Facile Large-Scale Synthesis of Urea-Derived Porous Graphitic Carbon Nitride with Extraordinary Visible-Light Spectrum Photodegradation

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ABSTRACT: We report the large-scale synthesis of porous graphitic carbon nitride (g-C3N4) in a direct heat treatment process by controlling the thermal condensation temperature of the low-cost urea precursor. An excellent linear relation between the yield of the urea-derived porous g-C3N4 (U-g-C3N4) and the input urea was experimentally demonstrated, and consequently, a large-scale yield >50 g in a batch was readily achieved. A series of morphology and structure characterizations revealed the actual evolutionary process of the temperature-dependent porous architecture of U-g-C3N4 and its inherent superiority. Furthermore, we demonstrated the extraordinary visible-light-driven photodegradation activity of large-scale U-g-C3N4 toward organic pollutants such as rhodamine B, safranine T, and α-naphthol. Such superior photodegradation performance and long-term photocatalytic stability, together with a scalable preparation method, may render as-fabricated U-g-C3N4 as a promising candidate for practical application in environmental remediation.

1. INTRODUCTION

Photocatalysis for conversion of solar into chemical energy is considered to be one of the more promising technologies to produce clean energy and remove environmental pollutants.1–6 Efficient photocatalysts operating under solar light have been actively pursued, and many attractive visible-light photocatalysts have been exploited.7–16 Graphitic carbon nitride (g-C3N4), which is constructed from N-bridged tri-s-triazine repeating units that form two-dimensional conjugated planes packed together via van der Waals interactions, has recently attracted much attention due to its promising photocatalytic applications in water splitting, photodegradation of organic pollutants, and photosynthesis via visible light.17–23 The merits of this metal-free photocatalyst include availability, ability of absorbing visible light, low-cost, and good stability.24–25 The photocatalytic activities of g-C3N4 are greatly influenced by the structure, including the electronic structure, nanostructure, crystal structure, and/or heterostructure.26,27 In recent years, many synthetic techniques and effective modification procedures have been proposed to optimize the photocactivity of g-C3N4 from the perspectives of structure design such as porous structure, nanosheets, helical nanorods, and hollow nanospheres.28–33 As usual, g-C3N4 can be prepared either through the thermal condensation of several low-cost nitrogen-rich precursors or through the hard or soft templating strategies using liquid precursors such as cyamamide molecules.34–36 However, most g-C3N4 materials derived from nitrogen-containing precursors such as cyamamide, melamine, and thiourea are always bulk and difficult to achieve superior photocatalytic performance, mainly resulting from low surface area and fast charge-carrier recombination.34,37 On the other hand, hard or soft templating-based synthetic routes for preparing morphology-defined g-C3N4 will inevitably involve cumbersome steps and complicated post-treatment processes, thus impeding further large-scale applications.35,38 Additionally, other studies indicate that, in some cases, porous g-C3N4 can also be obtained by template-free methods using complex precursors mediated by inhibitor or additives as starting materials.35 Recently, a simple, template-free method which can directly pyrolyze low-cost urea into porous g-C3N4 in air without the assistance of any other templates has been developed.39,40 Such fabricated urea-derived g-C3N4 photocatalysts have shown to be efficient in sunlight/visible-light-driven photocatalytic hydrogen production41 and in a certain visible photocatalytic activity for environmental pollutant treatment.42 For urea-derived polymeric g-C3N4 prepared by the pyrolysis process, it takes several hours (5–6 h) to complete the degradation of RhB.42 However, for practical applications in environmental purification, especially for visible-light-driven photodegradation of pollutants, the existing reported urea-derived g-C3N4 still suffers insufficient photo-
catalytic efficiency and limited production capacity.\textsuperscript{42–47} Indeed, the catalytic efficiency and photostable activity have been found to be strongly dependent on the porosity and specific surface area of g-C\(_3\)N\(_4\), which is closely related to the pyrolysis process, including the heating rate and annealing temperature.\textsuperscript{48,49} As such, studies on the inherent nature of porous g-C\(_3\)N\(_4\) with semiconductor characteristics such as visible-light response and facile diffusion of substrates in the pore channels, together with the actual evolutionary process of the porous architecture of g-C\(_3\)N\(_4\) related to its inherent superiority, are of particular importance for further improving the photocatalytic activity, which has not been reported until now. Furthermore, all existing reports of g-C\(_3\)N\(_4\) mainly focus on photodegradation of visible-light-response pollutants such as rhodamine B (RhB) and methyl orange (MO) and the photocatalytic degradation of biological stains such as safranine T (ST); pollutants with no absorption in the visible region, such as \(\alpha\)-naphthol (\(\alpha\)-NP), are rarely investigated. It is also worth mentioning that the current synthetic amount of urea-derived porous g-C\(_3\)N\(_4\) is limited to small-scale (usually <5 g) for lab study, and its synthesis and applicability to high-volume material production for practical photocatalytic applications remains untested.

