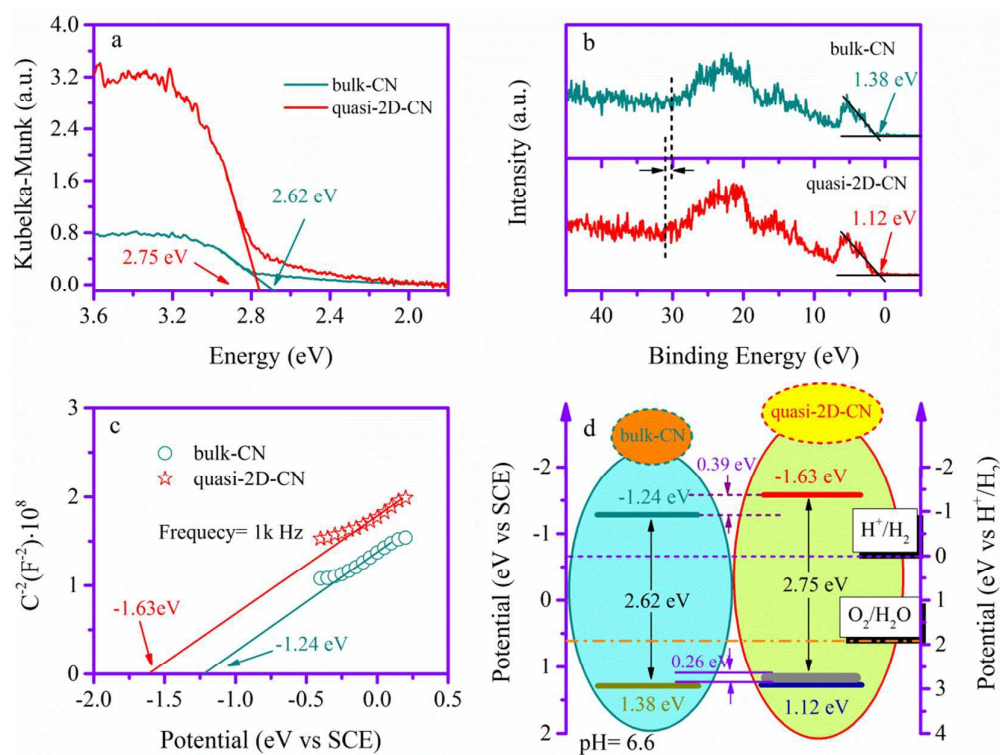


Fig.6 (a) UV-visible absorption spectra, (b) total densities of states of XPS valence band spectra, (c) electrochemical Motte-Schottky plots at frequency of 1k Hz and (d) schematic of electronic band structure of bulk-CN and quasi-2D-CN.

