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In situ growth of TiO$_2$ nanocrystals on g-C$_3$N$_4$ for enhanced photocatalytic performance

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Well dispersed TiO$_2$ nanocrystals with (001) facets were successfully grown in-situ on g-C$_3$N$_4$ through a facial solvothermal method. The resultant TiO$_2$/g-C$_3$N$_4$ composites exhibit remarkably higher efficiency for photocatalytic degradation of phenol as compared to pure catalysts (g-C$_3$N$_4$ or TiO$_2$) or mechanically mixed TiO$_2$/g-C$_3$N$_4$. The optimal composite with 11.2wt% TiO$_2$ showed the highest degradation rate constant, which is 2.8 times that of pure g-C$_3$N$_4$, 2.2 times that of pure TiO$_2$, and 1.4 times that of the mechanically mixed TiO$_2$/g-C$_3$N$_4$ respectively. The enhanced photocatalytic activity is mainly attributed to the effective charge separation derived from two aspects: (1) well matched energy level between the TiO$_2$ and g-C$_3$N$_4$; and (2) the uniform and close contact between the TiO$_2$ and g-C$_3$N$_4$ resulted from the in situ growth of highly dispersed TiO$_2$ nanocrystals. The TiO$_2$/g-C$_3$N$_4$ hybrid material prepared in this study is expected to provide a good foundation for the further design and synthesis of advanced TiO$_2$/g-C$_3$N$_4$-based functional materials and the in situ growth method developed is hopeful to provide a new strategy for the synthesis of other semiconductor-modified g-C$_3$N$_4$ materials.

Introduction

Semiconductor-based photocatalysis has been considered to be one of the most promising and attractive techniques in terms of solar energy conversion and treatment of organic pollutants$^{1,2}$. In the past decades, various semiconductor materials such as metal oxides$^{3-5}$, sulfides$^{6,7}$, and oxynitride$^{8,9}$ have been developed as photocatalysts under UV or visible light irradiation. Very recently, a polymeric semiconductor, graphite-like carbon nitride (g-C$_3$N$_4$)$^{10}$, has been reported as a metal-free and sustainable photocatalyst$^{11,12}$, which exhibits high photocatalytic performance for hydrogen production from water splitting. The catalytic performance of g-C$_3$N$_4$ for the photodegradation of organic pollutants in waste water was also investigated$^{13,14}$. However, the relatively low quantum efficiency of pure g-C$_3$N$_4$ still limits its practical application due to the fast recombination of photo-generated charge carriers$^{15,16}$. To resolve this problem, one of the efficient strategies is coupling g-C$_3$N$_4$ with other semiconductors to form heterojunction structures. Various semiconductors, such as, ZnO$^{17}$, TiO$_2$,$^{18,21}$ TaON$^{12}$, ZnWO$_4$,$^{23}$ BiP$_2$O$_7$,$^{24}$ and Bi$_2$WO$_6$ have been coupled with g-C$_3$N$_4$ to increase the separation efficiency of photo-generated electron-hole pairs, thus to promote the photocatalytic activity.

