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Effect of mesoporous FA-SiO_2 extracted from fly ash on the structural and photocatalytic properties of g-C_3N_4-based materials

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Abstract: In order to explore high value-added utilization pathways of fly ash, the mesoporous structure of silica extracted from fly ash (FA-SiO_2) was utilized to restrict the dicyandiamide (DCDA) thermal condensation process. This produced chemically bonded interacting composite photocatalysts of FA-SiO_2 and graphitic carbon nitride (g-C_3N_4). Compared with the spherical silica prepared using tetraethyl orthosilicate (TEOS-SiO_2), the mesoporous structure of FA-SiO_2 allowed DCDA to react in a smaller space, which facilitated the transformation of DCDA to melamine by the thermal degradation kinetics of FA-SiO_2/DCDA. This ultimately boosted the formation of an N-atom-removed triazine ring structure and a multistage structure combining lumps and rods in the composite photocatalysts of g-C_3N_4 and FA-SiO_2, which led to a higher visible-light utilization efficiency, a suitable valence-band position, and the photocatalytic activity for methylene blue reaching 3.56 times that of g-C_3N_4. The findings indicate that mesoporous FA-SiO_2 has the potential to remove the structural and photocatalytic properties of g-C_3N_4-based materials.

Key words: Fly ash; FA-SiO_2; g-C_3N_4-based materials; The structural and photocatalytic properties

1 Introduction

Photocatalysis is regarded as a green technology for the treatment of pollutants such as dyes and antibiotics, and is crucial for improving the current growing environmental pollution problem (Weng et al., 2018; Momin et al., 2024). Graphite-phase carbon nitride (g-C_3N_4) has attracted extensive research due to a series of excellent properties such as low cost, easy preparation, chemical stability, and a moderate band gap (Wang et al., 2018; Niu et al., 2018). g-C_3N_4 is usually prepared by thermal polymerization with nitrogen-rich materials such as dicyandiamide, melamine, or urea (Kumar et al., 2023), which results in the g-C_3N_4 exhibiting serious agglomeration, low specific surface area, and fewer surface active sites, as well as easy complexation of photogenerated electron-hole pairs (Momin et al., 2024). These drawbacks inhibit the photocatalytic performance of g-C_3N_4 (Yan et al., 2009; Lan et al., 2016).

Various adjusted structures have been used to improve the photocatalytic performance of g-C_3N_4, such as elemental doping, construction of heterojunction structures and defect engineering (Yang et al., 2022; Cheng et al., 2022; Yu et al., 2023; Wang et al., 2023). g-C_3N_4 can effectively control the structure of g-C_3N_4, which affects its photocatalytic properties (He et al., 2024). Yu et al. obtained g-C_3N_4 with a porous structure, high surface area, more amino functional groups, and a more stable chemical bonding structure by controlling the synthesis temperature of precursors (Huang et al., 2024). Yuan et al. also synthesized g-C_3N_4 with different chemical structures by controlling the polymerization temperature (Yuan et al., 2015). Instead of changing the synthesis temperature, Wan et al. controlled the polymerization of g-C_3N_4 by means of the limiting effect of the pores in Y-type zeolite. The result was g-C_3N_4 with a con-

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trolled degree of polymerization, which exhibited different photoluminescence properties due to the confining effect of sub-nanometer-sized cages in the molecular sieves (Wan et al., 2018).

Regulating by means of mesoporous structure materials is a feasible concept for the polymerization process of g-C_3N_4 . At this stage of exploration, a variety of mesoporous materials have been used to regulate the polymerization process of g-C_3N_4, such as zeolite molecular sieves, MOFs, clays, and mesoporous SiO_2 (Nair et al., 2024; Zhao et al., 2018; Chen et al., 2020; Khan et al., 2023). Compared to other substrates, mesoporous SiO_2 offers UV-visible transparency and chemical stability. It has been shown that g-C_3N_4 prepared with mesoporous SiO_2 modulation exhibits excellent photocatalytic activity, which is attributable to its intrinsic structure and the quantum confinement effect (Wang et al., 2019).

Fly ash is a solid waste discharged from thermal power generation which has a large storage capacity, is difficult to handle, and causes extensive pollution of the ecological environment. So, finding a way to comprehensively utilize it is an attractive topic for research. For example, fly ash can be embedded in MnO_2 for more effective mineralization of bisphenol-A and sorption of congo red (Angaru et al., 2024). In addition, the main components of fly ash are SiO_2 and Al_2O_3, which are effective resources for the preparation of SiO_2, $Al(OH)_3$, and Al_2O_3. However, the porous SiO_2 extracted from fly ash is rarely used to regulate the structure and properties of g-C_3N_4, especially analyzed the reason for regulation by thorough thermodynamic analysis.

In this study, we prepared mesoporous SiO_2 from fly ash to regulate the synthesis process of g-C_3N_4. Mixtures of SiO_2 and DCDA were prepared by a simple hydrothermal method, and the composite photocatalysts of SiO_2 and g-C_3N_4 were then calcined. We investigated the structure and performance of the photocatalysts by characterization methods such as FT-IR, XRD, SEM, and XPS. We also looked at the effects of different SiO_2 structures on the polymerization process of g-C_3N_4 during thermal decomposition by non-isothermal kinetic analysis.

2 Experimental section

2.1 Materials

The chemical reagents used in the experiment were of analytical grade. The tetraethyl orthosilicate (98%), Sodium carbonate (99.5%) and Dicyandiamide (99%) were produced by Shanghai Aladdin. The fly ash was produced by Huainan Mining Group Coal Preparation.

2.2 Silicon dioxide preparation

Silicon dioxide prepared from fly ash (the structural characterization is shown in Fig. S1): Sodium carbonate (10 g) and fly ash (10 g) were mixed, and then heated to 850 ℃ at an elevated rate of 10 ℃/min and held for 2h. The sinter was cooled naturally to room temperature and then ground into powder. The powder (5 g) was added to 40mL of 3 mol/L hydrochloric acid and stirred for half an hour, then centrifuged into the mixture. It was placed in a reaction vessel at 100℃ for 24h. The colloid was obtained and washed to neutral. Finally, it was freeze-dried to produce the powdered material, which was recorded as FA-SiO_2.

Silicon dioxide prepared from tetraethyl orthosilicate: Ethanol (50 mL), ammonia (10 mL, 25%), and 20 mL of deionized water were mixed at 35 ℃. The tetraethyl orthosilicate (5 mL) was added and stirred for 2 h. After centrifugation, the powder was washed with ethanol and dried at 60 ℃ to obtain a white powder, which was recorded as TEOS-SiO_2.