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Fig.7

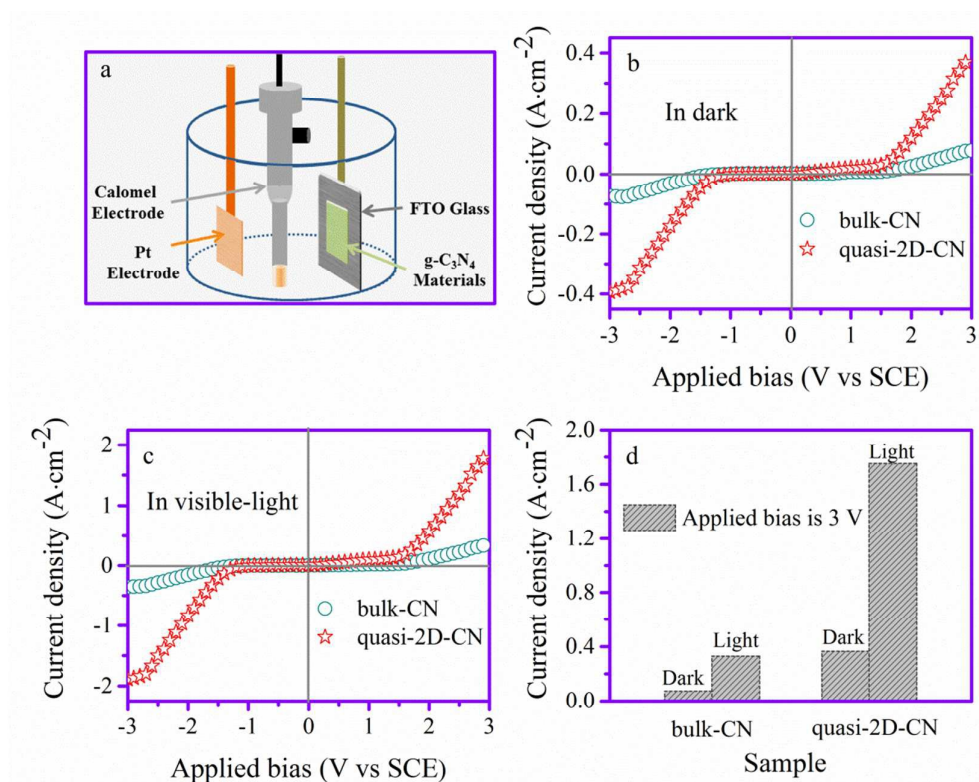


Fig.7 (a) Schematic of the test system of typical *I-V* curves. Typical *I-V* curves at (b) bulk-CN and quasi-2D-CN electrodes in dark, (c) in visible-light. (d) Compared with photocurrent density of bulk-CN and quasi-2D-CN electrode under 3V bias.

Fig.8

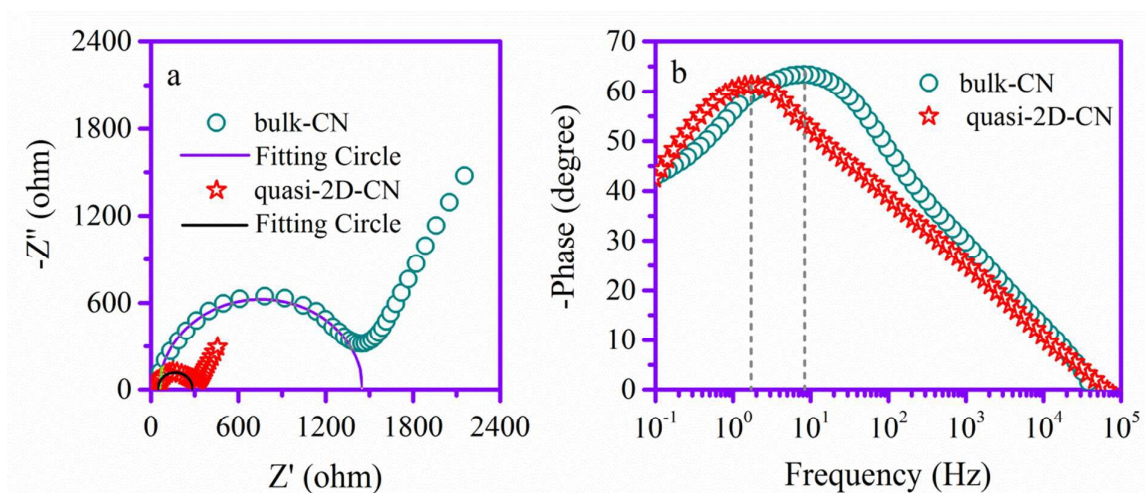


Fig.8 (a) EIS Nyquist plots and (b) Bode phase plots of bulk-CN and quasi-2D-CN, investigated by applying a sine wave current at frequency from 1M Hz to 0.01 Hz in dark.

