Exfoliated Graphitic Carbon Nitride Nanosheets/Gold Nanoparticles/Spherical Montmorillonite Ternary Porous Heterostructures for the Degradation of Organic Dyes

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ABSTRACT: Water-soluble organic carcinogenic pollutants have become a serious threat to both health and environment. Here, porous ternary spherical montmorillonite/exfoliated graphitic carbon nitride nanosheets/gold nanoparticles (SMT/g-C₃N₄/Au NPs) heterostructures were facile and green synthesized through a polydopamine chemistry method. These involved the coating of porous SMT with exfoliated g-C₃N₄ nanosheets and in situ growth of Au NPs. The prepared heterostructures exhibited a universal catalytic ability toward organic dyes, such as methylene blue (MB), rhodamine 6G, and Congo red, in the presence of sodium borohydride (NaBH₄). The catalytic activity would improve under high SMT/g-C₃N₄/Au NPs concentration, high temperature, and high pH values. For example, the apparent reduction rate constant (k_{app}) and turnover frequency (TOF) toward MB can reach 5.91 min⁻¹ and 302 h⁻¹, respectively, at 35 °C and pH values of 11. Furthermore, the influences of the pH values on the catalytic performance were investigated, and the reason can be attributed to the strong enhanced adsorption capacity of SMT/g-C₃N₄/Au NPs heterostructures toward organic dyes under the high pH values for facilitating electron transfer from NaBH₄ to organic dyes. Moreover, the SMT/g-C₃N₄/Au NPs heterostructures were quite stable, being recycled at least 10 times with almost unchanged k_{app} . The excellent catalytic performance and recyclability recommend our synthesized SMT/g-C₃N₄/Au NPs heterostructures for a wide range of applications in environment and wastewater treatment.

KEYWORDS: exfoliated g-C₃N₄, gold nanoparticles, porous heterostructures, catalyst, organic dyes

1. INTRODUCTION

Multifunctional materials, especially hybrid nanomaterials, with a high diversity of structures and compositions, have attracted increasing attention because of their excellent properties, which are exploitable in various fields, such as catalysis, wastewater treatment, medicinal chemistry, and energy storage.^{1–8} The rational control of dual or ternary heterostructures was achieved by applying a great number of approaches and strategies for their synthesis while using carbon oxide,^{9,10} carbonitride,^{11,12} silica oxide,¹³ and metal oxide¹⁴ as supports for various active sites. Among them, graphitic carbon nitride (g-C₃N₄), a fascinating 2D nanosheet semiconductor material with a graphite-like layer structure, is widely used as a catalytic support. With planar amino groups connected with tris-triazine in each layer and van der Waals forces between layers, it closely resembles graphene oxide.¹⁵ The g-C₃N₄ layer has a large surface area, providing a great number of active sites, favorable for enhancing the catalytic properties.¹⁶

So far, bulk g-C₃N₄ was usually prepared through thermal condensation of various carbon/nitrogen organic precursors.^{17–19} The g-C₃N₄ nanosheets can be obtained from bulk g-C₃N₄ by the liquid-phase exfoliation method in water,

isopropyl alcohol, and *N*-methylpyrrolidone and using ultrasound to accelerate the process.²⁰ Loading metal and metal oxide nanoparticles on the surface of g-C₃N₄ nanosheets not only can enhance their performances but also allows them to enrich the portfolio of applications with new applications.²¹ However, although the theoretical surface area of g-C₃N₄ nanosheets is large, the exfoliated g-C₃N₄ nanosheets would reaggregate in the aqueous solutions because of low surface energy, heavily limiting the application of g-C₃N₄ nanosheets in aqueous solution.²² Hence, it is greatly necessary to solve this issue to obtain advanced g-C₃N₄ nanosheet-based multifunctional materials for practical applications.

