Confining the polymerization degree of graphitic carbon nitride in porous zeolite-Y and its luminescence

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Graphitic carbon nitride (g-C₃N₄) has aroused broad interest in the field of photocatalysis and luminescence as a kind of metal-free semiconductor with a suitable band gap of ~2.7 eV. The properties largely depend on the polymerization degree of g-C₃N₄. This research exploits the nanocages of zeolite-Y to confine the polymerization of the melamine monomer to form g-C₃N₄. The composites are achieved via a facile two-step method, i.e., melamine–Na⁺ ion exchange reaction in the cage of the zeolite and subsequent calcination. BET measurement and transmission electron microscopy (TEM) confirm that the g-C₃N₄ is encapsulated in zeolite-Y, and the polymerization degree can be controlled by the melamine contents exchanged with Na⁺ in the cages of zeolite-Y. Photoluminescence and vibration spectroscopy also show the features of g-C₃N₄ with different polymerization degrees in the zeolite-Y composites. This research gives a perspective of fabricating subnanoscale g-C₃N₄ in porous zeolite, which may find potential applications in photocatalysis and optoelectronics.

1. Introduction

As a kind of carbon nitride allotrope, graphitic carbon nitride (g-C₃N₄) is composed of heptazine tectonic units and pendant amino groups. Benefitting from its special layer structure and electronic structure, g-C₃N₄ has become a novel organic and metal-free semiconductor with outstanding heat endurance and chemical resistance in the ambient environment. Owing to the suitable band gap of 2.7 eV, g-C₃N₄ also exhibits excellent photocatalytic properties under irradiation with visible light, including photo-degradation, photocatalytic NO removal and photocatalytic water splitting. Various synthetic methods and techniques, such as solvothermal synthesis, physical vapor deposition, chemical vapor deposition, thermal nitridation, etc., have been employed to produce g-C₃N₄. Additionally, a moderate approach ensuring the thermal condensation of simple organic monomers like melamine was reported to synthesize g-C₃N₄ as a low cost and simple synthetic method. Distinct photoluminescence (PL) properties can be acquired for the g-C₃N₄ with varied polymerization degrees, which was achieved via condensation of melamine at different synthetic temperature. With the ongoing condensation of melamine monomers, melon is the first formed polymeric C₃N₄ structure as an important intermediate precursor. Further reaction results in more polymerized and less defective g-C₃N₄. Thus, controlling the condensation of melamine is of significance. Differing from changing the synthetic temperature, we report on a new method to control the polymerization of g-C₃N₄ by utilizing the confining effect of zeolite-Y’s pores, which has not yet been reported to our best knowledge.

Zeolite-Y is built up by [AlO₄]₅⁻ and [SiO₄]⁴⁻ tetrahedra constituting an open 3D framework structure with cages and channels, which could accommodate particles smaller than 1.5 nm. It also can be viewed as silica structure with partial [SiO₄]⁴⁻ units substituted by [AlO₄]₅⁻, resulting in a negative charge of the structure stabilized by positive cations in the cages and channels. Zeolite-Y has been regarded as an outstanding host to encapsulate quantum dots (QDs) luminescent center, for preventing the QDs from attack of moisture, etc. Many approaches, including ion exchange, vapor impregnation and solid state diffusion, can be employed to introduce luminescent centers into the cages of zeolite-Y. Accordingly, the cations in the cages of zeolite-Y are supposed to be exchanged by the cationic amine, which would further condense to produce g-C₃N₄. Thus, utilizing the cages of zeolite-Y could be a feasible way to confine the polymerization of g-C₃N₄, which may find potential applications in photocatalysis, lighting device and chemical sensing, etc.

In this research, we report on a facile synthesis of porous zeolite-Y and g-C₃N₄ composites, aiming to confine the polymerization of g-C₃N₄ and tune the resulted luminescence. We successfully synthesized the zeolite-Y and g-C₃N₄ composites by two steps. Melamine is first dissolved in deionized water and introduced into the pores of zeolite-Y as precursor via an ion-exchange reaction. Through the thermal condensation of...
melamine in the second step, we eventually synthesized the zeolite-Y and g-C₃N₄ composites.