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Fig.9

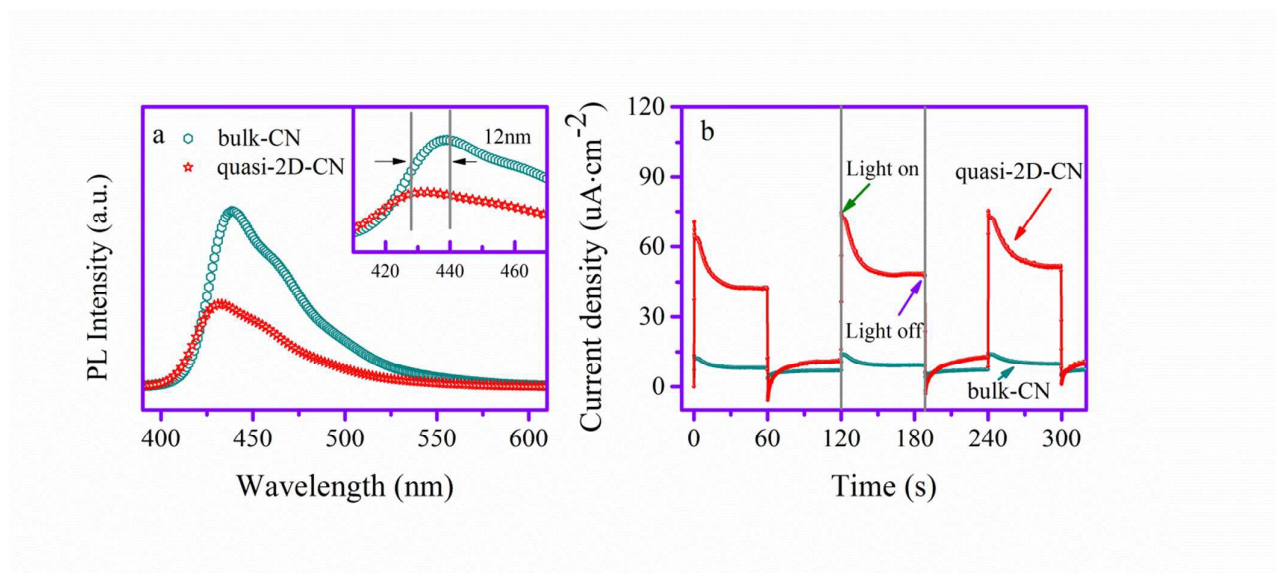


Fig.9 (a) Fluorescence emission spectra recorded at 298K and (b) periodic on/off photocurrent response under visible-light irradiation at bulk-CN and quasi-2D-CN electrodes in 0.5M Na_2SO_4 solution without ant bias potential.

Fig.10

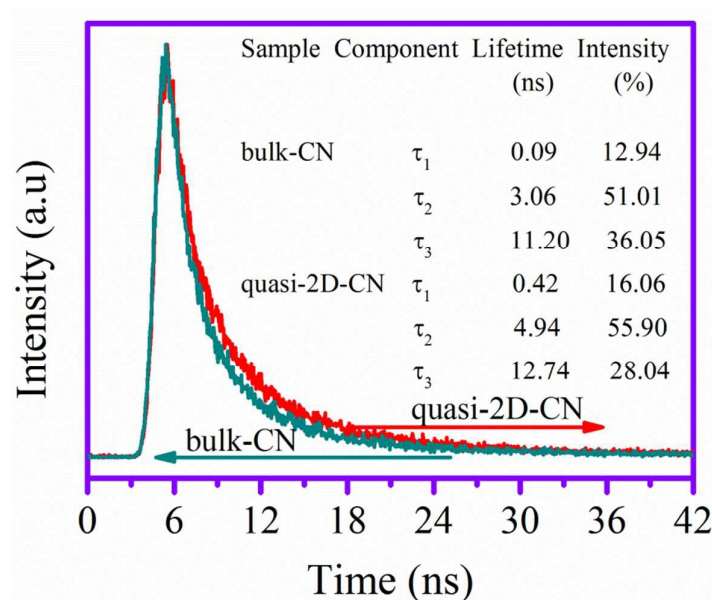


Fig.10 Time-resolved fluorescence decay spectra of bulk-CN and quasi-2D-CN monitored at 460 nm by time-correlated single-photon counting. The products are excited by the incident light of 380 nm from a picosecond pulsed light-emitting diode at room-temperature. The insert is the radiative fluorescence lifetimes and their relative percentages of photo-induced charge carriers in the bulk-CN and quasi-2D-CN.

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Fig.11

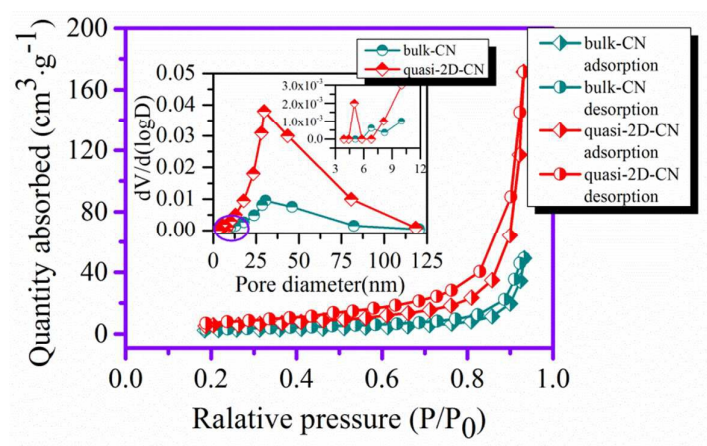


Fig.11 Nitrogen gas adsorption-desorption isotherm and (the insert) corresponding pore size distribution of bulk-CN and quasi-2D-CN materials.