Recently, nanoparticles or nanosheets such as Pd,²³ TiO₂,²⁴ CdS,²⁵ and SnNb₂O₆²⁶ were mixed with g-C₃N₄ nanosheets to fabricate g-C₃N₄ nanosheet-based 0D/2D, 1D/2D, and 2D/

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Scheme 1. Synthesis of 3D Porous SMt/g-C₃N₄/Au NPs Heterostructures, Emphasizing the Three Main Processes, i.e., Granulation of Mt, Coating of g-C₃N₄, and Au NPs Loading

2D heterostructures. In addition to the improved stability of g-C₃N₄ nanosheets, the high performances of the obtained materials were worth noting because of the synergistic effects of the two components of hybrid nanomaterials. Compared with 0D/2D and 1D/2D nanomaterials, 2D/2D nanomaterials own a much larger surface area and more available catalytic active sites. For example, such a 2D/2D heterostructure was synthesized by Chen et al. via the mixing of SnNb₂O₆ nanosheets with g-C₃N₄ nanosheets. The resulting nanomaterial exhibited a good catalytic performance toward the degradation of MB.²⁷ However, compared with g-C₃N₄ nanosheets, the size of these nanosheets (nanosupports) is too small to wrap the g-C₃N₄ nanosheets. That is, a great amount of the g-C₃N₄ surface denudes in suspensions, which still have a great chance to link together, bringing a serious aggregation problem. Therefore, the selection of a suitable larger 2D substrate to support g-C₃N₄ nanosheets is a promising method to address this shortcoming.

Nanomaterials, such as carbon nanotubes and montmorillonite (Mt), can form spherical 3D structures through spray-drying technology.^{28–30} The fabricated 3D porous structures can not only maintain the intrinsic properties of nanomaterials but also endow the materials with new properties such as large surface area, good flowability, and self-sedimentary capability, which are much more suitable as catalytic supports. Here, a 3D Mt stacked granule was selected as a support for g-C₃N₄ nanosheets, followed by the in situ growth of gold nanoparticles (Au NPs) on their surface through polydopamine chemistry. Au was chosen here because of its excellent electron-transfer ability.³¹ The organic pollutants, i.e., MB, Congo red, and rhodamine 6G, were selected as model molecules to evaluate the catalytic activity of the obtained material. The effects of the concentration of the catalyst, reaction temperatures, and pH values on the catalytic activity were further investigated, and the possible mechanism of catalytic activities depending on the pH values was proposed. Furthermore, the recyclability and stability of the catalyst were investigated. This work proposes a facile and effective strategy for producing porous heterostructures for a wide range of applications in the environment and wastewater treatment.

2. MATERIALS AND METHODS

2.1. Materials and Chemicals. Montmorillonite [Mt; (Na,K,Ca)_{0.33}(Al_{1.67}Mg_{0.33})Si₄O₁₀(OH)₂·nH₂O], dicyandiamide, chloroauric acid (HAuCl₄), dopamine hydrochloride, and sodium borohydride (NaBH₄) were purchased from Sinopharm Chemical Reagent Shanghai Co. Ltd., China. Tris-HCl buffer was received from Solarbio Science and Technology Co., Ltd., China. The organic dyes, methylene blue (MB), Congo red (CR), and rhodamine 6G (R6G) were obtained from Tianjin Guangfu Reagent Co., China. All of the chemicals and reagents were used as received without any further purification.

2.2. Fabrication of 3D Porous Spherical Montmorillonite (SMt)-Supported g-C₃N₄/Au NPs Heterostructures. SMt was prepared using our previously reported method.²⁹ The synthesis of g-C₃N₄ nanosheets was performed via calcination and ultrasonication from dicyandiamide. Typically, 10 g of dicyandiamide was introduced into a muffle furnace, and the temperature was raised to 550 °C within 4 h. The organic was calcined at this temperature for 4 h to obtain bulk g-C₃N₄. Then, the cooled yellow bulk g-C₃N₄ was suspended in an aqueous/isopropyl alcohol (75/25 wt %) mixed solvent to obtain a suspension with a solid concentration of 5 mg·mL⁻¹. Then the suspension was subjected to an ultrasound treatment for at least 2 h using an ultrasonic cell disruptor at 25 °C to obtain a canary-yellow suspension. Pyridinedithioethylamine (PDA)-coated SMt prepared by our previously reported method²⁹ was introduced to the canary-yellow suspension to obtain a mixture with a PDA-coated SMt concentration of 20 g·L⁻¹. After being shaken for 6 h, the product (SMt/g-C₃N₄) was washed at least five times, respectively, with deionized (DI) water and DI water containing 25 wt % isopropyl alcohol. SMt/g-C₃N₄ was collected and dried at 60 °C in a vacuum oven for at least 12 h to a constant weight. Then SMt/g-C₃N₄ was coated with PDA, and the process was the same with PDA-coated SMt. Then PDA-coated SMt/g-C₃N₄ was added in an aqueous solution containing 50 nm HAuCl₄. In the dark, after rotating for 6 h, the product was washed and dried like for the SMt/g-C₃N₄ process above. For control, SMt/Au NPs catalysts were fabricated through a polydopamine chemistry method.²⁹