2.3 Preparation of silicon dioxide and dicyandiamide composite precursor

Dicyandiamide (2.5 g) was added to 25ml of deionized water and stirred to dissolve at 70 ℃. Silicon dioxide (0.5 g) was added, then stirred for 2h. The obtained mixed liquid was placed in a room-temperature environment until crystallization occurred, and then filtered and dried to produce the precursor. The precursor obtained by crystallization of TEOS-SiO_2 and dicyandiamide was recorded as TEOS-SiO_2/DCDA, and the precursor obtained by crystallization of FA-SiO_2 and dicyandiamide was recorded as FA-SiO_2/DCDA.

2.4 Preparation of g-C_3N_4-based composite photocatalysts

The above-described precursors TEOS-SiO_2/DCDA and FA-SiO_2/DCDA were heated to 550 ℃ in N_2 atmosphere at a heating rate of 2.5 ℃/min and held for 4 h. The precursors were

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naturally cooled to room temperature and preserved by milling, and the resulting substances were recorded as TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4, respectively.

3 Results and Discussion

3.1 Structural study of silicon dioxide

Figs. S2 and S3 show the FTIR, XRD, and SEM spectra of silicon dioxide. It can be seen that the peak intensity and position of FA-SiO_2 remain basically the same compared to TEOS-SiO_2, implying successful extraction of FA-SiO_2 from fly ash (Kantor et al., 2022; Han et al., 2019; Du et al., 2018; Liu et al., 2019). The FA-SiO_2 exhibits a blocky structure made up of a combination of fine particles, which is different from the spherical shape of TEOS-SiO_2 (Fig. S3). As shown in Fig. 1, the specific surface area of FA-SiO_2 is 703.02 m^2/g, the average pore size is 4.99 nm, and the pore volume is 0.8135 cm^3/g. Unlike nonporous TEOS-SiO_2, the pore structure of FA-SiO_2 may limit the polymerization reaction of DCDA when used in FA-SiO_2/DCDA.

3.2 Structural study of the composite precursors of silicon dioxide and dicyandiamide

The structure of a precursor can affect the structure of the photocatalyst and subsequently catalytic performance, so it was important to investigate this aspect. Fig. 2a shows the FT-IR spectra of DCDA, TEOS-SiO_2/DCDA, and FA-SiO_2/DCDA. It is evident that TEOS-SiO_2/DCDA and FA-SiO_2/DCDA have similar infrared absorption spectra to DCDA, indicating that the basic structure of DCDA was preserved. TEOS-SiO_2/DCDA and FA-SiO_2/DCDA have new absorption peaks at 1090 cm^{-1} and 1074 cm^{-1}, which we attribute to the asymmetric stretching vibrational peak of Si-O-Si. This suggests the presence of a complex of SiO_2 and DCDA in the precursor. It is noteworthy that the absorption peak in TEOS-SiO_2/DCDA at 1090 cm^{-1} is significantly stronger than that of FA-SiO_2/DCDA at 1074 cm^{-1}, which could be attributed to the fact that DCDA is encapsulated on the surface of FA-SiO_2 during the crystallization process, making the vibrational peak of Si-O-Si difficult to discern. In addition, the peak of Si-O-Si in FA-SiO_2/DCDA appears at 1074 cm^{-1}, while the peak of Si-O-Si in FA-SiO_2 appears at 1091 cm^{-1} (Fig. S1a), which is slightly blueshifted compared to FA-SiO_2. The peak position of Si-O-Si in TEOS-SiO_2/DCDA remains basically the same as that of TEOS- SiO_2 (Fig. S1a). This may be due to the fact that FA-SiO_2 has a high specific surface area and pore volume, which causes interaction between DCDA and the skeleton structure of FA-SiO_2 during the crystallization process. Subsequently, internal stress is generated in the skeleton structure of FA-SiO_2, leading to a change in the atomic arrangement between DCDA and FA-SiO_2, and consequently to a change in the lattice constants of the complex, resulting in a slight blue shift in the peak position of Si-O-Si in TEOS-SiO_2/DCDA (Jia et al., 2023).

We examined the crystal structure of the precursor with XRD. As can be seen in Fig. 2b, the diffraction peaks of DCDA appear in both TEOS-SiO_2/DCDA and FA-SiO_2/DCDA, and the peak positions of the diffraction peaks are basically the same as that of DCDA, but there is a change in the intensity of the peaks. This suggests that the presence of SiO_2 affects the crystallinity of DCDA, and that TEOS-SiO_2 and FA-SiO_2 change the priority of surface crystal growth of dicyandiamide in the process of recrystallization.

Fig. 3 shows the SEM images of DCDA, TEOS-SiO_2/DCDA, and FA-SiO_2/DCDA. As shown in Fig. 3a, DCDA exhibits blocky aggregation. The microstructure of DCDA changed after it was compounded with TEOS-SiO_2 and FA-SiO_2. As shown in Fig. 3b, TEOS-SiO_2 particles with uniform particle size are stacked together, and DCDA filled in the pore structure formed by this particle stacking. Aggregation of fine particles was observed in FA-SiO_2/DCDA (Fig. 3c), which is consistent with the results shown in Fig. 3b, where the particles have infiltrated DCDA, indicating that an effective composite of FA-SiO_2 and DCDA has formed.

3.3 Structural study of composite photocatalysts

Fig. 4a shows the FTIR spectra of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4. For g-C_3N_4, the strong peak at 808 cm^{-1} is the out-of-plane bending vibration peak of the triazine ring in the g-C_3N_4 structure. The peaks in the region of 1200-1700 cm^{-1} correspond to the stretching vibrations of aromatic C-N and C=N inside and outside of the triazine ring in the g-C_3N_4 layer, and the broad peaks in the region of

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3100-3500 cm^{-1} are related to the terminal amino group of g-C_3N_4 vibrations (Meng et al., 2022; Zhang et al., 2018). Compared to pristine g-C_3N_4, the vibrational peaks of TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4 at 3100~3500 cm^{-1} are weak, indicating a decrease in the number of amines. The absorption peak of Si-O-Si in FA-SiO_2/g-C_3N_4 appeared at 1079 cm^{-1}, whereas the peak appeared at 1091 cm^{-1} for FA-SiO_2 (Fig. S1a) and was slightly blue-shifted. We attribute this to the interaction between FA-SiO_2 and g-C_3N_4 within the pore structure, which resulted in a change in the lattice constants of FA-SiO_2/g-C_3N_4 and led to the blue-shifted absorption peak of Si-O-Si, which was consistent with that of the precursor (Fig. 2a). The Si-O-Si absorption peak of TEOS-SiO_2/g-C_3N_4 appeared at 1090 cm^{-1}, and did not change significantly compared to the peak position of Si-O-Si in TEOS-SiO_2 (Fig. 2a). This could be attributed to the fact that the pore formed by the accumulation of TEOS-SiO_2 particles was too large to have a limiting effect on g-C_3N_4 polymerization. Compared with TEOS-SiO_2/g-C_3N_4, the absorption peaks of FA-SiO_2/g-C_3N_4 at 1079 cm^{-1} and 468 cm^{-1} were weakened, which may be due to the fact that FA-SiO_2 has a larger specific surface area and pore volume. g-C_3N_4 was encapsulated on the surface of FA-SiO_2, which was more completely complexed with g-C_3N_4, thus weakening the vibrational peaks of Si-O-Si.