Fig.12

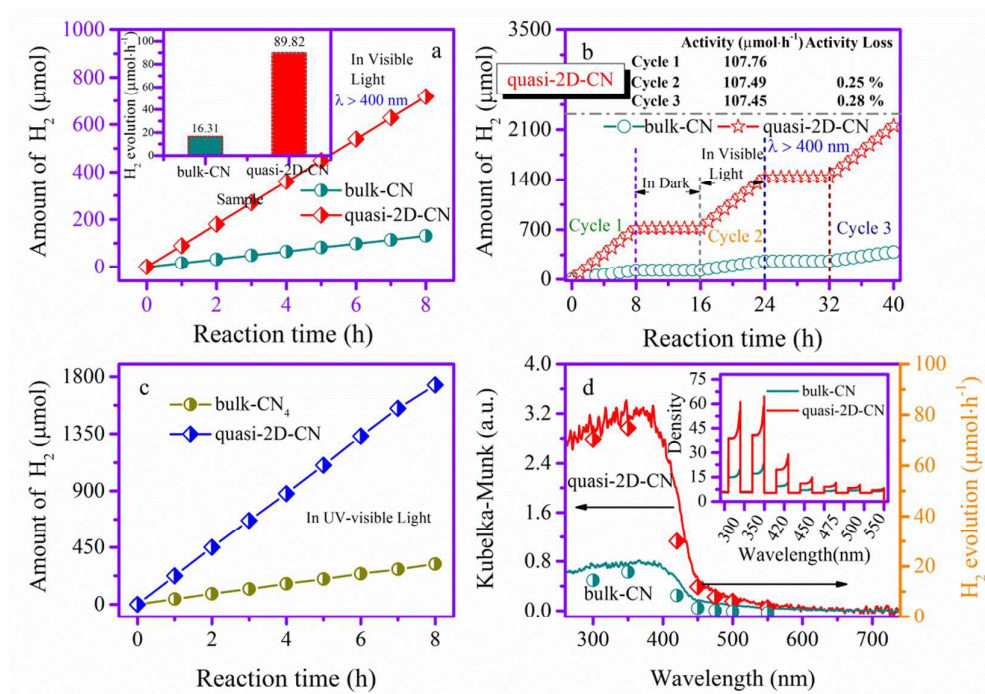


Fig.12 Photoactivity for H₂ production from water splitting containing 10 vol % triethanolamine scavenger, the insert is H₂ evolution rate per hour (b) long-time stability test over bulk-CN and quasi-2D-CN under visible-light irradiation (λ > 400nm), (c) Time vs H₂ production curves under UV-visible irradiation, (d) wavelength dependence of H₂ evolution by bulk-CN and quasi-2D-CN. For comparison, UV-visible absorption spectrum of quasi-2D-CN is also given. The insert is wavelength dependence of photocurrent density at bulk-CN and quasi-2D-CN electrodes in 0.5M Na₂SO₄ solution without any bias potential.

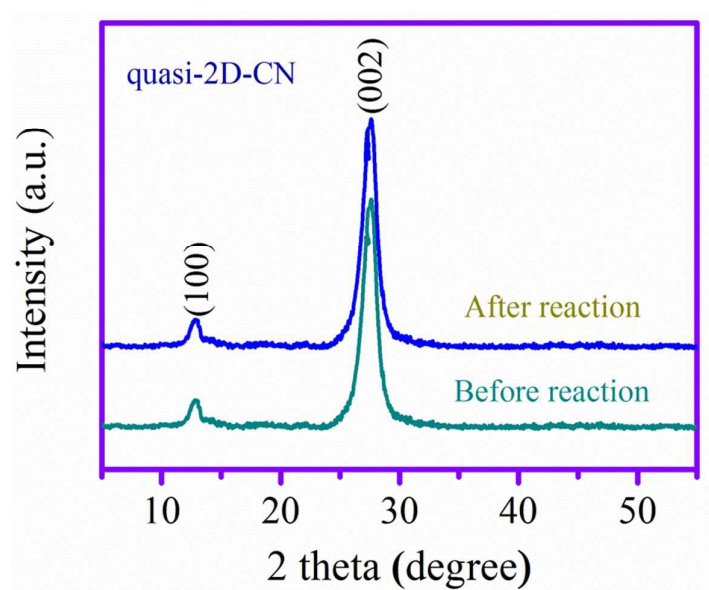
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Table.1

Table.1 Hydrogen evolution of quasi-2D-CN and comparison with other reported carbon nitrides and TEOA is triethanolamine.