2.3. Characterization. Fourier transform infrared (FT-IR) spectra were performed on a Nicolet iS50 Fourier transform infrared spectrometer (Thermo Electron Corp., United States) using KBr disks. The crystal structures of the synthesized samples were measured by X-ray diffraction (XRD; Bruker D8, Germany) using Cu K α radiation. The surface composition was examined by X-ray photoelectron spectroscopy (XPS; Thermo Escalab 250Xi, United States) using Al K α excitation. The morphology was analyzed by transmission electron microscopy (TEM; JEM-2200, Japan), cold-field-emission scanning electron microscopy (SEM; Jeol S4800, Japan), and atomic force microscopy (AFM; Multi-Mode 8, Veeco, United States). The content of Au NPs was measured by inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC II, PerkinElmer, Ltd., Hong Kong). The textural properties and ζ potential were examined by nitrogen physisorption (ASAP2020, Micromeritics, United States) and a Malvern Zetasizer (Nano ZS90, London, England), respectively.

2.4. Evaluation of the Catalytic Performances. The catalytic performances were evaluated in the catalytic reduction of organic dyes, i.e., MB, CR, and R6G, in the presence of NaBH₄. The samples made of SMt/Au NPs (without g-C₃N₄ nanosheets) were for control. The calibration curves were drawn for each model pollutant based on at least five concentrations (Figure S1). In a typical catalytic process, 20 mg of a solid-state sample was added in 500 mL of an organic dye solution (50 mg·L⁻¹), and then 50 mL of an aqueous solution containing 0.1 M NaBH₄ was added. The catalytic performances were examined based on the concentration of organic molecules before and after reactions evaluated by UV-vis spectrophotometry (PERSEE UT 1810, China). For the recycle experiments, after the reduction process was finished, the samples were separated from the mixture because of

Figure 1. (a) SEM image of SMt. (b) SEM image of SMt coated with small g-C₃N₄ nanosheets. (c) SEM image of SMt/g-C₃N₄/Au NPs. (d) High-resolution TEM image of SMt//g-C₃N₄. Inset: TEM image of SMt/g-C₃N₄/Au NPs. (e and f) AFM image and corresponding thickness analysis of g-C₃N₄ nanosheets.

the self-sedimentary property and reused consecutively for the next cycle. All of the reactions were in the dark.

2.5. Determination of the Point of Zero Charge (pH_{zpc}).

Typically, SMt/g-C₃N₄/Au NPs samples were added to 10 mL of a 0.1 M NaCl aqueous solution to obtain a suspension with a solid concentration of 30 g·L⁻¹. After adjustment of the pH values to 3, 5, 7, 9, 10, and 11, respectively, the solution was fully mixed using an MX-RL-Pro rotator at a speed of 50 rpm for 24 h. Two data graphs were drawn to understand the pH_{zpc}.

2.6. Adsorption Experiment. A total of 20 mg of samples was added to a 100 mL aqueous solution containing 25 mg·L⁻¹ organic dyes. The UV-vis absorption spectra at different intervals were recorded to monitor the whole process. The removal percentage (*R*)

was obtained from the equation $R = (C_0 - C_t)/C_0 \times 100\%$, where *C*₀ and *C*_{*t*} are the initial dye concentration and concentration of the reaction time, respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis of 3D Porous SMt/g-C₃N₄/Au NPs Heterostructures. The main steps involved in the synthesis of 3D porous SMt/g-C₃N₄/Au NPs heterostructures are illustratively depicted in Scheme 1. First, the 2D Mt was dispersed in an ethanol solution, followed by a spray-drying technique to obtain a spherical 3D porous structure. Then, surface functionalization was performed with dopamine.

Figure 2. (a) FT-IR spectra and (b) XRD patterns of samples. (c) XPS spectrum of SMt/g-C₃N₄/Au NPs. Inset: High-resolution XPS spectrum of Au 4f. (d) N₂ adsorption–desorption isotherms of samples.