We analyzed the XRD spectra of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4. As shown in Fig. 4b, there are two distinct characteristic diffraction peaks at 13.1° and 27.4° for pure g-C_3N_4, which correspond to the (100) crystallographic plane of the triple-S-triazine unit planar structure and the (002) crystallographic plane of the interlayer stacked conjugated aromatic structure, respectively. For TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4, the broad peak at 15.0° to 25.0° and the characteristic diffraction peak at around 27° imply the existence of SiO_2 and g-C_3N_4 in the photocatalysts. It is worth noting that the characteristic peak at around 27° underwent a small leftward shift compared to pristine g-C_3N_4, indicating an improvement in the interlayer spacing of g-C_3N_4.

The surface chemical states of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 were analyzed by XPS. As shown in Fig. 5a, the elements C, N, and O were detected in g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4, while the element Si was also detected in TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4 (the content of each element is shown in Table S1).The elemental contents of C and N in FA-SiO_2/g-C_3N_4 were higher than in TEOS-SiO_2/g-C_3N_4, indicating that the content of g-C3N4 in FA-SiO_2/g-C_3N_4 was higher than in TEOS-SiO_2/g-C_3N_4, which might be due to the facts that the specific surface area and pore volume of FA-SiO_2 were higher than those of TEOS-SiO_2, and that more dicyandiamide was adsorbed within the pore structure during the preparation process, while the closed environment within the pores also favored the conversion of DCDA to g-C_3N_4.

Fig. 5b shows the C 1s spectrum of the photocatalyst. For g-C_3N_4, the C 1s spectrum can be deconvoluted into three peaks at 284.8 eV, 286.19 eV, and 288.12 eV. They correspond to the indeterminate carbon adsorbed on the surface of the photocatalyst, the C-NHx bond, and the N-C=N bond in the carbon-nitrogen heterocycle, respectively. The ratios of various chemical bonds containing C elements are given in Table 1, from which it can be determined that the content of N-C=N bonds in g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 increases sequentially. This may be caused by the restricted reaction space of DCDA (Fig. 3b,c). When FA-SiO_2 has a mesoporous structure, the polymerization reaction of DCDA occurs in a smaller space, and the more localized space restricts the polymerization of DCDA into the more triazinyl ring structure of g-C_3N_4. As shown in Fig. 5c, the N 1s spectrum of g-C_3N_4 contains three components located at 398.61 eV, 399.89 eV, and 400.98 eV, and the peak at 398.61 eV can be attributed to carbonitrides. We attribute the peak at 398.61 eV to C=N-C in the carbon-nitrogen heterocycle, the peak at 399.89 eV to N-$(C)_3$, and the peak at 400.98 eV to the amino functional group (C-N-H). The ratios of various chemical bonds containing N elements are given in Table 1. It is clear that the C=N-C content in TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4 is reduced in comparison to that in g-C_3N_4, which may be due to the removal of N atoms from the CN framework structure. This would be in agreement with the FTIR analysis (Fig. 4a). The synthesis pathway of the SiO_2 and g-C_3N_4 composites is shown in Fig. S4. The Si 2p spectra are shown in

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Fig. 5d: the Si 2p peaks of SiO_2 in TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4 appear at 104.08 eV and 103.92 eV, respectively. It is worth noting that a new Si 2p peak appears at 106.97 eV, which indicates that the chemical bonding between SiO_2 and g-C_3N_4 may have been established at the interface (Sun et al., 2021).

The microstructure and morphology of the three photocatalysts were investigated using SEM. The results showed that the microstructure of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 was very different. g-C_3N_4 had an obvious lamellar stacking structure (Fig. 6a). As seen in Fig. 6b, g-C_3N_4 filled in the pores formed by the stacking of TEOS-SiO_2 particles, consistent with the results observed in the precursor (Fig. 3b). A multistage structure combining lumps and rods was observed in FA-SiO_2/g-C_3N_4 (Fig. 6c). FA-SiO_2 has a large pore volume and mesoporous structure, which adsorbs DCDA during preparation of the precursor. The DCDA adsorbed within the pores releases ammonia during the polymerization process, resulting in extrusion of the g-C_3N_4 formed by polymerization within the pores. Thus, the unique nanoscale rod-like g-C_3N_4 structure is formed, which explains the blueshift of Si-O-Si absorption peaks. We observed this shift in the composite FA-SiO_2/g-C_3N_4 under infrared light when under the effect of stress. The nanorod-like structure of g-C_3N_4 in FA-SiO_2/g-C_3N_4 effectively increases its contact area with pollutants, which improves photocatalytic activity. The elements in FA-SiO_2/g-C_3N_4 were detected using an energy spectrometer (EDS) (Fig. 6d), which showed that the samples contained the elements C, N, O, and Si. This matched the XPS detection results (Fig. 5a), further proving that an effective composite of FA-SiO_2 and g-C_3N_4 was formed.

3.4 Thermal decomposition kinetics study

We investigated the effect of precursor structure on the structure of the composite catalysts using thermal decomposition kinetic analysis. The DCDA, TEOS-SiO_2/DCDA, and FA-SiO_2/DCDA were tested by thermal analysis at heating rates of 5, 15, and 25 ℃/min. The TG curves of the three precursors were similar at different heating rates, indicating that the thermal decomposition process of the three precursors was approximately the same, but that there were differences in the temperature-related changes of the three precursors at various stages. From Fig. 7a and d, it is evident that the heating process of DCDA can be divided into five stages. In order to investigate the effect of the introduction of TEOS-SiO_2 and FA-SiO_2 on the polymerization process of DCDA in the precursors, we processed and analyzed the thermal decomposition kinetic data for the second stage of the three different precursors.

