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Facile Synthesis of Few-layer-thick Carbon Nitrides Nanosheets by Liquid Ammonia-Assisted Lithiation Method and their Photocatalytic Redox Properties

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High-quality few-layer-thick graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) nanosheets (NSs) were fabricated by a simple, highly efficient, and rapid method namely, liquid ammonia (LA)-assisted lithiation. Li intercalation occurred in less than half an hour, importantly, the degree of Li intercalation was indicated by the color change of LA solution from deep blue to colorless. The obtained products were carefully investigated by field-emission transmission electron microscopy, field-emission scanning electron microscopy, atomic force microscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy, Raman scattering spectrometry, UV-visible absorption spectrometry, photoluminescence, soft X-ray absorption and nonresonant soft X-ray emission spectroscopy, and X-ray absorption near-edge structure analyses. Because of the lack of high-temperature or high-energy treatment, high-yield few-layer-thick g-C\textsubscript{3}N\textsubscript{4} NSs were produced with trace O\textsubscript{2} impurity. Interestingly, while maintaining the similar crystal structure and chemical stoichiometric ratio relative to the parent bulk materials, the surface structure, electronic and optical properties were significantly varied. Moreover, compared to the bulk counterparts, the as-prepared g-C\textsubscript{3}N\textsubscript{4} NSs show clearly enhanced photocatalytic redox activity with respect to both photocatalytic H\textsubscript{2} evolution and hydroxyl radical generation. LA-assisted lithiation is a general method and could be easily extended to exfoliate diverse other layered materials such as molybdenum and tungsten sulfides.

INTRODUCTION

Two-dimensional (2D) NSs have attracted tremendous attention owing to their unusual properties resulting from their unique surface atomic geometry and electronic structure.\textsuperscript{1–3} As a typical example, graphene, a 2D single layer of carbon atoms, has demonstrated exceptional properties and a wide range of applications in nanoelectronics, photodetectors, capacitors, and catalysis.\textsuperscript{4–6} These have triggered keen interests to synthesize atomic-thick NSs other than graphene and investigate their properties. To date, inspired by the available routes to fabricate graphene and graphene oxide, several ultrathin 2D NSs have been obtained by diverse methods such as mechanical cleavage,\textsuperscript{7} ball milling,\textsuperscript{8} ultrasonication in common solvents,\textsuperscript{9} and ion intercalation.\textsuperscript{10, 11} Unfortunately, these available pathways are limited in regards to yield, purity and efficient. For instance, Ramakrishna et al use the n-butyl lithium in hexane as the intercalation agent to insert lithium ions and then ultrasonication in water to peel off the nanosheet.\textsuperscript{5} Nevertheless, long reaction time (e.g. 3 days) and poor controllability over lithium insertion process restrict its popularization. Alternatively, electrochemical lithiation has been used to exfoliate MoS\textsubscript{2}, WS\textsubscript{2}, etc.\textsuperscript{12–14} which is inconvenient to manipulate (complicated fabrication of lithium battery) and high output is inaccessible. Despite the scientific and technological importance and significant efforts, the progress in this field is still limited. Therefore, a facile, effective, and versatile method for the fabrication of single- or few-layer ultrathin 2D NSs is highly desirable and is of special interest owing to its unique and fascinating properties, providing additional opportunities for the applications of 2D-layered materials.

Recently, as a new type of 2D-layered material, metal-free graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) NSs have received increasing attention.\textsuperscript{12–14} In particular, this fascinating semiconductor with a bandgap of ~ 2.64 eV has been intensively investigated as an alternative metal-free visible-light-responsive photocatalyst.\textsuperscript{15–21} g-C\textsubscript{3}N\textsubscript{4} has a graphite-like structure with strong C–N covalent bonding in the in-plane direction and weak van der Waals forces between the C–N layers with a layer distance of ~ 3.3 nm.\textsuperscript{15–21} This intrinsically layered structure allows to exfoliate bulk materials to afford a monolayer or atomically thick g-C\textsubscript{3}N\textsubscript{4} NSs.\textsuperscript{12–14} Compared to the bulk g-C\textsubscript{3}N\textsubscript{4}, the highly anisotropic 2D NSs may possess a much higher specific surface area, a larger bandgap because of the quantum size effect, improved electron transport ability along the in-plane direction, and increased lifetime of photoexcited charge carriers because of a higher separation efficiency.\textsuperscript{12–14} Liu et al. reported that g-C\textsubscript{3}N\textsubscript{4} NSs with a thickness of ~ 2 nm can be obtained by the thermal oxidation etching of bulk g-C\textsubscript{3}N\textsubscript{4} in air.\textsuperscript{12} However, the thermal oxidation etching afforded only ~ 6 wt% yield.\textsuperscript{9} Zhang et al
reported a water-mediated exfoliation method to prepare g-C_3N_4 NSs.\textsuperscript{13} The exfoliation process was significantly influenced by the surface energy of the solvent molecules. Yang et al. reported an isopropanol-mediated exfoliation method to obtain g-C_3N_4 NSs with enhanced performance in photocatalytic H_2 evolution.\textsuperscript{14} Although solvent-mediated exfoliation methods are feasible, their efficiency is low. Therefore, it is still a challenge to develop an effective method to fabricate few-layer-thick g-C_3N_4 NSs.