Basically, the dopamine polymerized, generating polydopamine, whose role was to coat the surface of SMt and provide additional sites for the adsorption and reduction of g-C₃N₄ and HAuCl₄, respectively.^{32–34}

3.2. Morphological and Structural Studies. A controllable morphology with an improved regularity and particle size upon granulation is important for a reproducible surface functionalization and catalytic performance but also ensures an enhanced capability of recovery and reuse, as compared with the amorphous and nanosized pristine Mt.²⁹ The morphology of the samples was analyzed by SEM (Figure 1a–c), TEM (Figure 1d), and AFM (Figure 1e,f). Parts a–c of Figure 1 display the SEM images of the granulated Mt (SMt), SMt wrapped with small g-C₃N₄ nanosheets (SMt/g-C₃N₄), and Au NPs loaded onto the surface of SMt/g-C₃N₄ through PDA chemistry (SMt/g-C₃N₄/Au NPs). It can be seen that these particles with sizes of about 20 μm display similar spherical morphologies irrespective of the applied treatment. However, the surface of the particles shows several differences as a result of the treatment. Therefore, SMt displays a uniformly rough surface, whereas the PDA-modified SMt/g-C₃N₄ surface presents multiple laminations because of the deposition of tiny exfoliated g-C₃N₄ nanosheets on the external surface. Parts d and e of Figure 1 show the TEM image of SMt/g-C₃N₄ nanosheets and AFM image of g-C₃N₄ nanosheets, respectively. The TEM image shows close contact between g-C₃N₄ nanosheets and SMt, which is well consistent with the results of SEM. As observed from measurement of the AFM image (Figure 1f), the thickness of the g-C₃N₄ nanosheets is about 1.5 nm. The black spots with a size of about 80 nm observed in the TEM image of SMt/g-C₃N₄/Au NPs heterostructures are assigned to the Au NPs (inset of Figure 1d).

The chemical structures of SMt, g-C₃N₄ nanosheets, PDA-modified SMt, SMt coated with g-C₃N₄ nanosheets, and SMt/

g-C₃N₄/Au NPs were analyzed by FT-IR, as shown in Figure 2a. The spectrum of g-C₃N₄ nanosheets displays a large band between 3000 and 3500 cm⁻¹, which is assigned to the typical stretches of N–H.²⁰ The band at 2150 cm⁻¹ is characteristic of the stretching vibration of cyano terminal groups. The vibrational bands located between 900 and 1700 cm⁻¹ are ascribed to the s-triazine derivatives.¹² Clearly, these typical g-C₃N₄ peaks can be observed in the spectra of g-C₃N₄-modified SMt samples, suggesting the good wrapping of g-C₃N₄ nanosheets on the surface of SMt. In addition, the FT-IR spectrum of SMt/g-C₃N₄/Au NPs is very similar to that of SMt/g-C₃N₄, indicating preservation of the SMt/g-C₃N₄ structure after in situ growth of Au NPs on its surface. Furthermore, the wrapping of g-C₃N₄ nanosheets on PDA-modified SMt was confirmed by the ζ potential. The obtained values for SMt, PDA-modified SMt, g-C₃N₄, SMt/g-C₃N₄, and SMt/g-C₃N₄/Au NPs were –42.2, –38.4, –29.2, –30.3, and –8.9 mV, respectively. The ζ potential of SMt/g-C₃N₄ is very similar to that of g-C₃N₄, strongly demonstrating the coating of SMt with g-C₃N₄ nanosheets.

The samples were further analyzed by XRD, XPS, and N₂ adsorption to assess their crystalline phases, surface chemical composition, and texture, respectively. Figure 2b illustrates the XRD patterns of the samples. The diffractogram of g-C₃N₄ displays a strong typical diffraction peak at 27.7°. The XRD pattern of SMt/g-C₃N₄/Au NPs display, in addition to the peaks of Mt and g-C₃N₄, four new peaks at 38.1°, 44.4°, 64.4°, and 77.8°, corresponding to the (111), (200), (220), and (311) planes, respectively, of Au(0) (JCPDS 04-784).²⁹ Remarkably, the intensity of g-C₃N₄ is decreased as a result of the exfoliation process. The surface chemical composition and oxidation states of elements in the SMt/g-C₃N₄/Au NPs heterostructure were analyzed by XPS, as shown in Figure 2c. The XPS survey spectrum exhibits the peaks corresponding to