The activation energy was determined by the Flynn-Wall-Ozawa method. Taking the conversion rate α as 0.1-0.9, we calculated the activation energy E of the three precursors. E represents the magnitude of the reaction resistance during the thermal condensation reaction of the precursors; the larger the resistance of the thermal condensation reaction, the larger the value of E. Compared with DCDA, E of the precursors TEOS-SiO_2/DCDA and FA-SiO_2/DCDA decreased (Fig. 8a), which could be attributed to the fact that the introduction of SiO_2 improves aggregation of DCDA in the unit space, and makes the reaction easier to carry out, facilitating the formation of the triazine ring. This would be in accord with the XPS analysis. With the increase of conversion α, the activation energy of TEOS-SiO_2/DCDA gradually rose higher than that of FA-SiO_2/DCDA. This might be related to the mesoporous structure of FA-SiO_2, which restricts the reaction of dicyandiamide in FA-SiO_2/DCDA and forces it to take place in a smaller space, fostering the conversion of dicyandiamide to melamine.

As shown in Fig. S4, the value of P(u)/P(0.5) was obtained by substituting the value of activation energy E into the formula. We searched for a curve of the mechanism function of the experimental response by plotting the P(u)/P(0.5)-α relationship and comparing it with the standard curve of G(α)/G(0.5)-α. Specifically, we looked at the degree of agreement of the scattering points with the theoretical curve. After comparative calculations, DCDA conformed to a mechanism function of $G(\alpha) = 1-(2\alpha)/3-(1-\alpha)2/3$ with a standard deviation of 0.26. Both TEOS-SiO_2/DCDA and FA-SiO_2/DCDA conformed to a mechanism function of $G(\alpha) = -\ln(1-\alpha)$ with standard deviations of 0.28 and 0.39, respectively.

The value of A can be calculated by substituting the calculated E value and the mechanism function into the formula, keeping in mind that $Y = \ln(E/\beta R) + \ln P(u)$ and $X = \ln G(\alpha)$, plotting the Y-X scatterplot,

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and linearly fitting the resulting data points with an intercept of -lnA. In this experiment there were three different values for the rate of warming β, which resulted in three different values of A. Fig. 8b depicts the relationship between the warming rate β and the finger front factor A for the three materials. The finger forward factor A is used to describe mutual collisions of atoms. The more intense the collisions, the larger the A value. In this experiment, the order of A values for the three precursors in descending order is: DCDA, TEOS-SiO_2/DCDA, and FA-SiO_2/DCDA. The introduction of SiO_2 alters the aggregation of DCDA, resulting in a decrease in the collision probability, and thus TEOS-SiO_2/DCDA and FA-SiO_2/DCDA have a lower finger prefactor A than does DCDA. In addition, FA-SiO_2/DCDA has a lower finger prefactor A than DCDA. The mesoporous structure of FA-SiO_2 in FA-SiO_2/DCDA makes DCDA react in a smaller space, and the particles are limited by the space. This reduces the collision probability, resulting in a lower A-value for FA-SiO_2/DCDA than or TEOS-SiO_2/DCDA.

3.5 Photocatalytic performance study

The photocatalytic performance of the three photocatalysts was evaluated by measuring the degradation rate of methylene blue (MB) solution under simulated visible light. As shown in Fig. 9a, the degradation rate of g-C_3N_4 was 12.8% under continuous irradiation for 60 min, and the degradation rates of TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4 under the same conditions were 18.9% and 37.3%. Their photocatalytic activity was 1.53 times and 3.56 times higher, respectively, than that of g-C_3N_4 (Fig. 9b). The enhanced photocatalytic performance of TEOS-SiO_2/g-C_3N_4 may be related to the removal of N atoms in the CN framework (Li et al., 2023). FA-SiO_2/g-C_3N_4 exhibited the best photocatalytic activity, which we attribute to the fact that not only was the chemical structure of FA-SiO_2/g-C_3N_4 improved, but also the mesoporous structure of FA-SiO_2. This caused the FA-SiO_2/g-C_3N_4 to form a more complex multilevel structure in terms of the microscopic morphology. The nanorod-like structure of g-C_3N_4 in FA-SiO_2/g-C_3N_4 can effectively increase the contact area with pollutants, which improves its photocatalytic activity. In addition, after 5 cycles of experiments, there was no significant change in the photocatalytic degradation efficiency (Fig. 9c).

To explore the photocatalytic remediation of methylene blue, we determined the LC-MS of MB (Figs. S6 and S7). Characteristic liquid-chromatography peaks caused by the original MB molecules can be observed in Fig. S6a, and correspond to the peaks at m/z 284 and 285 in the mass spectrum (Fig. S6b) (Gnaser et al., 2005). Multiple new substance peaks were observed in the liquid chromatogram of MB after photocatalytic degradation (Fig. S7a), indicating the presence of multiple MB degradation intermediates in the solution after the catalytic degradation reaction. Except for the peak located at the retention time of 3.65 min, the other peaks have small areas and low content, so further analysis was not necessary (Fig. S7b). Among them, the peak located at m/z 269.96 represents the intermediate product of MB molecule losing one CH_3, while the peak at m/z 256 originates from the intermediate product of MB molecule losing two CH_3 (bansode et al., 2017). Based on the above LCMS results, it can be concluded that MB molecules are degraded in the form of dihydroxylation.

Next, we measured the optical properties of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 composites by UV-Vis diffuse reflectance spectroscopy (DRS). As shown in Fig. 10a, g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 all have significant absorption in the visible region. The UV-visible diffuse reflectance spectra of TEOS-SiO_2/g-C_3N_4 are slightly blueshifted in comparison to the pristine g-C_3N_4, which suggests that the visible absorption becomes poorer, possibly due to the fact that the TEOS SiO_2/g-C_3N_4 has a thinner stacked layer of g-C_3N_4 (Attri et al., 2023). FA-SiO_2/g-C_3N_4, on the other hand, exhibits a redshift towards longer wavelengths, indicating that FA-SiO_2/g-C_3N_4 has higher visible-light utilization compared to g-C_3N_4, which could be attributed to the better internal light reflection arising from the interlaced rod-like and layered multilevel structure (Wang et al., 2023). This may improve photocatalytic performance as well. From the equations $\alpha h\nu = A (h\nu - Eg)^{1/2}$ and $Eg = 1240/\lambda$ (α, h, ν, Eg, A, and λ are the absorption coefficient, Planck's constant, optical frequency, bandgap energy, scaling factor, and wavelength, respectively), it can be calculated that the g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4

bandgap-energy values (Eg) are 2.81 eV, 2.83 eV, and 2.78 eV, respectively (Fig. 10b).