Herein, we report a large-scale synthesis of urea-derived porous g-C\(_3\)N\(_4\) (denoted as U-g-C\(_3\)N\(_4\)) using direct pyrolysis of the urea precursor using a moderated heating rate of 3 °C/min. The experiment data showed a good linear relationship between the yield of the U-g-C\(_3\)N\(_4\) catalyst and the input of urea precursor, and consequently a yield of U-g-C\(_3\)N\(_4\) more than 50 g per batch was readily achieved. The actual evolutionary process of the temperature-dependent porous architecture of U-g-C\(_3\)N\(_4\) and its inherent superiority were experimentally traced. Specially, it was found that the homemade large-scale U-g-C\(_3\)N\(_4\) via pyrolysis of urea at 600 °C exhibited extraordinary visible-light-driven photodegradation toward organic pollutants such as RhB, ST, and \(\alpha\)-NP. Notably, the complete degradation of RhB (\(C_0 = 2.5 \times 10^{-5}\) mol/L) was performed within 25 min of visible irradiation using only 10 mg of photocatalyst, and this result was found to be obviously better than those reported previously.\textsuperscript{42,44,46,47} Such scalable preparation method, superior photodegradation performance, and proven long-term photostability of g-C\(_3\)N\(_4\) could allow for the practical application in environmental remediation.

2. EXPERIMENTAL SECTION

2.1. Materials. Urea (Beijing Shiji, A.R. 99%), ethanol [Sinopharm Chemical Reagent Beijing Co. (Beijing, China), 99.7%], rhodamine B [Fisher Scientific (Hong Kong) Co., Ltd.], safranine T (Aladdin A.R. 85%), \(\alpha\)-naphthol (Beijing ruida fine chemical Co., Ltd.), and deionized (DI) water used in this study were of analytical grade and used without further purification.

2.2. Method. U-g-C\(_3\)N\(_4\) was synthesized via pyrolysis of the urea precursor. Typically, urea was first placed in an oblong aluminum box with a cover (the length, width, and height were 21.0, 11.5, and 6.3 cm, respectively), and then wrapped using aluminum foil. The sealed precursor was directly heated at 600 °C for 2 h at a heating rate of 3 °C/min and then cooled to room temperature naturally. The resultant powder (U-600) was obtained by centrifuging, rinsing and quickly drying at 80 °C in a vacuum drying oven (−0.1 MPa). In parallel, U-100, U-200, U-300, U-400, U-500, U-550, and U-650 samples were synthesized by the same experimental procedure except using different thermal polymerization temperatures.

Small-Scale Synthesis of U-g-C\(_3\)N\(_4\): A small quantity of urea (\(M_0 = 2.5 \text{ g} < M_0 = 45 \text{ g}\)) was loaded into a miniature reactor. The mass of resultant small-scale synthetic U-g-C\(_3\)N\(_4\) was weighed and recorded as \(M_1\).