C, Si, N, O, Al, Mg, and Au, in well agreement with the chemical composition of bulk SMt/g-C₃N₄/Au NPs heterostructures. As shown in the inset of Figure 1c, the high-resolution XPS spectrum of Au 4f displays two peaks at 84.3 and 87.8 eV, which correspond to the binding energy of Au 4f_{7/2} and Au 4f_{5/2} of Au(0), confirming the existence of this element on the surface of the synthesized SMt/g-C₃N₄/Au NPs heterostructure.^{9,34} The Au content was calculated as 2.7 wt % by ICP-MS, which is similar to the result reported otherwise.³⁴ Considering the size of Au NPs and the quite homogeneous dispersion on the surface of the composite (Figure 1c), this content is enough for the catalytic reduction of organic pollutants in wastewater. The pore structure and specific surface area were analyzed by N₂ adsorption. As shown in Figure 2d, all of the samples exhibit isotherms of type IV with hysteresis of type IIB typical for slitlike mesopores. Compared with pristine Mt (Figure S3), the SMt, SMt/g-C₃N₄, and SMt/g-C₃N₄/Au NPs samples showed a significantly increased pore volume and specific surface area (Table 1).

Table 1. Mesoscale Properties of Mt, SMt, SMt/g-C₃N₄, and SMt/g-C₃N₄/Au NPs

sample	BET surface area (m ² ·g ⁻¹)	pore volume (cm ³ ·g ⁻¹)
Mt	7.9	0.10
SMt	60.2	0.36
SMt/g-C ₃ N ₄	60.5	0.26
SMt/g-C ₃ N ₄ /Au NPs	52.1	0.22

Above all, the stable structure of fabricated SMt/g-C₃N₄/Au NPs via polydopamine chemistry can effectively enhance the electron-transfer capacity of Au NPs due to an increase in the

local electron concentration through electron transfer from the g-C₃N₄ nanosheets to Au NPs. Furthermore, the strong adsorption capacity of porous SMt and π - π electron interaction of g-C₃N₄ nanosheets with organic dyes containing a benzene ring can significantly enhance the concentration of organic pollutant near the Au NPs, facilitating the uptake of electrons via organic pollutant. Hence, our synthesized SMt/g-C₃N₄/Au NPs heterostructures possess the character of abundant active sites, large specific surface area, and adsorption ability, indicating great potential in the fast catalytic reduction of organic pollution in wastewater.

3.3. Catalytic Properties of 3D Porous SMt/g-C₃N₄/Au NPs Heterostructures.

Au NPs supported on a conducting or semiconducting substrate can rapidly transfer electrons, which is significantly important for chemical catalytic reduction of organic pollutants in wastewater.⁹ Herein, g-C₃N₄, a semiconducting material, was coated on PDA-modified SMt and used to load Au NPs. The high catalytic performance of the prepared heterostructure was first assessed in the degradation of several pollutants, among them, MB, an organic pollutant with strong carcinogenicity. A very low concentration of MB in aqueous solution can alter the refractive index, greatly influencing the physiological activity of aquatic creatures.³⁵ The catalytic reduction of MB in water was investigated using NaBH₄ as a reduction agent. As shown in Figure 3a, the absorption peak of MB is placed at 665 nm. After 1 min of reaction, the intensity of the peak decreased, and this decrease continued as the time was prolonged, so that no absorption was noticed after 5 min of reaction. As illustrated in Figure S4, the color of the MB solution changed from bright blue to colorless with the reaction time, indicating the catalytic reduction of carcinogenic MB to an inactive form, leuco-methylene blue (LMB).^{28,36} The reaction rates of all three

Figure 3. (a–c) Time-resolved UV–vis spectra of organic dyes. (d) Plot of $\ln(C_t/C_0)$ versus reaction time for the catalytic reduction of organic dyes. Reaction conditions: initial concentrations of organic dye (25 mg·L⁻¹), NaBH₄ (0.05 M), and SMt/g-C₃N₄/Au NPs (200 mg·L⁻¹), pH 7, *T* = 25 °C.