The potentials of the conduction band (CB) and valence band (VB) have a large influence on the catalytic performance of photocatalysts. The valence band potentials of the three photocatalysts were determined by UPS tests. As shown in Fig. 11a-c, the second cutoff edge potential (Ecut) of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 was 17.38, 15.69, and 15.62 eV, respectively, and the Fermi edge potential (EFM) was 1.94, 0.42, and 0.48 eV, respectively. According to the equation EVBE = hν -(Ecut - EFM) (where hν = 21.22 eV), the EVBE of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 was 5.78, 5.95, and 6.08 eV, respectively. 0 V vs RHE (Reversible Hydrogen Electrode) is equal to -4.44 eV vs Evac (Vacuum Energy Level). The VB edge potential of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 is 1.34, 1.51, and 1.64 eV, respectively. The variations in the TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4 valence band potentials could be attributed to the interaction between SiO_2 and g-C_3N_4. It makes the electron-cloud density of the N atom of g-C_3N_4 in TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4 decrease (Fig. 11c), which causes the valence band potential to change due to the variation of the local electric field. In addition, based on the equation ECB=EVB-Eg, the conduction band potentials of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 were obtained as -1.47, -1.32, and -1.14 eV, respectively. The energy-level structures of the three photocatalysts are shown in Fig. 11d. It is clear that the valence band of FA-SiO_2/g-C_3N_4 is in a more positive position, indicating that the oxidation performance due to photoexcitation is stronger than that of g-C_3N_4 or TEOS-SiO_2/g-C_3N_4, which is favorable for the catalytic degradation of MB (Zhang et al., 2020).

The electron transfer between FA-SiO_2 and g-C_3N_4 was important for photocatalytic activity. Transient photocurrent density responses are shown in Fig. 12a. The FA-SiO_2/g-C_3N_4 had the strongest light response. This may be due to the chemical bonding between SiO_2 and g-C_3N_4, which can effectively transfer the electrons between the two materials.

To investigate the active free radicals during photocatalysis, we used ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), benzoquinone (BQ), and isopropanol (IPA) as quenchers for holes (h^+), superoxide radicals ($\bullet O^{2-}$), and hydroxyl radicals (•OH), respectively. From Fig. 12b, one can see that H^+, $\bullet O^{2-}$, and •OH all participate in the catalytic degradation of MB. A comparison of the degradation rates shows that h^+ dominates the catalytic reaction process.

4 Conclusions

In this study, mesoporous FA-SiO_2 and spherical TEOS-SiO_2 were prepared to modulate the polymerization process of g-C_3N_4. The results show that both the mesoporous structure of FA-SiO_2 and the stacking pore structure of TEOS-SiO_2 improve the chemical structure of g-C_3N_4. FA-SiO_2/g-C_3N_4 forms a multilevel structure that combines blocks and rods because of the limiting effect of the mesoporous structure of FA-SiO_2, which improves visible-light utilization. We investigated the non-isothermal pyrolysis kinetics of different precursors in a nitrogen atmosphere by the TG-DTG method. The mesoporous structure of FA-SiO_2 allows the polymerization reaction of DCDA to occur in a smaller space, which is more favorable for the conversion of DCDA to g-C_3N_4. Photocatalytic experiments showed that the photocatalytic activity of TEOS-SiO_2/g-C_3N_4 and FA-SiO_2/g-C_3N_4 for methylene blue is 1.53 and 3.56 times higher than that of g-C_3N_4, respectively. Compared with TEOS-SiO_2/g-C_3N_4 and pristine g-C_3N_4, the correction of the valence band of FA-SiO_2/g-C_3N_4 leads to its stronger oxidizing ability and higher visible-light utilization efficiency. All of this leads to FA-SiO_2/g-C_3N_4 exhibiting the strongest photocatalytic ability.

Acknowledgments

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Author contributions

Qingbo YU designed the research. Xianhua LI processed the corresponding data. Qingbo YU wrote the first draft of the manuscript.

Conflict of interest

Xianhua LI and Qingbo YU declare that they have no conflict of interest.

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Electronic supplementary materials

Table S1, Figs. S1–S7

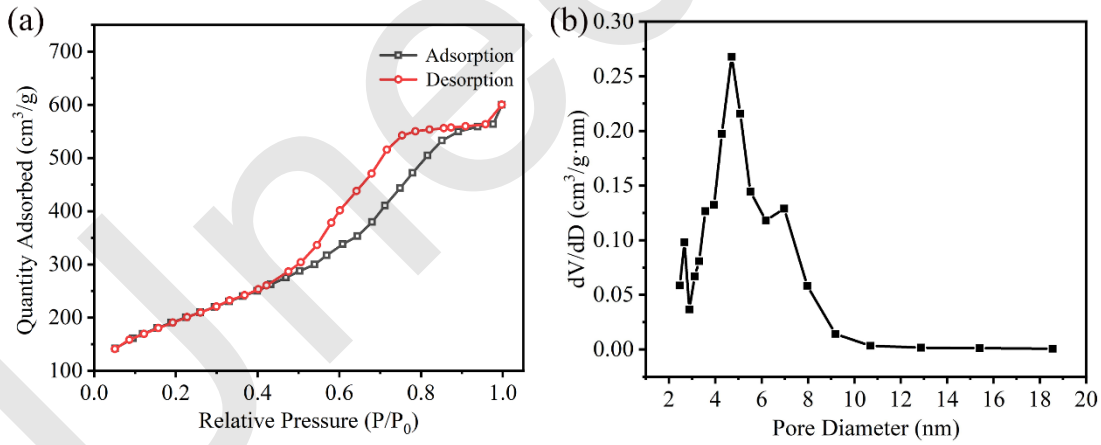

Fig. 1 (a) N_2 adsorption desorption isotherm of FA-SiO_2; (b) Aperture distribution curve.

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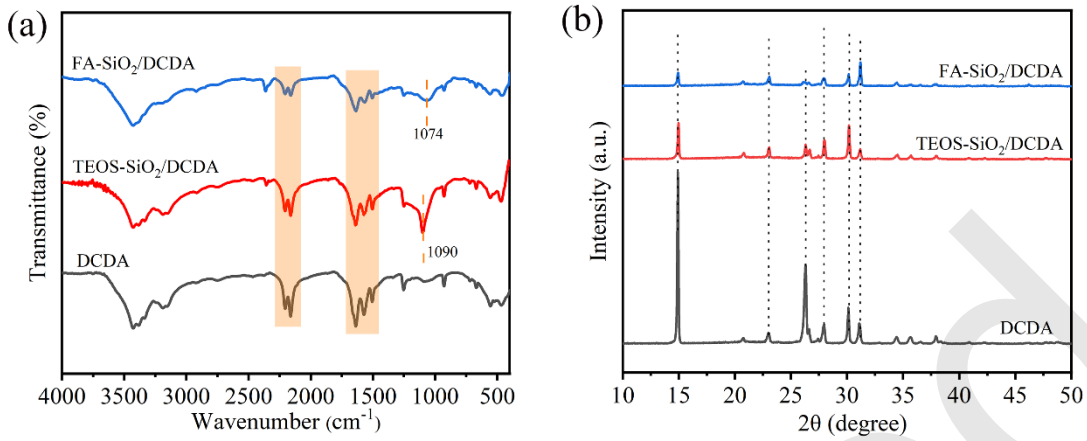