Large-Scale Synthesis of U-g-C\(_3\)N\(_4\): A large amount of urea (100 g < \(M_0 = 1000 \text{ g}\)) was loaded into a volume-expanding reactor and then pyrolyzed, following the same experimental process. The mass of the resultant small-scale synthetic U-g-C\(_3\)N\(_4\) was weighed and recorded as \(M_2\).

2.3. Characterization. Powder X-ray diffraction (XRD) analysis was performed on an X-ray diffractometer (X’Pert PRO MPD, Panalytical) using Cu Kα radiation in 2θ range from 10° to 70° with a scanning rate of 5°/min. The surface morphology of samples was determined from scanning electron microscopy (SEM) images on a Hitachi S-4700 microscope. Transmission electron microscopy (TEM) images were characterized on a JEOL JEM-3010 microscope. The Brunauer–Emmett–Teller (BET) specific surface area and the Barrett–Joyner–Halenda (BJH) pore-size distribution were taken using a Quantachrome Quadsorb SI instrument. Thermogravimetric analysis (TGA) curves were recorded on a Netsch STA449C thermal analysis apparatus under the flow of argon at a heating rate of 3 °C/min. The optical properties of U-600 and P-25 were studied using the adsorption spectra recorded on an ultraviolet–visible (UV–vis) spectrophotometer (Lambda 950 UV/vis).

2.4. Photocatalytic Activity. The photocatalytic activity was evaluated by decomposition of RhB, ST, and \(\alpha\)-NP under visible-light irradiation (420 nm < \(\lambda < 780 \text{ nm}\)) using a 300 W Xe lamp (CEL-HXF300; the spectrum of the light source is shown in Figure S1) with a 420 nm cutoff filter. A 10 mg sample of the photocatalyst was added to 60 mL of RhB (2.5 \times 10^{-5}\) mol/L), ST (7.5 \times 10^{-5}\) mol/L), or \(\alpha\)-NP (2.5 \times 10^{-5}\) mol/L). Before illuminating, the suspension was stirred in the dark for 30 min to establish an adsorption–desorption equilibrium. The suspension was exposed to the visible light under magnetic stirring. At regular intervals of visible-light irradiation, samples were withdrawn and centrifuged for removing solid particles for analysis. The concentration of pollutant solution was determined by a UV–vis spectrophotometer (Shimadzu UV-2501PC). The degradation curves of RhB under visible-light irradiation in the presence of large-scale synthetic U-g-C\(_3\)N\(_4\) (i.e., U-550, U-600, U-650) and recyclability experiment were carried out in the conditions as mentioned above.

2.5. Detection of Reactive Oxidative Species. The reactive oxidative species in the photodegradation were detected using in situ trapping experiments. The detection process was similar to the photodegradation experimental process. Three different scavengers, such as p-benzoquinone (BQ, \(O_2^-\) radicals scavenger), disodium ethylenediaminetetra-acetate (EDTA, holes scavenger) and isopropanol (IPA, -OH radicals scavenger), were added to the RhB solution prior to illumination in three separate photodegradation systems. The concentration of the scavengers was controlled to be 1.0 mM.

3. RESULTS AND DISCUSSION

3.1. Large-Scale Synthesis of U-g-C\(_3\)N\(_4\): As is well-known, large-scale synthesis of catalyst products is essential for practical industrial application.\textsuperscript{46} However, currently reported U-g-C\(_3\)N\(_4\) synthesized via pyrolysis of the low-cost precursor, urea, is still limited to small-scale production.\textsuperscript{50,46,51} In this
work, the feasibility of large-scale production of U-g-C_{3}N_{4} via polycondensation of urea was demontrated. The typical preparation procedure for U-g-C_{3}N_{4} is schematically illustrated in Figure 1a. For synthesis of small-scale U-g-C_{3}N_{4}, the initial amount of the urea precursor loaded into a miniature reactor was controlled to be in the range of 2.5 g < M_{0} < 45 g, and consequently the maximum yield of the resultant U-g-C_{3}N_{4} was ca. 2.07 g. To study the relation between the input of precursor and the yield of U-g-C_{3}N_{4}, the small-scale synthetic U-g-C_{3}N_{4} experiments applying six different input amounts of urea (i.e., 2.5, 6.25, 12.5, 25, 35, and 45 g) were performed in this work. Notably, an excellent linear relation between the yield of small-scale U-g-C_{3}N_{4} and the input of urea precursor was demonstrated, with the correlation coefficient R^{2} reaching 0.99 (Figure 1b). Such a linear relation result motivated us to consider if there is any possibility to achieve high yield of U-g-C_{3}N_{4} by simply boosting the amount of urea initially added in the reaction system. Following this research route, we subsequently carried out the synthesis of large-scale U-g-C_{3}N_{4} using large amounts of the urea precursor, i.e., 100 g < M_{0} <