Materials	method	H ₂ evolution ($\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$)	Light (nm)	Sacrificial reagent	Ref
Quasi-2D-CN	Liquid exfoliation	898.2	$\lambda>400$	10% TEOA	This work
Monolayer-C ₃ N ₄	Sonication-assisted chemical exfoliation	252	$\lambda>400$	10% TEOA	13
g-C ₃ N ₄ nanosheet	Thermal oxidation	780	$\lambda>420$	10% TEOA	17
g-C ₃ N ₄ nanosheet	Sonication-assisted Liquid exfoliation	900	$\lambda>420$	10% TEOA	19
S-doped bulk-C ₃ N ₄	S doping	380	$\lambda>420$	10% TEOA	29
N-doped bulk-C ₃ N ₄	N-self doping	560	$\lambda>400$	10% TEOA	31
Defected g-C ₃ N ₄	Hydrogen treatment	230	$\lambda>420$	20% TEOA	32
TiO ₂ -In ₂ O ₃ @ g-C ₃ N ₄	Surface modification	160	$\lambda>400$	25 % methanol	33

Fig.13

**Fig.13** XRD patterns of quasi-2D-CN before and after reaction

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Fig.14

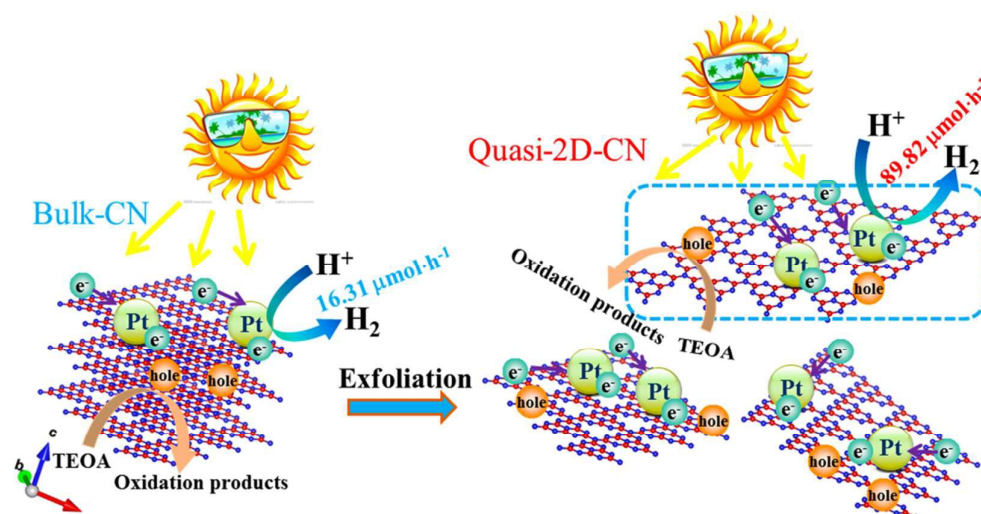
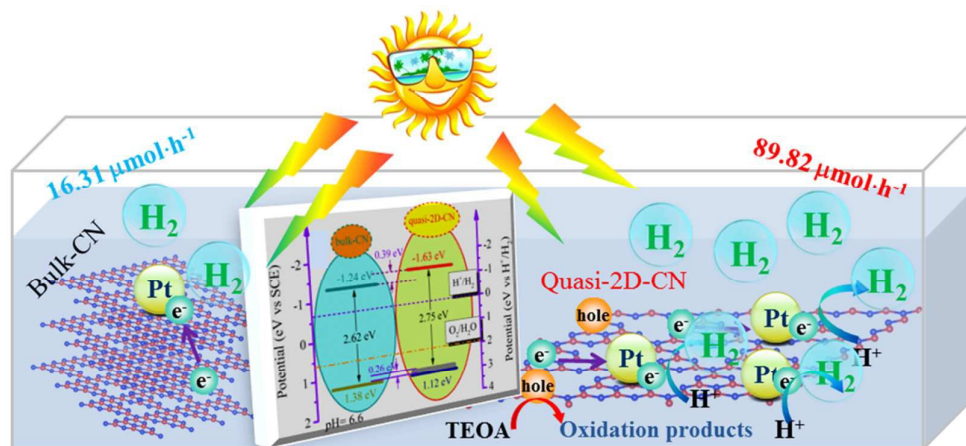


Fig.14 Schematic illustration of the visible-light photocatalytic performance of Pt-deposited bulk-CN and quasi-2D-CN, TEOA is triethanolamine.



Graphical abstract

Compared to bulk polymeric graphitic carbon nitride, quasi-two-dimension structure possesses unique electronic structure, enlarged bandgap,

prolonged lifetime, increased surface area and enhanced electronic transport, and exhibits highly efficient hydrogen production from water under visible light.