Herein, we report a simple and efficient method to fabricate few-layer-thick g-C_3N_4 NSs by a LA-assisted lithiation method. Because of the high surface/bulk ratio, the as-prepared g-C_3N_4 NSs exhibited enhanced photocatalytic performance compared to their bulk counterpart. Significantly, this LA-assisted lithiation method is versatile and effective to exfoliate other 2D-layered materials such as MoS_2 and WS_2 in a large scale and high yield, providing additional opportunities to meet the intense demand for practical catalytic, biological, and electrical applications. To the best of our knowledge, this is the first report on the synthesis of few-layer-thick 2D g-C_3N_4, MoS_2, and WS_2 NSs by the LA-assisted lithiation method.

1. EXPERIMENTAL

1.1 Preparation of bulk g-C_3N_4: Melamine (10 g, Alfa Aesar, 99.999%) was heated at 550 °C for 2 h under the protection of 20 standard cubic centimeter per minute (sccm) N_2 (99.999%) with a ramp rate of 3 °C/min for both heating and cooling processes, affording yellow g-C_3N_4 powder (yield: ∼3 g).

1.2 Preparation of few-layer-thick g-C_3N_4 NSs: First, the Li intercalation of g-C_3N_4 was carried out in LA using a Schlenk line (see ESI Fig.S1). 0.3 g as-prepared bulk g-C_3N_4 yellow powder and 0.01 g of Li pieces (Alfa Aesar, 99.999%) (molar ratio, 2:1) were placed at the bottom of a silica tube. This process was performed in an argon-filled glove box (Mbraun, Unilab, Germany) to prevent air and water contamination. Then, the silica tube was placed in a bath of 70:30 alcohol/ice water mixture, in which the yellow g-C_3N_4 powder was immersed. Then, the reaction was by shaking the tube, thus contacting the LA with Li; the blue color (characteristic color of e\(^-\)(NH\(_3\))\(_2\)O) gradually faded within 30 min. Finally, the ammonia was carefully removed by evaporation. After the intercalation, the Li-intercalated sample was exfoliated and ultrasonicated in deionized (DI) water for 30 min. During this process, a large number of bubbles were observed, and an opaque suspension of the product was obtained.

After the suspension was centrifuged at 3,000 rpm to remove the residual unexfoliated g-C_3N_4 particles and washed five times with DI water, the products was characterized. The preparation of MoS\(_2\) and WS\(_2\) NSs is similar to that of g-C\(_3\)N\(_4\) NSs as mentioned above.

1.3 Characterization: X-ray diffraction (XRD) data were collected using a high-resolution powder diffractometer (Rigaku D/max 2500, CuK\(_\alpha\), \(\lambda = 0.15418\) nm) at room temperature. Raman scattering measurement was performed at room temperature using a Raman system (JY-HR800) equipped with a 532 nm line from a solid-state laser. An FEI Sirion-200 field-emission scanning electron microscopy (SEM) and a JEM-2100F field-emission transmission electron microscopy (TEM) operating at 200 keV were used to characterize the synthesized materials. The point resolution of the high-resolution TEM (HRTEM) was ∼ 0.19 nm. The thickness of the material was analyzed by atomic force microscopy (AFM) using a Bruker DI MultiMode-8 system. For the chemical compositions analysis, the samples were analyzed using a K-Alpha X-ray photoelectron spectroscopy (XPS) system using an Al K\(_\alpha\) X-ray source and the binding energy values were measured with respect to the C1s peak at 283.5 eV. For the optical measurement, UV-visible absorption spectra were recorded using a UV-visible spectrophotometer (UV2550, Shimadzu, Japan), and photoluminescence (PL) spectroscopy was measured using a Horiba JY HR800 instrument. N\(_2\) adsorption–desorption isotherms were measured using an F-sorb X400 surface area analyzer. All the samples were outgassed at 150 °C for 10 h prior to the N\(_2\) adsorption measurements. Soft X-ray absorption (XAS) and nonresonant soft X-ray emission spectroscopy (XES) spectroscopic measurements of C and N K-edges were conducted using the new XES endstation that is currently being commissioned on the resonant elastic and inelastic X-ray scattering (REIXS) beamline at the Canadian Light Source (CLS). The Rowland circle spectrometer with a microchannel plate imaging detector on that endstation was configured for an approximate resolving power of 10\(^5\) for the XES measurements. The incident light was supplied by the monochromator with a resolution of better than 5×10\(^{-5}\) for the XAS measurements, and the data were collected using total electron yield (TEY). The XAS and XES measurements were calibrated by graphite (285.4 eV) and h-BN (400.9 eV) at C and N edges, respectively. The X-ray absorption near-edge structure (XANES) measurements at C K and N K-edges were collected at the spherical grating monochromator (SGM) beamline at the CLS, the University of Saskatchewan, Canada.