Among the many kinds of semiconductors mentioned above, TiO$_2$ has been regarded as one of the most attractive candidates due to its non-toxicity, good stability, high activity and its appropriate band position which can well matched with that of g-C$_3$N$_4$ to promote efficient separation of photo-generated charge carriers$^{25-28}$. Therefore, great efforts have been made to prepare and study TiO$_2$/g-C$_3$N$_4$ composed photocatalysts. For example, Zhu et al.$^{18}$ prepared TiO$_2$/g-C$_3$N$_4$ composite with evident performance enhancement by ball milling of TiO$_2$ and g-C$_3$N$_4$. Fu et al.$^{32}$ reported a solid-state approach to synthesizing g-C$_3$N$_4$ coated TiO$_2$ nanocomposites from urea and commercial TiO$_2$ precursors. Park et al developed novel visible light active graphic carbon nitride TiO$_2$ composite through a thermal transformation methodology. In view of the previous studies, there are mainly three strategies for the preparation of the TiO$_2$/g-C$_3$N$_4$ composite: (1) mixing the pre-synthesized TiO$_2$ and g-C$_3$N$_4$ by means of heating, grinding or ball milling$^{30,33}$; (2) calcinating commercial available TiO$_2$ or pre-synthesized TiO$_2$ with precursors of g-C$_3$N$_4$$^{34,35}$; (3) in situ growth of TiO$_2$ on pre-synthesized g-C$_3$N$_4$$^{36-39}$. The first method by using physical mixing is easy to operate and beneficial for scale up, however, uniform mixing and close contact between the two components may not be quite easy to achieve. The second method allows for selection or structure design of the TiO$_2$ for use, but the high temperature calcinations is prone to resulting in aggregation of TiO$_2$ which may bring negative impact on the improvement of photocatalytic activity. The third method by in situ growth of TiO$_2$ doesn’t have the mentioned drawbacks of the former two methods, however, because of the rapid hydrolysis of titanium precursor, it’s
difficult to achieve ultradispersed TiO$_2$ nanocrystals on the surface of g-C$_3$N$_4^{26}$ and controlling the microstructures of coupled TiO$_2$ with desired dispersity and size distribution is still a great challenge$^{41}$. Herein, we developed a facial solvothermal method for the in situ growth of TiO$_2$ nanocrystals on g-C$_3$N$_4$. It is remarkable to find that TiO$_2$ nanocrystals with small particle size (<20 nm) are highly dispersed on the surface of the g-C$_3$N$_4$. In addition, exposed high energy (001) facet of TiO$_2$ nanocrystals was found, which has been widely evidenced by theoretical and experimental researches to be more reactive than the thermodynamically stable (101) facets due to their higher surface energy$^{42}$. The resultant TiO$_2$/g-C$_3$N$_4$ composites exhibit considerable higher efficiency for photocatalytic degradation of phenol as compared to pristine catalysts (g-C$_3$N$_4$ or TiO$_2$) or mechanically mixed TiO$_2$/g-C$_3$N$_4$. The mechanism for the enhanced photocatalytic performance has also been discussed. The TiO$_2$/g-C$_3$N$_4$ hybrid material prepared by this facial solvothermal method is expected to provide a good foundation for the further design and synthesis of advanced TiO$_2$/g-C$_3$N$_4$-based functional materials.

Experimental details

Synthesis of g-C$_3$N$_4$

g-C$_3$N$_4$ was synthesized by heating melamine powder. 6 g of melamine powder was put into an covered alumina crucible and heated in a muffle furnace. At first, the powder was heated to 500 °C at a speed of 2 °C min$^{-1}$ and kept in this temperature for 2 h, then heated to 520 °C in 10 min and keep 2 h. After cooling to room temperature, the light yellow g-C$_3$N$_4$ was obtained. The product was grounded into powder for further usage.

Preparation of TiO$_2$/g-C$_3$N$_4$

1.5 mL of TBOT was added into 20 mL of ethanol under vigorous agitation. After stirring for 15 min, little yellow transparent solution was obtained. This solution was labeled as A. During the procedure, pay attention to moisture to prevent hydrolysis of titanium source. At the same time, 0.5 g of ammonium acetate (AMAT) was dissolved into 15 mL of ethanol followed by 15 min vigorous stirring. After that, a certain amount of g-C$_3$N$_4$ was added into this solution. The suspension was labeled as B. The two solutions of A and B were mixed at room temperature and shifted into 100 mL of Teflon reaction kettle. Then 30 mL of anhydrous ethanol was added to make the total volume became 65 mL and the filling rate reached about 65%. After screwing and sealing the stainless steel outer sleeve well, the Teflon reaction kettle was kept in a 180 °C electric thermostatic blast dryer for 18 h and then cooled to room temperature. The suspension was centrifuged for 15 min at a speed of 4000 r min$^{-1}$, followed by multiple ultrasonic washing with ethanol. Then the sample was dried in 60 °C vacuum oven overnight. The samples were labeled as TiO$_2$/g-C$_3$N$_4$(m), where m represented the quality of g-C$_3$N$_4$ added in the preparation process. Furthermore, we also prepared compared sample, and the specific process is as follow: 0.8 g g-C$_3$N$_4$ was mechanically ground with 0.1 g TiO$_2$ nanocrystalline, then was labelled g-C$_3$N$_4$+TiO$_2$(8:1).