Figure 4. Effect of the (a) SMT/g-C₃N₄/Au NPs concentration, (b) reaction temperature, and (c) pH values on the catalytic performance. (d) Time-resolved UV-vis spectra of MB organic dye. Reaction conditions: 25 mg·L⁻¹ MB, 250 mg·L⁻¹ SMT/g-C₃N₄/Au NPs, pH 11, and temperature 35 °C.

reduction reactions were obtained from the kinetic equation $\ln(C_t/C_0) = k_{app}t$ (Figure 3d), where the concentration of C was obtained from the corresponding calibration curves (Figure S1).³⁷ The reaction rate, k_{app} , is the slope of $\ln(C_t/C_0)$ and the time t curve. Good linearity was obtained for all three catalytic reactions, which implies pseudo-first-order kinetics. The experiment without SMT/g-C₃N₄/Au NPs heterostructures was carried out to highlight the catalytic role of the material. As shown in Figure S5, the absorbance of MB at 665 nm is almost unchanged. Besides, the experiments of SMT/g-C₃N₄ heterostructures without Au NPs and only SMT were for control. As shown in Figures S6 and S7, after reactions of 5 and 6 min, the absorbance value slightly decreased from 1.6 to 1.5 and from 1.5 to 1.4 for SMT/g-C₃N₄ heterostructures and SMT, respectively. An obvious peak at 665 nm can be observed.

To prove the significant role of g-C₃N₄ nanosheets in the catalytic process, Au NPs-supported SMT (Au NPs concentration, 19.8 wt %) without g-C₃N₄ nanosheets was prepared and used as a control. As shown in Figures S8 and S9, the catalytic reduction toward MB required 8 min to complete and the k_{app} value was as low as 0.29 min⁻¹. Considering the high Au NPs concentration of the SMT/Au NPs catalyst, about 8 times higher than SMT/g-C₃N₄/Au NPs heterostructures, it can be affirmed that the heterostructures containing g-C₃N₄ nanosheets exhibited a much higher catalytic activity toward the MB model organic dye. It can be assumed that the high catalytic activity is significantly influenced by the g-C₃N₄ nanosheets. The g-C₃N₄ nanosheets can adsorb organic dyes containing a benzene ring via π - π electron interactions.

Furthermore, electron transfer from the g-C₃N₄ nanosheets to Au NPs occurs, increasing the local electron density for a facile uptake of electrons by the organic pollutants.¹³ These results demonstrate that the SMT/g-C₃N₄/Au NPs heterostructures can indeed effectively catalyze the reduction of MB in the presence of NaBH₄.

Other organic pollutants, CR and R6G, were selected to highlight the catalytic universality of the SMT/g-C₃N₄/Au NPs heterostructures. As shown in Figure 3b,c, the absorption peaks at 510 and 526 nm, corresponding to CR and R6G, respectively, both decreased within 4 and 6 min, respectively, in the presence of the catalyst and NaBH₄.

Moreover, the effects of the concentration of catalyst, reaction temperature, and pH on the catalytic activities toward MB were investigated. As shown in Figure 4a, the k_{app} value of the MB reduction in the presence of SMT/g-C₃N₄/Au NPs was linearly increased from 0.266 to 1.652 min⁻¹ as the solid concentration increased from 140 to 320 mg·L⁻¹. Considered in our experiment, NaBH₄ is excessive, and the increased K can be attributed to the increased catalytic area for electron transfer from NaBH₄ to MB. The influence of the reaction temperature on k_{app} is depicted in Figure 4b. The value of k_{app} increased from 0.52 to 0.81 min⁻¹ as the temperature increased from 18 to 35 °C.

The influence of the pH value on the reaction rates is depicted in Figure 4c. As was already discussed above, the degradation of organic dyes is based on electron transfer from the electron donor (NaBH₄) to the electron acceptor (organic dyes) using a catalyst as a "relay". However, this process is strongly influenced by the pH. According to the empirical