1.4 Photocatalytic redox properties: The photocatalytic H\(_2\) production experiments were performed in a 100-mL 3-neck Pyrex flask at ambient temperature and atmospheric pressure, and the outlets of the flask were sealed with silicone rubber septums. A 350-W xenon arc lamp, which was positioned 20 cm away from the reactor, was used as the light source to trigger the photocatalytic reaction. The focused intensity on the flask was ∼ 20 mW/cm\(^2\). In a typical photocatalytic experiment, 50 mg of the sample was dispersed in 80 mL of an aqueous solution containing 10% v/v triethanolamine scavenger. The decomposition of 6 wt % Pt catalyst was conducted by directly dissolving H\(_2\)PtCl\(_6\) into the above 300 mL solution. Before the irradiation, the system was bubbled with N\(_2\) for 40 min to remove the dissolved O\(_2\), ensuring anaerobic condition. H\(_2\) was analyzed using a gas chromatograph (GC-14C, Shimadzu, Japan, TCD, N\(_2\) as the carrier gas and 5 Å molecular sieve column). Hydroxyl radical (OH\(^-\)) reactions were performed as follows: 5 mg sample was suspended in 80 mL of an aqueous solution containing 0.01 M NaOH and 3 mM terephthalic acid. Before the exposure to irradiation, the suspension was stirred in dark for 30 min. Then, 5 mL of the
solution was taken out every 10 min under $\lambda > 400$ nm and centrifuged for fluorescence spectrum measurements. During the photoreactions, no $O_2$ was bubbled into the suspension. The fluorescence signal of the generated 2-hydroxy terephthalic acid was measured using a Hitachi F-4500 fluorescence spectrophotometer with an excitation wavelength of 320 nm.

2. RESULTS AND DISCUSSION

The real-time Li intercalation of bulk $g$-$C_3N_4$ in LA is shown in Fig. 1. Initially, bulk $g$-$C_3N_4$ powder exhibits yellow color (Fig. 1a), while the LA solution with dissolved Li in silica tube exhibits deep indigo blue color (Fig. 1b). After mixing them and shaking for 10 min, the Li ions gradually inserted into the $g$-$C_3N_4$, and the color of the resulting LA solution gradually faded to deep green (Fig. 1c). The color of the solution continually faded during the shaking, became colorless after 30 min (Fig. 1d), the yellow color originates from the suspended $g$-$C_3N_4$ fragments), indicating that most of the Li ions intercalated into the $g$-$C_3N_4$ NSs and small amounts of Li ions are left in the LA solution. Next, the lithium-intercalated $g$-$C_3N_4$ was ultrasonicated in DI water prior to its exfoliation into a well-dispersed transparent NS suspension.

![Fig. 1](image1.png)

Fig. 1 Real-time Li intercalation of bulk $g$-$C_3N_4$ in LA.

Further, the chemical composition of $g$-$C_3N_4$ NSs was investigated by energy-filtered TEM (Fig. 3 and ESI, Fig. S3). The uniform distribution of C and N elements confirms that this method facilitates a nondestructive exfoliation of $g$-$C_3N_4$, and no residual Li element was detected. Further, the SEM images (ESI, Fig. S4) show that the as-exfoliated $g$-$C_3N_4$ NSs maintained the same lateral scale range as the parent (bulk) $g$-$C_3N_4$, but show a few-layer-thick feature in thickness.