Photocatalytic activity test

The photocatalytic activity of the samples was tested by degradation of phenol at room temperature using a 300 W Xe lamp with AM 1.5 filter to simulate solar light source. 0.04 g catalyst powder was put into 40 mL of 10 mg L$^{-1}$ phenol aqueous solution. And it’s worth noting that the concentration are the same for all investigated catalysts. At first, the system was stirred in darkness for 30 min to make the catalyst dispersed in phenol solution and reach the adsorption-desorption equilibrium. After 30 min dark reaction, 2 mL of solution was taken out to determine the adsorption ability of every sample. Then light irradiation was turn on, after which 2 mL of solution were taken out per 30 min. All the solution samples obtained were centrifuged at the speed of 1200 r min$^{-1}$ for 10 min, then the concentration of phenol was tested by HPLC.

Results and discussions

The TiO$_2$ nanocrystals were grown onto g-C$_3$N$_4$ by a solvothermal treatment of TBOT and g-C$_3$N$_4$ in ethanol in the presence of AMAT at 180 °C for 18 h. Fig. 1 shows the TEM and HRTEM images of a representative sample (TiO$_2$/g-C$_3$N$_4$(1.5)), which was demonstrated to have the best photocatalytic activity. From Fig.1 a and b we could see that TiO$_2$ nanoparticles were well dispersed on the surface of g-C$_3$N$_4$ with particle size less than 20 nm. The HRTEM image shows the characteristic lattice fringe of (001) and (101) facets (Fig. 1c), indicating the existence of exposed high energy (001) facet in the TiO$_2$ nanoparticles. The corresponding FFT pattern demonstrates that the TiO$_2$ is in the form of a single crystal and the angle between

![Fig. 1](image-url)
The crystal structure of the samples was determined by XRD, as shown in Fig. 3. Two pronounced peaks can be found in bare g-C$_3$N$_4$ at about 13.5 and 27.4°, which accord with the characteristic interplanar stacking peaks of aromatic systems and the inter-layer structural packing, indexed as the (100) and (002) crystal planes for graphitic materials, respectively. The XRD pattern of bare TiO$_2$ which was prepared in the absence of g-C$_3$N$_4$ exhibits diffraction peaks with standard peak position and peak shape of anatase TiO$_2$ (JCPDF No. 21-1272), which corresponds in turn from left to right to (101), (103), (004), (112), (200), (105), (211), (206) and (116) crystal planes of anatase TiO$_2$. It can be seen that the same anatase phase can be identified in the TiO$_2$/g-C$_3$N$_4$ nanocomposites with the bare TiO$_2$. As the content of g-C$_3$N$_4$ increased in the compositon catalysts, the diffraction peak of g-C$_3$N$_4$ at about 27.4° gradually increases. Except for the peak at 27.4°, there are no obvious changes of the positions, intensities, and widths of characteristic diffraction peaks of anatase TiO$_2$. This fact suggests that the existence of g-C$_3$N$_4$ has no significant influence on the phase structure of the TiO$_2$ particles. In addition, the XRD peaks of this heterogeneous catalyst were composed by the superposition of characteristic peaks of g-C$_3$N$_4$ and TiO$_2$, which inferred that TiO$_2$ grew on the surface of g-C$_3$N$_4$ without any disturbing to the internal structure of g-C$_3$N$_4$.

The surface composition and chemical status of the elements in the prepared TiO$_2$/g-C$_3$N$_4$ sample were analysed by XPS. Fig. 4 and Fig. 5 illustrates the XPS survey spectrum and high-resolution XPS spectra of different elements. The survey spectrum (Fig. 4) shows that the TiO$_2$/g-C$_3$N$_4$ surface is composed of C, N, O and Ti. From the XPS spectrum of C 1s shown in Fig. 5a, two peaks can be distinguished to be centred at 284.2 and 287.4 eV, respectively. The peak at 284.2 eV is exclusively assigned to the adventitious hydrocarbon from the XPS instrument. Another one at 287.4 eV is identified as carbon atoms that have one double and two single bonds with three N neighbours. Fig. 5b is the high-resolution N 1s spectrum of the TiO$_2$/g-C$_3$N$_4$ (0.5). The asymmetrical feature of the observed N 1s peaks suggests the coexistence of distinguishable models. A signal deconvolution after Gaussian curve fitting is also displayed in Fig. 5b, pointing out chemically different N species in
the g-C$_3$N$_4$, with their N 1s binding energy at 398.5, 399.6 and 400.8 eV, respectively. The N 1s binding energy of 398.5 eV can be assigned to sp2-hybridized nitrogen (C=N=C)$^{30}$. The other two peaks at 399.6 and 400.8 eV can be attributed to tertiary nitrogen (N–(C)$_3$) and amino functional groups with a hydrogen atom (C–N–H), respectively.$^{51}$ The presence of the N–(C)$_3$ group confirm the polymerization of melamine.$^{52}$ From Fig. 3c and d, Ti 2p can be observed at binding energy of around 458.0 (Ti 2p$_{3/2}$) and 463.8 eV (Ti 2p$_{1/2}$)$^{52}$, while O 1s at binding energy of 529.4 and 531.6 eV, which are in good agreement with previous reports.$^{54}$