Fig. 2 (a) FT-IR spectra and (b) XRD spectra of DCDA, TEOS-SiO_2/DCDA, and FA-SiO_2/DCDA

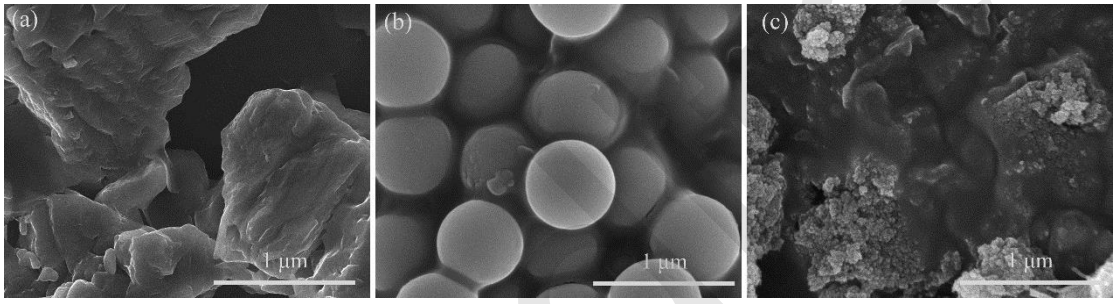

Fig. 3 SEM of (a) DCDA, (b) TEOS-SiO_2/DCDA, and (c) FA-SiO_2/DCDA

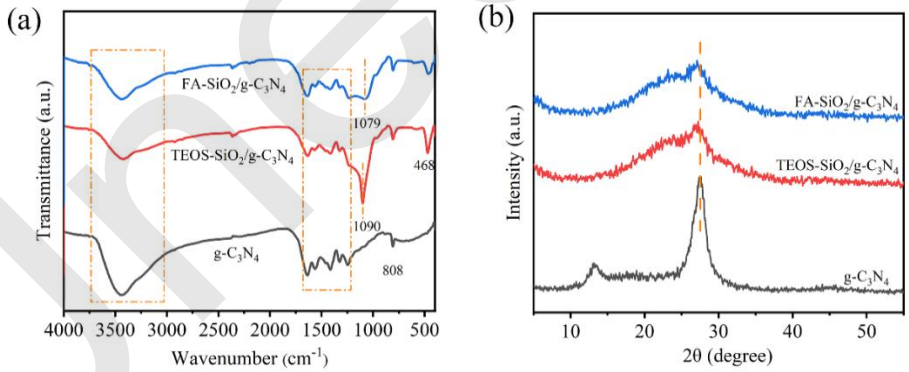

Fig. 4 (a) FT-IR and (b) XRD spectra of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4

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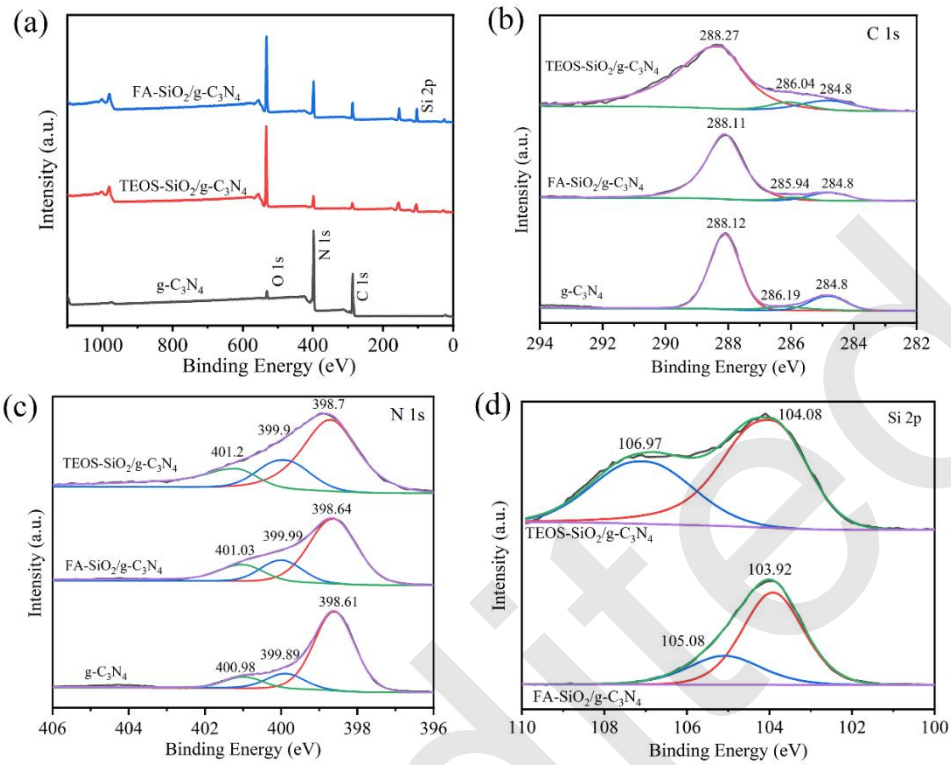

Fig. 5 (a) full XPS spectrum; high-resolution XPS spectrum of (b) C 1s, (c) N 1s, and (d) Si 2p picture of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4