Figure 1. (a) Schematic of the formation of U-g-C_{3}N_{4} from urea and picture of the large-scale synthesized U-g-C_{3}N_{4}. Linear fit curve of small-scale (b) and large-scale (c) synthesis of U-g-C_{3}N_{4}.

Figure 2. (a) XRD pattern and (b) SEM image of U-g-C_{3}N_{4}. (c) TEM image of U-g-C_{3}N_{4} with an inset showing the porosity within the U-g-C_{3}N_{4} sheets. (d) N_{2} adsorption–desorption isotherm and BJH pore-size distribution (inset) of U-g-C_{3}N_{4}.
1000 g in the reaction system (Figure 1c). As expected, a yield of U-g-C3N4 that was more than 50 g per batch was readily achieved. Furthermore, the excellent linear relation remained unchanged even when the amount of input urea was increased to 1000 g during the synthetic procedure. In addition, a comparison of this synthesis method of porous g-C3N4 with those reported in the literature is listed in Table S1; the table shows obvious advantages of this method. This facile large-scale preparation method could allow for the industrial application of U-g-C3N4.

3.2. Characterizations and Evolutionary Process of U-g-C3N4. Evidence for the formation of U-g-C3N4 was obtained by XRD analysis, as shown in Figure 2a. The intense diffraction peak at 27.5° is assigned to the (002) reflection of a graphitic-like aromatic structure, and the relatively weak peak at 12.8° corresponds to the in-plane repeating motifs of the continuous heptazine network.17,41,52 The two characteristic peaks that are always assigned to typical g-C3N4 polymer match well to that of the g-C3N4 reported previously.53−55 The SEM image at a low magnification (Figure 2b) and TEM image at a high magnification (Figure 2c) show that the as-prepared U-g-C3N4 possesses a porous stacked layered morphology. A typical type IV isotherm featuring a pronounced H3-type hysteresis loop demonstrates the existence of mesopores in the polymeric frameworks of U-g-C3N4 (Figure 2d), in agreement with the result of the honeycomb pore structure of U-g-C3N4, as shown in the inset of Figure 2c. The BJH pore-size distribution graph (inset of Figure 2d) reveals that the U-g-C3N4 sample has a broad pore size distribution ranging from 3 to 120 nm. The average pore diameter is measured to be 15.7 nm. Indeed, such porous architecture is associated with high specific surface area, good mass diffusion, and efficient separation of photoinduced

Figure 3. SEM images of U-0 (a), U-100 (b), U-200 (c), U-300 (d), U-400 (e), U-500 (f), U-550 (g), U-600 (h), and U-650 (i).

Figure 4. SEM images of U-550 (a), U-600 (b), and U-650 (c). TEM images of U-550 (d), U-600 (e), and U-650 (f).
electrons and holes and thus is beneficial for the enhancement of photocatalytic performance,\textsuperscript{56−58} which will be discussed in detail in the following section. The above results demonstrate the successful fabrication of U-g-C\textsubscript{3}N\textsubscript{4} by the simple thermal polycondensation method using urea as a cheap precursor.