![Fig. 2](image2.png)

Fig. 2 (a) TEM image of $g$-$C_3N_4$ NS. Inset shows the HRTEM image of the selected area indicated by a box. (b) EDS of the as-exfoliated $g$-$C_3N_4$ NSs deposited on a Cu foil. (c) AFM image of the as-exfoliated $g$-$C_3N_4$ NSs. (d) The corresponding height image of a random $g$-$C_3N_4$ NS.

To better understand the crystal structure, the as-prepared g-$C_3N_4$ NSs were characterized by XRD as shown in Fig. 4. Clearly, the exfoliation of few-layer-thick $g$-$C_3N_4$ NSs from bulk $g$-$C_3N_4$ induced considerable change in the XRD pattern. In contrast to bulk $g$-$C_3N_4$, the typical diffraction peak at $13.1^\circ$, which stems from the lattice planes parallel to the $c$-axis, disappeared in the XRD pattern of $g$-$C_3N_4$ NSs. Moreover, the intensity of the diffraction peak at $27.6^\circ$ corresponding to the (002) plane decreased remarkably. Both these changes confirm that the bulk $g$-$C_3N_4$ was successfully exfoliated into few-layer-thick NSs, consistent with the abovementioned characterization results.

![Fig. 3](image3.png)

Fig. 3 Energy-filtered TEM images of C and N elements in the as-prepared g-$C_3N_4$ NSs.
The electronic structure of the as-prepared g-C₃N₄ NSs was investigated by the combined analysis of optical absorption and PL spectra. As shown in Fig. 5a, the intrinsic absorption peak of g-C₃N₄ NSs shows a distinct blue shift of ~10 nm compared to bulk g-C₃N₄. The PL spectra show a clear blue shift from 459 nm (bulk g-C₃N₄) to 449 nm (g-C₃N₄ NSs) (Fig. 5b). Both these typical blue shifts can be attributed to the quantum confinement effect resulting from the shifting of conduction and valence bands in opposite directions. In addition, g-C₃N₄ NSs shows a stable PL peak without apparent shift under different excitation wavelength (Fig. S8) and varied excitation intensity (Fig. S9), implying its intrinsic stimulated emission mechanism.

It is well established that XANES is highly sensitive and can be used to determine the changes in the valence of atoms in a matrix. To further investigate the electronic and chemical structures of the as-prepared g-C₃N₄ NSs, C and N K-edge XANES and XES spectra of the g-C₃N₄ NSs were obtained using the bulk g-C₃N₄ as the reference. The identical XES and similar XANES spectra (Fig. 6a) between the g-C₃N₄ NSs and bulk matrix proved that the as-prepared g-C₃N₄ NSs maintained the major structure as the bulk material. The XES spectra of g-C₃N₄ (Fig. 6a), both NSs and bulk material, are close to that of graphite, but apparently different from crystalline β-C₃N₄ because of the difference in bonding.

The XANES spectrum of g-C₃N₄ at the C K-edge is composed of a sharp π∗ (C=N) transition at ~288 eV and a broad σ∗ peak at ~294 eV. The N K-edge XANES spectra (Fig. 6b) are composed of a broad σ∗ transition peak located at 407 eV and two π∗ peaks located at 399 and 402 eV, which have been assigned to the pyridine- and graphite-like N bonding in g-C₃N₄, respectively. Interestingly, the surface-sensitive TEY mode XANES measurements show clear structural differences in the g-C₃N₄ NSs than bulk-sensitive XES measurements. The g-C₃N₄ NSs exhibit a stronger π∗ feature in both the C and N K-edge.
XANES spectra, predicting a better electronic conductivity. Furthermore, the $\sigma^*$ peak in the C K-edge XANES in the g-C$_3$N$_4$ NSs shifted to a higher energy direction, indicating that the shortening of C–N bonds in plane was probably induced by the presence of a strain in g-C$_3$N$_4$ NSs after the exfoliation, and similar results have been observed in graphene.\textsuperscript{24, 25} Moreover, the XANES spectra of g-C$_3$N$_4$ NSs at the C and N K-edges show a lower-energy shoulder beside the first $\pi^*$ orbital, indicating the presence of more dangling bonds in g-C$_3$N$_4$ NSs. The spectrum of g-C$_3$N$_4$ NSs is slightly broader with higher intensity, indicating that the g-C$_3$N$_4$ NSs have better electronic conductivity (Fig. 6c).