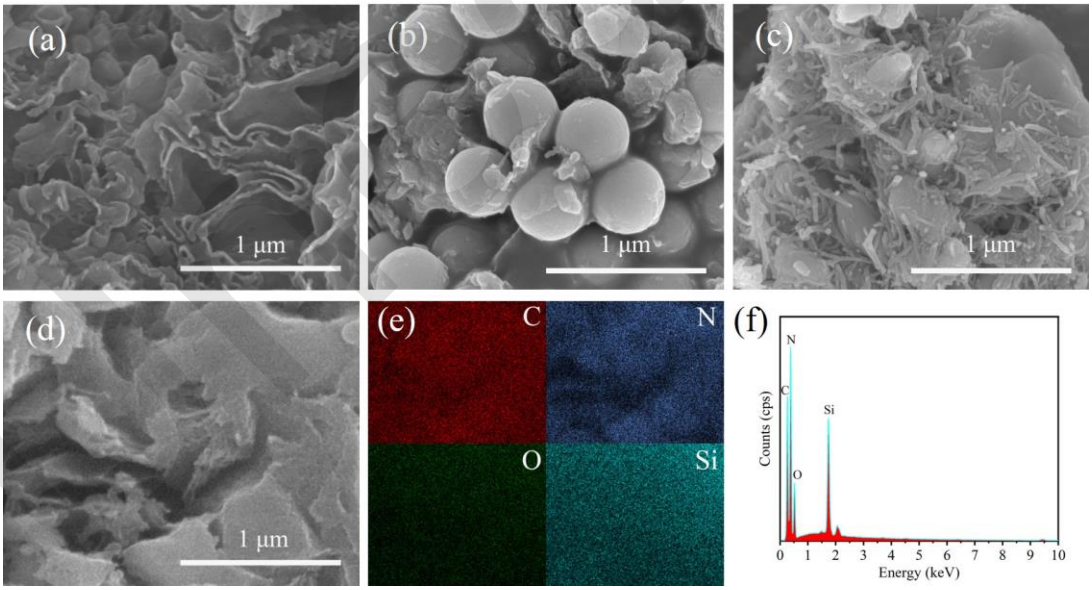

Fig. 6 SEM of (a) g-C_3N_4, (b) TEOS-SiO_2/g-C_3N_4, and (c) FA-SiO_2/g-C_3N_4; SEM image (d) and the corresponding elemental mapping (e) and EDS spectrum (f) of FA-SiO_2/g-C_3N_4

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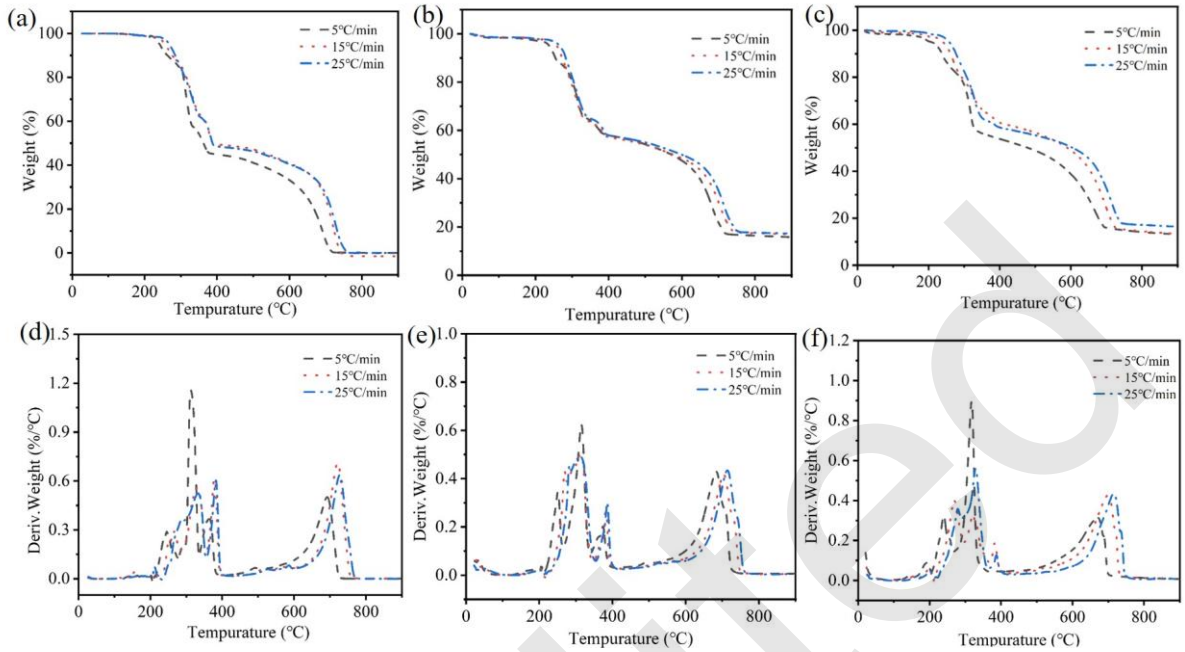

Fig. 7 TG curves of (a) DCDA, (b) TEOS-SiO_2/DCDA, and (c) FA-SiO_2/DCDA; DTG curve of (d) DCDA, (e) TEOS-SiO_2/DCDA, and (f) FA-SiO_2/DCDA.

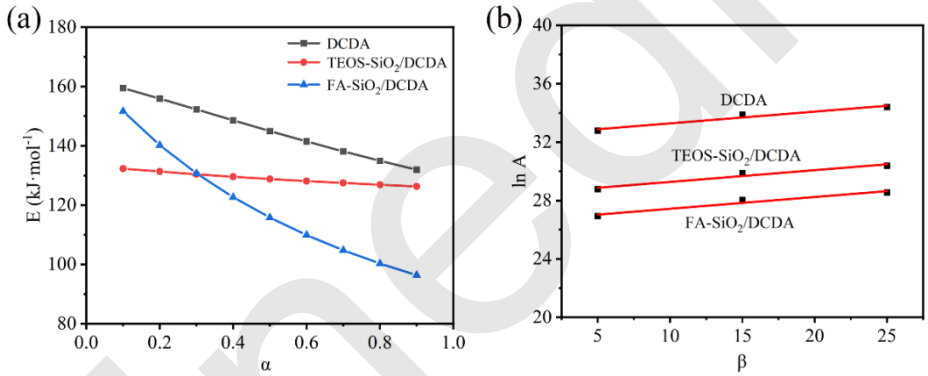

Fig. 8 (a) Relationship between conversion α and activation energy E and (b) Relationship between pre-exponential factor A and heating rate β.

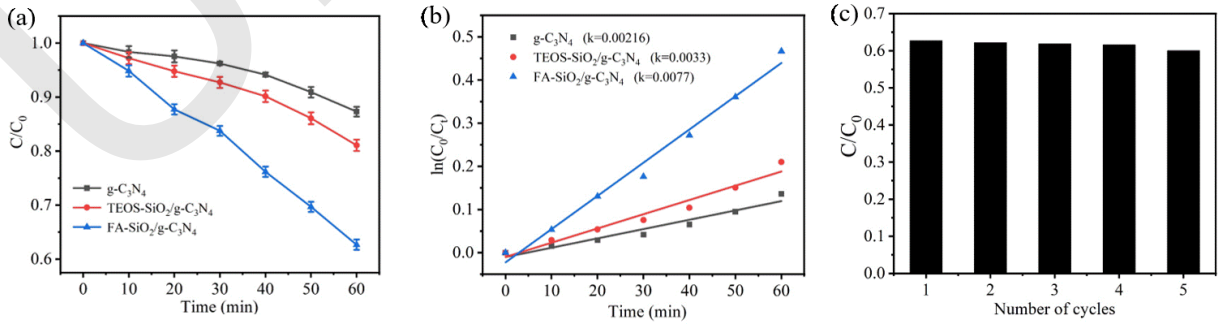

Fig. 9 (a) Photocatalytic degradation curve; (b) kinetic fitting of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4 and (c) photocatalytic cycle test of FA-SiO_2/g-C_3N_4