In thermal polycondensation synthesis of g-C\textsubscript{3}N\textsubscript{4} derived from nitrogen-containing precursors, the precursor mass and heating temperature would influence the microstructure annealing.\textsuperscript{59,60} However, in this study, temperature was a predominantly controlling factor for the formation of porous structure because we had used a large reactor with enough volume to eliminate the influence of precursor mass. To gain deep insight into the actual evolutionary process of the U-g-C\textsubscript{3}N\textsubscript{4} architecture, a series of temperature-dependent experiments were also performed. SEM and TEM in combination with TGA and XRD were used to reveal the layered structure and pore formation process (Figures 3 and 4; Figures S2 and S3). As can be seen in Figure 3a, U-0 (i.e., nonheat-treated urea) exhibits bulk morphology. When the heating temperature rises to 100 °C, the bulk morphology is maintained (Figure 3b). Correspondingly, no obvious weight loss is observed in TGA thermograms at the low-temperature range, and little difference is observed in the XRD patterns between U-0 and U-100. Upon continuously increasing the heating temperature up to 200 °C, a porous structure initially appears within the microtexture of U-200 (Figure 3c), and simultaneously a sharp weight loss largely associated with urea decomposition occurs. During this heating process, urea is melted and vaporized with vigorous gas evolution.\textsuperscript{61} The few changes in the XRD pattern of U-200 demonstrates that the main composition of U-200 is still urea. As for U-300, more enlarged pores caused by the aggregation of intermediate products, i.e. cyanuric acid, ammelide, and ammeline (Figure 3d), and a weight loss around 300 °C (Figure S2) together with a change in the XRD pattern (Figure S3) are directly visualized.\textsuperscript{61,62} Under the heating temperatures ranging from 400 to 500 °C, the produced intermediates further polymerize to form melon (Figure 3e,f),\textsuperscript{17,41} which can be demonstrated by XRD patterns of U-400 and U-500. Note that the layer structure and the pore channels become discerned at 550 °C, which is higher than the polymerization temperature (525 °C) of g-C\textsubscript{3}N\textsubscript{4}\textsuperscript{17} (Figures 3g and 4a,d). When the temperature climbs to 600 °C, a large number of tiny pores within the loose layered g-C\textsubscript{3}N\textsubscript{4} texture are generated (Figures 3h and 4b,e). However, the excessively high heating temperature at 650 °C causes the collapse of the loose porous g-C\textsubscript{3}N\textsubscript{4} structure (as shown in Figures 3i and 4c,f). The XRD patterns of U-550, U-600, and U-650 show that the peak at 27.5° becomes sharp with increasing heating temperature, indicating the proceeding of polymerization of g-C\textsubscript{3}N\textsubscript{4}.

N\textsubscript{2} adsorption−desorption isotherms, BET specific surface areas, and BJH pore-size distributions were also measured to reveal the actual evolutionary process of the porous architecture. Considering that the polymerization of urea-derived intermediates occurred above 389 °C,\textsuperscript{17,41} the samples of U-400 to U-650 were analyzed herein. As can be seen in Figure 5a, all samples possess type IV adsorption−desorption isotherms, which is characteristic of mesoporous materials. BET surface areas are shown in the inset of Figure 5a. One can see that the specific surface area of samples gradually enlarges as the heating temperature increases from 400 to 600 °C and decreases when the temperature further increases from 600 to
650 °C. The largest surface area is obtained by the U-600 sample. The BJH pore-size distribution of samples is also examined, as shown in Figure 5b. One can see that U-400 exhibits only a small peak around 4 nm in the pore-size distribution curve. As the heating temperature increases from 400 to 550 °C, the peak around 4 nm gradually grows up and simultaneously an obvious peak around 12 nm appears, suggesting that the amount of pores increases during the heat treatment process in the wide pore diameter distribution. When the temperature reaches 600 °C, the pore volume is measured as the largest among all samples, with three peaks around 4, 6, and 17 nm, and the pore diameter distribution widens up to 120 nm. However, the pore-size distribution of the resulting U-650 sample narrows as compared to that of U-600. Especially, the pore volume in the region of pore diameter >10 nm decreases obviously, mainly because of the collapse of pore structure of U-g-C3N4. This is in good accord with the results of SEM (Figures 3i and 4c) and TEM (Figure 4f) images.