2. Experimental section

Materials and chemicals: Melamine powders (Aladdin, 99%) and Na⁺–zeolite-Y (SiO₂/Al₂O₃ = 5.1, Alfa Aesar).

The zeolite-Y and g-C₃N₄ composites (simplified as CN₁₋₄, r refers to the initial mass of melamine dissolved in 50 mL deionized water), were generally synthesized by two steps. Typically, the melamine exchanged zeolite-Y was firstly prepared. Detailedly, the amount of r g (r = 1.2, 1.4 or 2.0) of melamine powders were stirred and dissolved in 50 mL deionized water in a water bath at 80 °C for 0.5 h. Then 1.0 g of zeolite-Y was added in melamine solution and magnetically stirred in a water bath at 80 °C for 48 h. The melamine-ion was introduced into the pores of zeolite-Y via the ion-exchange reaction. The as-prepared precursors were repeatedly centrifuged and then washed with deionized water (for twice), and finally dried in air at 80 °C for 12 h. In a second step, the as-prepared precursors were calcined at 550 °C under N₂ atmosphere for 3 h. The CN₁₋₄ products were used directly for further investigation.

Bulk g-C₃N₄ was synthesized by direct heating 2 g of melamine powders at 550 °C under N₂ atmosphere for 3 h. X-ray diffraction (XRD) patterns of the samples were measured on a Rigaku D/max-IIIA X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) images were obtained using an FEI Nova Nano SEM 430 field-emission scanning electron microscopy. The transmission electron microscopy (TEM) images and elemental mapping of resin-embedded sections of CN₁₋₄ were recorded on a JEOL JEM-2100F transmission electron microscope. The specific surface area of the samples was checked by BET measurement (Quantachrome Autosorb-IQ). PL and excitation spectra were recorded on an Edinburgh Instruments FLS 920 spectrometer with a red-sensitive photomultiplier tube (R928). Fluorescence lifetimes were measured on a Hamamatsu Photonics C11367-11. Raman scattering spectroscopy measurements were carried out with 785 nm excitation using a micro-Raman spectroscopy (HORIBA JOBIN YVON LabRAM Aramis). Fourier transform infrared (FTIR) spectroscopy was carried out on Thermo Fisher NICOLET IS 50.

3. Results and discussion

3.1 Synthesis, structure and morphology

Fig. 1 depicts the schematic synthetic procedure of CN₁₋₄. Fig. 2a shows XRD patterns of the bulk g-C₃N₄, the raw zeolite-Y and CN₁₋₄ (r = 1.2, 1.4, 2.0), respectively. For the pattern of bulk g-C₃N₄ (orange), two major peaks at around 12.9° and 27.6° are assigned to the in-plane structure packing of aromatic systems of (100) plane and the interlayer stacking of conjugated aromatic systems of (002) plane, respectively, indicating that it is the typical graphitic phase. It can be seen that both the patterns of CN₁₋₄ (red) and raw zeolite-Y (olive) are in good agreement with reference pattern (black bar), which suggests that the porous zeolite framework is maintained for CN₁₋₄. Differently, the CN₁₋₄ (r = 1.4 and 2.0) are almost amorphous with only one declined diffraction peak at around 6.7°, which show slightly shift to higher diffraction angle compared to that of the raw zeolite-Y. It is the typical fingerprint of zeolite-Y with microporous structure, suggesting that the framework of the CN₁₋₄ (r = 1.4 and 2.0) do not totally collapse.