Notably, the band structure determined by XES and XAS is seemingly different from the results of UV-visible and PL measurements. The UV-visible result (Fig.5a) indicates that the bandgap widens, while the XES and XAS results indicate that the bandgap narrows. A possible reason for this discrepancy is that XAS at TEY is surface sensitive (< 5 nm deep), while XES is bulk sensitive. All these results confirm a rich electronic structure as the bulk counterpart. Notably, no clear blue shift was observed in the Raman spectra of g-C$_3$N$_4$ NSs,\textsuperscript{13} probably because of the identical lateral scale as the bulk g-C$_3$N$_4$ (ESI, Fig.S4) in which the phonon confinement effect does not act differently. Moreover, for both the g-C$_3$N$_4$ bulk and NS materials, there are no shifts in the C peak, which was located at ~ 1350 and 1580 cm$^{-1}$, respectively, confirming the high purity of the as-exfoliated g-C$_3$N$_4$ NSs.

Significantly, this LA-assisted lithiation method can also be applied to exfoliate diverse 2D-layered material such as MoS$_2$ and WS$_2$. The AFM analyses (ESI, Fig.S7) of the as-prepared MoS$_2$ and WS$_2$ NSs showed an average thickness of ~ 3.5 and ~ 3.0 nm, respectively, confirming that few-layer-thick MoS$_2$ and WS$_2$ NSs were successfully obtained. It is well known that LA is transparent and colorless in nature, while Li metal is dissolved in LA to generate metal cations, Li$^+$ and solvated electron, e$^-$ (NH$_3$)$_n$, exhibiting a deep blue color arising from the presence of solvated electrons.\textsuperscript{26–34} Therefore, the entire process of Li insertion into the g-C$_3$N$_4$ matrix can be visualized by the color fading of the LA solution. The basic reaction corresponding to Fig. 1b can be described by Eq. (1).

$$\text{Li} + \text{NH}_3(l) \rightarrow \text{Li}^+ + e^- (\text{NH}_3)_n \quad (1)$$

It is proposed that, in addition to Li$^+$ ion diffusion, the Li$^+$ ions probably penetrated the C$_3$N$_4$ interlayers (Step 1, Fig. 7), involving the in-situ redox reactions catalyzed by LA, which can be described by Eq.(2).

$$\text{xLi}^+ + \text{C}_3\text{N}_4\text{(bulk)} \rightarrow \text{xLi} + \text{C}_3\text{N}_4^{4+} \quad (2)$$

It is rationalized that the lithiation was much faster than the traditional Li intercalation only based on the diffusion of Li$^+$ ions.\textsuperscript{7} These Li$^+$ located between the interlayers to form a charged g-C$_3$N$_4$ material, which was subsequently compensated by the solvated electrons to form a neutral g-C$_3$N$_4$ material with intercalated metallic Li during the shaking, as shown by Eq.(3)

$$\text{xLi} + \text{C}_3\text{N}_4^{4+} + e^- (\text{NH}_3)_n \rightarrow \text{Li@C}_3\text{N}_4\text{(bulk)} \quad (3)$$

During these processes, the characteristic deep blue color of e$^-$ (NH$_3$)$_n$ gradually faded because of the decrease in e$^-$ (NH$_3$)$_n$ concentration, corresponding to Fig. 1c. After the insertion of metallic Li into the interlayers, the interlayer distance increased, thus weakening the van der Waals interactions between the layers (Step 2, Fig. 7). To examine the possible reaction between g-C$_3$N$_4$ and ammonia, the structure of bulk g-C$_3$N$_4$ before and after soaked in ammonia (without lithium) was compared by XRD analysis (ESI, Fig. S11). It can be seen that no crystal structure change was found, implying bulk g-C$_3$N$_4$ is inert to liquid ammonia. Next, the products were exfoliated in DI water by ultrasonication. (Step 3, Fig. 7). In this step, metallic Li reacts with H$_2$O to form LiOH and H$_2$, thus pushing the layers apart...
from each other. In fact, a large number of bubbles were observed during the exfoliation. Thus, isolated few-layer-thick g-C$_3$N$_4$ NSs were obtained. The corresponding reaction process can be described by Eq.(4).

$$\text{Li@C}_3\text{N}_4 + \text{H}_2\text{O} \rightarrow \text{C}_3\text{N}_4(\text{NS}) + \text{LiOH} + \text{H}_2 \uparrow \ (4)$$