3.3. Photocatalytic Activity. The photocatalytic activity of U-550, U-600, and U-650, obtained via the large-scale synthetic procedure, were evaluated by the degradation of RhB solution under visible-light irradiation (420 nm < λ < 780 nm). As a reference, the photodegradation experiment based on commercial P-25 was also conducted (Figure 6). Figure 6a shows that an adsorption–desorption equilibrium is reached within 30 min in the dark, and the amount of organic pollutant adsorbed to the surface of the catalysts is less than 15%. The amount of RhB adsorbed on different g-C3N4 samples follows the order of U-550 < U-650 < U-600, consistent with their specific surface areas. As such, the photodegradation yield is calculated after subtraction of this adsorbed fraction. From Figure 6a, one can observe that no obvious degradation of RhB occurs under visible irradiation without photocatalysts. The slightly decreased concentration of RhB by P-25 appears mainly because of the self-sensitization-induced degradation of RhB.63 Apparently, the as-prepared three U-g-C3N4 photocatalysts such as U-550, U-600, and U-650 exhibit visible-light photocatalytic activity that is much higher than that of P-25 in the degradation of RhB. The photocatalytic activity follows a trend in a sequence of U-600 > U-650 > U-550. This is understandable because U-600 possesses relatively higher specific surface area and sufficient pore channels in comparison with the other samples, as demonstrated above. Specifically, U-600 reaches a RhB degradation rate of 100% after irradiation for 25 min, which is superior to that of P-25 with a degradation rate of 16%, owing to the obviously enhanced optical absorption capability in visible light as compared to P-25 (Figure S4). Figure 6b shows the temporal evolution of the spectral changes of RhB mediated by the U-600 sample. The absorption peaks decrease gradually with increasing irradiation time and disappear after 25 min, which means RhB is exhaustively degraded. It is worth noting that such an excellent photocatalytic performance that takes just 25 min for only 10 mg of U-g-C3N4 to completely degrade the target pollutant (RhB) is much better than that of urea-derived g-C3N4 by the direct thermal polymerization method previously reported (Table S2).

For better understanding of the photodegradation performance of the large-scale U-g-C3N4 photocatalyst, the degradation of the ST biological stain and the α-NP compound with no absorption in visible region were also performed under otherwise identical conditions. As can be seen in Figure 7a, U-g-C3N4 achieves a 95% degradation rate of ST after 30 min of light radiation, which is much higher than that of P-25 with a degradation rate of only 12%. Furthermore, it is found that all the absorption peaks of ST decrease rapidly with increasing irradiation time and disappear after 25 min, which means ST is exhaustively degraded. It is worth noting that such an excellent photocatalytic performance that takes just 25 min for only 10 mg of U-g-C3N4 to completely degrade the target pollutant (RhB) is much better than that of urea-derived g-C3N4 by the direct thermal polymerization method previously reported (Table S2).
disappear after irradiation for 30 min (Figure 7b). Figure 7c shows that U-g-C₃N₄ significantly outperformed the commercial P-25 catalysts in photodegradation of α-NP under visible light, and the characteristic absorption bands of α-NP decrease as the illumination time increases (Figure 7d). These results suggest the versatility and effectiveness of the U-g-C₃N₄ photocatalyst in the visible-light-induced photodegradation of organic pollutants.