formula, $\log t_{1/2} = \text{pH} - (0.034T - 1.92)$, where $t_{1/2}$ is the half-life and T is the reaction temperature (expressed in Kelvin), the half-life of self-hydrolysis of NaBH_4 in water increases from 0.36 s to 430 days as the pH value increases from 6 to 14.³⁸ Although the catalytic process is ended within a few minutes, a too fast self-hydrolysis of NaBH_4 at low pH requires a high concentration of electron donor. Hence, the range of pH from 6 to 11 was selected for this work. As shown in Figure 4c, the value of k_{app} greatly increased from 0.52 to 5.91 min^{-1} as the pH value changed from 6 to 11. The experiments using $\text{SMt/g-C}_3\text{N}_4$ without Au NPs at different pH values were carried out for control. As shown in Figure S10, after reaction for 5 min, the absorbance value decreased from 1.4 to 1.0 for $\text{SMt/g-C}_3\text{N}_4$ heterostructures at pH 11, which is similar to the result at pH 7 (Figure S6). This result demonstrates that there is no change in the catalytic activity of $\text{SMt/g-C}_3\text{N}_4$ under different pH values. All of these results revealed that the catalytic performance can be enhanced by controlling the concentration of $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs heterostructures, reaction temperature, and pH value. As shown in Figure 4d, the catalytic process can be finished within 30 s and k_{app} can reach 5.91 min^{-1} at a catalyst concentration of $250 \text{ mg}\cdot\text{L}^{-1}$, a pH value of 11, and a temperature of 35°C , which is much higher than those reported for other systems, e.g., Au-based catalyst (1.05 min^{-1} for SMt and 1.80 min^{-1} for Fe_3O_4 and MgAlCe-LDH , respectively; Table 2).^{29,39,40} In

Table 2. Comparison of the Catalytic Performances of $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs with Other Catalysts Reported in the Literature

catalyst	k_{app} (min^{-1})	ref
$\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs	5.91	this work
SMt/Au NPs	1.05	29
$\text{Fe}_3\text{O}_4/\text{Au}$ NPs	1.80	39
MgAlCe-LDH/Au NPs	1.80	40

addition, the TOF of the $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs heterostructures toward MB degradation was calculated as 302 h^{-1} , according to the moles of MB catalytically reduced per mole of Au NPs, which is also much higher than that reported for SMt (13.2 h^{-1}) and Fe_3O_4 (115 h^{-1}), demonstrating the high catalytic performance of the synthesized 3D $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs heterostructures.^{29,39}

3.4. Proposed Mechanism of the Catalytic Reaction Depending on the pH. The influence of the pH value on

k_{app} is much greater than that of other parameters, which is supported by the considerable increase in k_{app} as the pH increased from 6 to 11. To understand the reaction mechanism at the molecular level, depending on the pH, MB reduction was selected as the model reaction. The catalytic reduction of MB was performed in the presence of NaBH_4 and a Au-based catalyst. It is well-known that the catalytic activity strongly depends on the number of active sites, that is, Au NPs. Under acidic or neutral conditions, Au ions can remain stable. However, Au NPs would release Au ions under alkaline conditions, which would locate near the surface of Au NPs.⁴¹ ICP-MS was employed here to detect the release of Au ions in the solution at different pH values. The concentration of the Au ion at pH 7 is 3 ppb, and the values were almost unchanged with increased pH values. On the other hand, the pH value would affect the adsorption behavior by changes of the charge density of the adsorbent and protonation state in the aqueous solution.¹⁶ As shown in Figure S11, the removal percentages (R) of $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs heterostructures toward MB increased from 6% to 59% as the pH value increased from 4 to 11. It is worth noting that R increased under alkaline conditions. Hence, the pH_{zpc} was detected to reveal the dependence between the pH and adsorption profile.⁴² From Figure 5, the pH_{zpc} is known as 7.02. At a solution pH value higher than 7.02, the surface of the $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs heterostructures is negatively charged and strong electrostatic attraction would happen with a cationic dye, such as MB.^{43,44} Thus, a higher adsorption value was obtained at the high pH value. The high concentration of organic dyes near the heterostructures facilitates electron transfer from NaBH_4 to organic dyes, leading to a remarkable increase in the apparent reduction rate constant (k_{app}). For example, as shown in Figure S12, the blue color of the MB solution rapidly condenses the surface of the $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs heterostructures within 3 s and then instantaneously vanishes within 9 s. The proposed mechanism of the catalytic reaction rate dependent on the pH values is shown in Figure 6.