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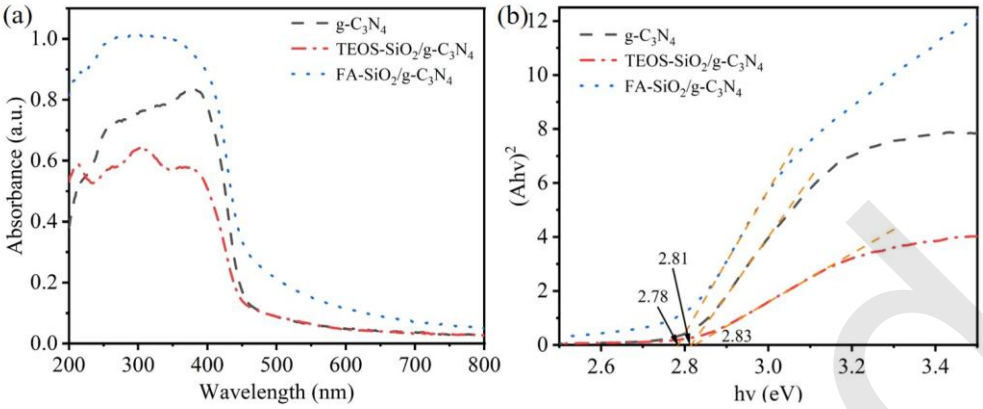

Fig. 10 (a) UV-visible diffuse reflectance spectrum and (b) relationship between $(Ahv)^2$ and hv of g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4

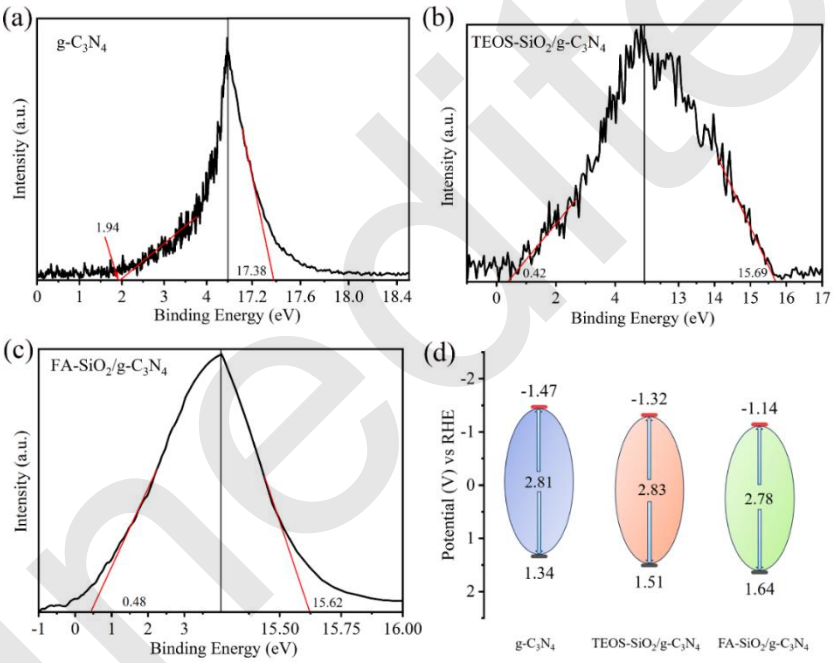

Fig. 11 UV photoelectron spectra of (a) g-C_3N_4, (b) TEOS-SiO_2/g-C_3N_4, and (c) FA-SiO_2/g-C_3N_4; (d) Energy-level structural diagram

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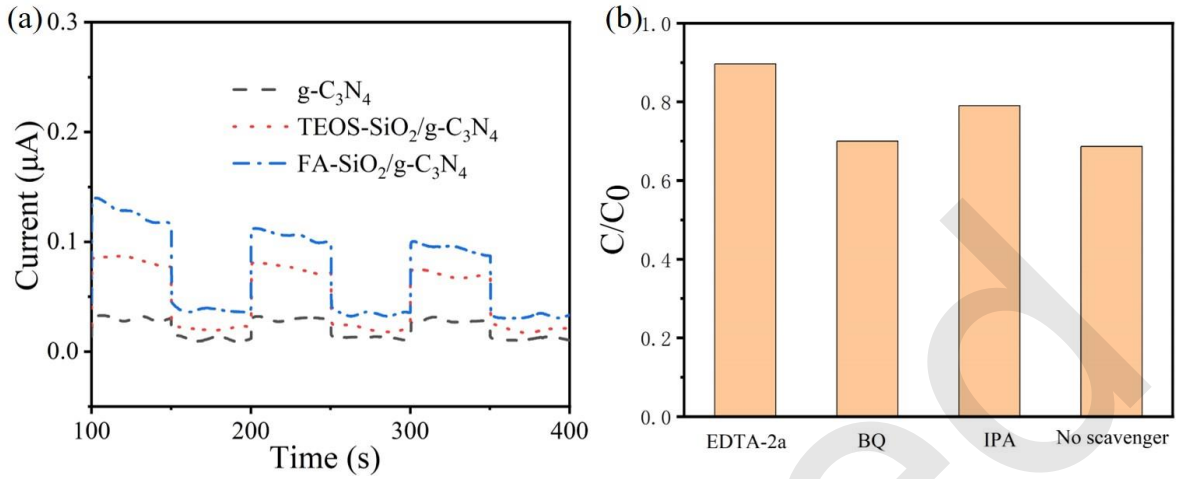

Fig. 12 (a) Transient photocurrent density responses; (b) the MB photocatalytic degradation rate of FA-SiO_2/g-C_3N_4 after adding different free radical quenchers

Table 1 Proportion of chemical bonds containing C and N in g-C_3N_4, TEOS-SiO_2/g-C_3N_4, and FA-SiO_2/g-C_3N_4

Chemical bond / Sample	C–C (%)	C–NHx (%)	N–C=N (%)	C=N–C (%)	N–$(C)_3$ (%)	C–N–H (%)
g-C_3N_4	15.94	7.05	77.01	71.98	15.65	12.37
TEOS-SiO_2/g-C_3N_4	10.66	6.71	82.63	58.13	20.43	21.44
FA-SiO_2/g-C_3N_4	10.44	2.14	87.42	64.31	17.27	18.42

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