3.4. Role of Reactive Species and Proposed Photocatalytic Mechanism. In general, many reactive species including h⁺, ·OH, and ·O₂⁻ are expected to be involved in the photocatalytic reaction. The effects of some scavengers on the photodegradation of RhB were examined in an attempt to propose the possible photocatalytic reaction mechanism. The p-benzoquinone, disodium ethylenediaminetetraacetate, and isopropanol were used as ·O₂⁻, h⁺, and ·OH scavengers, respectively. As shown in Figure 8a, the photocatalytic activity of U-g-C₃N₄ is greatly suppressed by the addition of BQ as ·O₂⁻ scavenger, indicating that ·O₂⁻ is the main active species in the photocatalytic reaction. Conversely, no obvious decrease in the photocatalytic activity is observed by introduction of IPA and EDTA, which means ·OH and h⁺ radicals are not the dominating active species in the photocatalytic reaction. From Figure 8b, one can see that the conduction edge potential of U-g-C₃N₄ (~1.3 V vs NHE) is more negative than the standard redox potential O₂/·O₂⁻ (~0.046 V vs NHE) to reduce the molecular oxygen to yield ·O₂⁻ which then induces the degradation of RhB. When the VB potential of U-g-C₃N₄ (+1.4 V vs NHE) is compared with the standard redox potential of OH⁻/·OH (~1.99 V vs NHE), it is found that the VB potential of U-g-C₃N₄ is more negative than the standard redox potential of OH⁻/·OH. Hence, the photoinduced h⁺ cannot oxidize OH⁻ to generate ·OH radicals. It further indicates the main reactive species involved in the photocatalytic degradation of RhB over the U-g-C₃N₄ photocatalyst are ·O₂⁻ instead of the photoinduced h⁺ and ·OH. The proposed photocatalytic mechanism of U-g-C₃N₄ is that the visible-light irradiation can induce the generation of a large number of ·O₂⁻ with high oxidation activity in the presence of U-g-C₃N₄, thus resulting in the degradation of organic pollutants.

3.5. Reusability. The stability of a photocatalyst is also very important from the point of view of its practical application. To check the stability of the fabricated large-scale U-g-C₃N₄, we carried out the recycled photodegradation of RhB under visible-light irradiation. As shown in Figure 9, no obvious decay of photocatalytic efficiency is observed after five consecutive cycles. The as-prepared U-g-C₃N₄ material maintains its extraordinary photocatalytic performance in every cycling run. Figures S5 and S6 show the SEM images and XRD patterns of U-g-C₃N₄ before and after photodegradation of RhB, and one can see that no obvious changes of the U-g-C₃N₄ sample are presented after the photodegradation experiments. Therefore, U-g-C₃N₄ can be regarded as a stable high-performance visible-light photocatalyst for photodegrading organic pollutants, possessing great prospects in environmental protection.

4. CONCLUSIONS
The U-g-C₃N₄ photocatalyst has been successfully synthesized from the low-cost urea precursor via a simple pyrolysis procedure. We demonstrate that large-scale synthesis of U-g-C₃N₄ can easily be achieved by adjusting the constituent ratio of reactants added initially. A series of characterizations reveal the temperature-dependent evolutionary process of the porous architecture, and it is found that 600 °C is an optimal temperature for the formation of porous layered U-g-C₃N₄. The fabricated large-scale U-g-C₃N₄ exhibits extraordinary visible-light-driven photodegradation toward organic pollutants such as RhB, ST, and α-NP and excellent long-term photocatalytic degradation stability and reusability. Such superior photodegradation performance and long-term photocatalytic stability, together with a scalable preparation method, could allow for the practical application of g-C₃N₄ in environmental remediation. Thus, this work opens further opportunities for significant improvement of g-C₃N₄ toward industrial applications in the domain of photocatalysis.
Spectrum of the light source; thermogravimetric analysis of urea; XRD patterns of U-0, U-100, U-200, U-300, U-400, U-500, U-550, U-600, and U-650; UV–visible absorption spectra of U-g-C3N4 (U-600) and P-25; SEM images of U-g-C3N4 before and after using for photodegradation of RhB; XRD patterns of U-g-C3N4 before and after using for photodegradation of RhB; comparison of different methods for preparation of porous g-C3N4; and RhB photodegradation performance comparisons between previously reported urea-derived g-C3N4 and as-prepared U-g-C3N4.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported financially by National Natural Science Foundation of China (21176019, 21377011, 21476019) and Beijing Higher Education Young Elite Teacher Project (YETP0487).

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