3.5. Recyclability. Developing cost-effective catalysts is highly desirable for real applications. However, the cost of a catalyst is related to many factors, among them, the recyclability. To examine the ability of the prepared catalyst to be used for several cycles consecutively, the reduction of MB in the presence of $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs was performed for 10 cycles (Figure 7a). As can be seen, after 10 successive cycles, k_{app} still remains above 90%. This performance can be explained by the stability of Au NPs and $\text{g-C}_3\text{N}_4$ nanosheets

Figure 5. pH_{zpc} determination of the $\text{SMt/g-C}_3\text{N}_4/\text{Au}$ NPs heterostructures by two different plots.

Figure 6. Proposed mechanism of the catalytic reduction of MB at low and high pH values.

Figure 7. (a) Recyclability of SMt/g-C₃N₄/Au NPs in the reduction of MB. (b) SEM image of SMt/g-C₃N₄/Au NPs. TEM images of (c) fresh and (d) SMt/g-C₃N₄/Au NPs heterostructures after 10 cycles.

on SMt due to the adhesion of polydopamine (Figure 7b–d). On the other hand, the 3D micro-sized heterostructures can be easily recovered from the mixture through the self-sedimentary property without any devices involved. Furthermore, the Au content of the catalysts after recycling 10 times was calculated by ICP-MS, and a value of 2.7 wt % was obtained, which is consistent with the result of fresh SMt/g-C₃N₄/Au NPs. All of

these results prove the excellent recyclability of the synthesized SMt/g-C₃N₄/Au NPs heterostructures.

3.6. Practical Application of Porous SMt/g-C₃N₄/Au NPs Heterostructures. Seawater from the Yellow Sea, Yantai, Shandong Province, China, was used to prove the feasibility of the prepared heterostructures for real applications. After the sand settled down at the bottom of the beaker, 10 mL of a MB aqueous solution (250 mg·L⁻¹) and 10 mL of a NaBH₄

Figure 8. Application of synthesized SMt/g-C₃N₄/Au NPs for catalytic reduction of MB in seawater. Reaction conditions: 25 mg·L⁻¹ MB, 200 mg·L⁻¹ SMt/g-C₃N₄/Au NPs heterostructures, 0.05 M NaBH₄, pH 7, *T* = 25 °C.

aqueous solution (0.5 M) were added to the clear seawater (80 mL). As shown in Figure 8, the bright-blue color of the mixture became light blue within 2 min, while the solution became colorless after 5 min. As can be seen, at the end of the reaction, the synthesized SMt/g-C₃N₄/Au NPs heterostructures had already settled down at the bottom of the vessel. Hence, these results prove the applicability of the synthesized heterostructures for the fast and efficient treatment of real wastewaters.

4. CONCLUSIONS

In conclusion, 3D porous SMt/g-C₃N₄/Au NPs heterostructures were synthesized using SMt as the substrate to support exfoliated g-C₃N₄ nanosheets and Au NPs through polydopamine chemistry. The synthesized SMt/g-C₃N₄/Au NPs heterostructures exhibited a universal catalytic activity toward three organic dyes—MB, CR, and R6G—under neutral pH and 25 °C. The catalytic rate would accelerate under alkaline conditions, high temperature, and high SMt/g-C₃N₄/Au NPs concentration. For example, the reaction rate was higher ($k_{\text{app}} = 5.91 \text{ min}^{-1}$) under alkaline conditions (pH 11), high temperature (35 °C), and high SMt/g-C₃N₄/Au NPs concentration (250 mg·L⁻¹). The influence of the pH value on the catalytic performance was systematically investigated. The reason can be attributed to the increased adsorption ability of SMt/g-C₃N₄/Au NPs heterostructures toward organic dyes for fast electron transfer from NaBH₄ to organic dyes. Furthermore, the synthesized 3D heterostructures proved to be stable and could be easily recovered and reused 10 times with almost unchanged k_{app} . Our strategy used herein to

prepare g-C₃N₄ nanosheets-based multifunctional materials with high catalytic performance may extend to other composite systems designed for catalytic applications in wastewater treatment, medical chemistry, and energy storage.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.0c01355>.

Calibration curves of organic dyes, photographs of synthesized samples, N₂ adsorption curve of Mt, time-resolved UV–vis spectra of MB catalyzed by SMt, SMt/g-C₃N₄, and SMt/Au NPs, plot of $\ln(C_t/C_0)$ versus reaction time, and photographs of catalytic processes (PDF)

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Notes

The authors declare no competing financial interest.

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