Fig. 2b and c depict the SEM images of CN₁₋₄ and raw zeolite-Y, respectively. Obviously, the particles of the CN₁₋₄ are angular with similar morphology and smooth surfaces compared to that of the raw zeolite-Y, suggesting that the exchanged melamine may take reaction inside the pores of zeolite-Y during calcination. It can be seen that both the CN₁₋₄ and CN₁₋₄ exhibit red shift in the sequence of r = 1.2, 1.4, 2.0, which is owed to the different polymerization degrees of g-C₃N₄. This is ascribed to the encapsulation of g-C₃N₄ in the cages of zeolite-Y with diameter of subnanoscale, resulting in a quantum...
confinement effect on the electronic structure of the encapsulated g-C$_3$N$_4$. \cite{24,25,26,39,40} Accordingly, all the excitation spectra in Fig. 5b show similar trend.

With the help of Gaussian fitting of the PL peaks, we could obtain a clear understanding of these peaks. The fitted results of the CN$_{1.4}$–Y sample are depicted in Fig. 6a. It can be seen that the PL spectrum of CN$_{1.4}$–Y sample has four emission peaks centered at P$_1$ (396 nm), P$_2$ (427 nm), P$_3$ (467 nm) and P$_4$ (491 nm), respectively. According to the previous research on g-C$_3$N$_4$,\cite{19,41,42} the band-gap states of g-C$_3$N$_4$ are comprised of a sp$^2$ C–N σ band, sp$^3$ C–N π band and the lone pair (LP) state of the bridge nitride atom (Fig. 6b). The P$_1$, P$_2$, and P$_4$ originate from...
the different transitions: \( \sigma^*-\text{LP} \), \( \pi^*-\text{LP} \) and \( \pi^*-\pi \), respectively. The fitting peak positions of \( \text{CN}_r-\text{Y} \) are depicted in Fig. 6c. The red shift of \( P_1 \) and \( P_2 \) reflects the extension of the encapsulated g-C\(_3\)N\(_4\) network, proving that the subnanocages of zeolite-Y can control the polymerization degree of g-C\(_3\)N\(_4\). It is strongly evidenced by the emission blue shift of \( \text{CN}_{1.2}-\text{Y} \) compared with that of \( \text{CN}_r-\text{Y} \) (\( r = 1.4 \) or 2.0).\(^{19,20}\) According to Füle et al., the size of the sp\(^2\) carbonic clusters should be within the range of 0.94–1.15 nm in order to enable the direction transition between the \( \pi \) and \( \pi^* \) bands.\(^{38,41,43}\) The appearance of the \( \pi^*-\pi \) transition bands of \( \text{CN}_r-\text{Y} \) (\( r = 1.2, 1.4, 2.0 \)) samples, corresponding to the peak \( P_4 \), directly proves that g-C\(_3\)N\(_4\) is encapsulated in the pores of zeolite-Y with a diameter of subnanoscale. The peak position of \( P_3 \) remains at around 467 nm, which is probably due to the presence of NH\(_2\) on the edge and the defect of C≡N.\(^{38}\) It can be further proved in the FTIR spectroscopy.

The PL decay curves of the bulk g-C\(_3\)N\(_4\) and \( \text{CN}_r-\text{Y} \) (\( r = 1.2, 1.4, 2.0 \)) are presented in Fig. 6d, which are all monitored at their dominant emission peaks under the 320 nm excitation. All the samples show a fast decay component of 1.7–3.1 ns, which indicates that they share the same origin of \( \sigma^*\text{-LP} \). While the samples other than \( \text{CN}_{1.2}-\text{Y} \) exhibit a more complicated long decay, suggesting that a multiple process such as charge-carrier trapping may be involved for these higher polymerized samples.\(^{19,44}\)

Low temperature PL measurements of the \( \text{CN}_{1.2}-\text{Y} \), \( \text{CN}_{1.4}-\text{Y} \) and bulk g-C\(_3\)N\(_4\) were carried out and the results are given in Fig. 7a, b and c, respectively. All their emissions are gradually

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**Fig. 4**  (a) TEM image of the \( \text{CN}_{1.2}-\text{Y} \). (b–f) The elemental mapping of C, N, Al, Si and O in the same particles.