Notably, the as-proposed LA-assisted lithiation method is better than those reported by Zhang et al. and Kaner et al., owing to five outstanding merits of our study: (1) In particular, the large-scale production (~10 g) of g-C$_3$N$_4$, MoS$_2$, and WS$_2$ NSs (for one time) has been achieved with a high yield of ~85%. (2) Compared to the conventional methods, this method is less time-consuming. Most of the reactions were completed in <30 min; for MoS$_2$, this process occurred in ~5–10 min. (3) A significant feature of this method is that the degree of Li intercalation can be visually observed from the clear color changes in the LA solution from deep blue color to colorless, while the Li intercalation process can be tuned by the shaking speed of the silica tube. (4) In the absence of high-temperature treatment or oxidation process, the as-prepared NSs obtained by a low-temperature synthesis exhibited the same crystal structure and chemical stoichiometric ratio of parent (bulk) materials, exhibiting the intrinsic features of the parent (bulk) material. (5) The LA-assisted lithiation method also expands the range of layered materials that can be inserted by metallic Li than the special one. Moreover, it should be noted that the metals, Na and K, can also be used to exfoliate the 2D-layered compounds by the similar route. Thus, this route can be defined as LA-assisted alkali metal intercalation strategy.

![Fluorescence spectra of 2-hydroxyterephthalic acid (TAOH) solution generated by g-NCNS under irradiation with visible light (λ > 400 nm)](image)

Fig. 8 (a) Time-dependent H$_2$ production of bulk g-C$_3$N$_4$ (black curve) and g-C$_3$N$_4$ NSs (red curve) under visible light irradiation (λ > 400 nm). (b) Fluorescence spectra of 2-hydroxyterephthalic acid (TAOH) solution generated by g-C$_3$N$_4$ NS under λ > 400 nm.

The intriguing surface characteristics, electronic and electrical properties, and optical responses of the as-prepared g-C$_3$N$_4$ NSs make it promising for diverse applications. As a proof of concept, the advantage of g-C$_3$N$_4$ NSs as a photocatalyst was demonstrated in this study. The photocatalytic activity of the as-prepared g-C$_3$N$_4$ NSs was first evaluated in the photocatalytic H$_2$ evolution from a water/triethanolamine solution. Under visible light irradiation, while a trace amount of H$_2$ was detected using bulk g-C$_3$N$_4$ as the photocatalyst, the as-prepared g-C$_3$N$_4$ NSs showed extensively enhanced photocatalytic H$_2$ evolution at a steady rate (Fig. 8a), indicating the stability of g-C$_3$N$_4$ NSs as photocatalysts. Here, the as-prepared g-C$_3$N$_4$ NS exhibited an average hydrogen evolution rate of ~8 µmol h$^{-1}$ within 0 ~ 5 h, which is about twice than that of bulk parent material as obtained in Wang et al.’s work. Moreover, the g-C$_3$N$_4$ NSs also showed great ability in activating H$_2$O molecules to produce highly reactive hydroxyl radicals (Fig. 8b), which can be used as reactive oxidative species to trigger various oxidation reactions for environmental remediation and organic transformations. The enhanced photocatalytic activity of g-C$_3$N$_4$ NSs can be attributed to the increased surface area (ESI, Fig. S10), abundant dangling bonds, and modified electronic structures as demonstrated previously. The high surface/bulk ratio and more dangling bonds in g-C$_3$N$_4$ NSs provide abundant reactive sites. The few-layer-thick thickness and better electronic conductivity shorten the bulk diffusion length and promote the bulk transport rate of charge carriers with the consequence of reduced recombination probability. Moreover, the surface atomic geometry and the band structure engineering associated with few-layer-thick g-C$_3$N$_4$ NSs will also contribute a lot, as has been primarily demonstrated in several photocatalysts such as ZnO and TiO$_2$.

3. CONCLUSIONS

In summary, we developed a simple, highly efficient, and large-scale synthesis method to fabricate g-C$_3$N$_4$ NSs and other 2D-layered materials such as MoS$_2$ and WS$_2$ NSs from their parent (bulk) materials. The synthetic process was well controlled to achieve few-layer-thick NSs, and the reaction progress could be visualized by the clear color fading from deep blue to colorless without destroying its entire crystal structure. The enhanced photocatalytic performance of g-C$_3$N$_4$ NSs than its bulk counterpart was attributed to the increased surface area, abundant dangling bonds, and modified electronic structures. This novel route is advantageous over others in terms of both high yield (~85%) and large-scale synthesis (~10 g in one time), representing a promising alternative to the current methods in practical applications such as large-scale production of NSs.

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