**Fig. 5**  (a) The normalized PL emission spectra of the \( \text{CN}_r-\text{Y} \) (\( r = 1.2, 1.4, 2.0 \)) and bulk g-C\(_3\)N\(_4\). (b) The normalized excitation spectra of the \( \text{CN}_r-\text{Y} \) (\( r = 1.2, 1.4, 2.0 \)).
enhanced with the decline of temperatures. While the peak locations and profiles remain unchanged for CN1.4–Y and bulk g-C3N4 as the temperature decreases. Differing from this phenomenon, the edge at short wavelength shows red shift for CN1.2–Y as the temperature decreases, which could ascribed to the lower polymerization degree of g-C3N4 for CN1.2–Y than that of CN1.4–Y and bulk g-C3N4.

3.3 Raman spectroscopy and FTIR spectroscopy
To further identify the composition of the composites, Raman spectroscopy of the raw zeolite-Y, melamine, bulk g-C3N4 and all CNr–Y (r = 1.2, 1.4, 2.0) samples were recorded and the results are presented in Fig. 8a. Typical Raman peaks of bulk g-C3N4 locate at around 707 and 1233 cm⁻¹, which are induced by the heptazine ring breathing mode and stretching vibration modes of C=N and C–N hetero-cycles, respectively. These features
Removing the Raman peaks of zeolite-Y, it could be seen that a broad band located in the range of 3000–2506 cm$^{-1}$, which are assigned to the absorbed H$_2$O molecules and CN composites.

However, for bulk g-C$_3$N$_4$, the peaks at around 3400 cm$^{-1}$ are assigned to the characteristic breathing mode of the tri-s-triazine units. While it superposes the peaks originated from zeolite-Y. The peaks in the 1000–1700 cm$^{-1}$ region are assigned to the typical stretching modes and rotation vibration of C–N and C≡N heterocycles in the network. The appearance of these peaks for CN$_{1.2}$–Y ($r = 1.2, 1.4, 2.0$) samples evidently indicate the formation of g-C$_3$N$_4$ in the cages of zeolite-Y. Apparently, these peaks are strong for bulk g-C$_3$N$_4$. While for the CN$_r$–Y, the interaction of laser beam with CN$_r$ is much weaker when taking the FTIR measurement since the CN characteristic breathing mode of the tri-s-triazine units. It is reasonable to infer that the confining effect on condensation degree of melamine in the pores of zeolite-Y would result in a lot of −NH$_2$ groups and C≡N as defects existing in the edge of the g-C$_3$N$_4$ network. The defects cause the appearance of P$_2$ in the PL peaks for CN$_r$–Y ($r = 1.2, 1.4, 2.0$), again proving that the g-C$_3$N$_4$ are encapsulated in the pores of zeolite-Y.

4. Conclusion

In conclusion, we successfully synthesized the porous zeolite-Y and graphitic carbon nitride composites via a facile two-step method. Firstly, we introduce melamine into the pores of zeolite-Y via ion-exchange reaction and the resulted products are the precursors for next step. Secondly, the aimed CN$_r$–Y products are synthesized in situ via the thermal condensation of melamine. Various characterizations, including the PL spectroscopy, evidence the formation of the g-C$_3$N$_4$ encapsulated in the pores of zeolite-Y. Owing to the confining effect of the subnanoscale cages in zeolite-Y, the CN$_r$–Y with controlled polymerization degree of the encapsulated g-C$_3$N$_4$ can be gained. The dimension of the polymeric network of the g-C$_3$N$_4$ in the composites extends and results in red shifting of PL peak as the content of the melamine monomers is elevated. The research gives new clues to fabricate organic semiconductors with different polymerization degree in a porous zeolite, which may be intriguing in photocatalysis and optoelectronics.

Conflicts of interest

There are no conflicts to declare.
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