UV-vis diffuse reflectance spectroscopy (DRS) was carried out to investigate the optical properties of the TiO$_2$/g-C$_3$N$_4$ materials. Fig.6 is the results of UV-Vis diffuse reflectance spectra (DRS) of different samples. From the spectra we could see that a sharp fundamental absorption edge for TiO$_2$ was 390 nm and the main absorption edge of the pure g-C$_3$N$_4$ occurs at 450 nm. The optical absorption of TiO$_2$/g-C$_3$N$_4$ is enhanced distinctly in both UV and visible light region compared to that of pure g-C$_3$N$_4$. This suggests that the growth of the TiO$_2$ on g-C$_3$N$_4$ can possibly cause modifications to g-C$_3$N$_4$ in the fundamental process of electron–hole pair formation during irradiation$^{54}$, which will be favorable for the photocatalytic reaction.

**Photocatalytic activity and enhancement mechanism**

The photocatalytic activity of the catalysts was evaluated by the photocatalytic degradation of phenol. It can be seen from Fig.7a that, after 90 min photocatalytic reaction, the degradation rate of phenol solution was 81% at the present of pure TiO$_2$. The degradation rate of phenol solution which was added pure g-C$_3$N$_4$ was only 70%. However, with the hybrid catalysts, the degradation all reached 100% within 90 min, suggesting the TiO$_2$/g-C$_3$N$_4$ composites exhibited higher photocatalytic activity than both the pure TiO$_2$ and pure g-C$_3$N$_4$ sample. From Fig. 7a we can also find that, with the content of g-C$_3$N$_4$ increase from 0.5 g to 1.5 g which means an increase of dispersion degree of TiO$_2$ nanocrystals on g-C$_3$N$_4$ as discussed above, the photocatalytic activity was enhanced gradually, proving the high dispersion of TiO$_2$ nanocrystals is beneficial for the enhancement of the photocatalytic activity. When the content of g-C$_3$N$_4$ reached 1.5 g, the as-prepared photocatalyst exhibited the highest photocatalytic activity. Significantly, the TiO$_2$/g-C$_3$N$_4$ (1.5) presents an obvious increase in the catalytic activity for phenol decomposition, which induced 100% degradation within 50 min. We can further describe and compare the photocatalytic properties of TiO$_2$/g-C$_3$N$_4$ (1.5) with pure g-C$_3$N$_4$ and pure TiO$_2$ by the photocatalytic degradation rate constants which was shown in Fig. 7b and determined by the first-order kinetic equation ln (C/C) = kt. Remarkably, the average value of rate
The photocatalytic degradation results to 10 mg/L phenol of different catalysts in the light source of 300 W Xenon lamp coupled with AM 1.5.

Fig. 7 The photocatalytic degradation results to 10 mg/L phenol of different catalysts in the light source of 300 W Xenon lamp coupled with AM 1.5.

Fig. 8 Thermal gravimetric (TG) analysis of TiO$_2$/g-C$_3$N$_4$ (1.5).

by TG. Fig. 8 showed the TG results of heating TiO$_2$/g-C$_3$N$_4$ (1.5) from 40 °C to 880 °C in the air at the heating rate of 10 °C/min. Because g-C$_3$N$_4$ became unstable when the temperature reached 600 °C in the air, at 700 °C, g-C$_3$N$_4$ sublimated off completely by converting into nitrogen and cyano fragments. When the temperature was raised from 40 °C to 880 °C, the g-C$_3$N$_4$ had completely sublimed away, and the leaving matter all was TiO$_2$. So we got the ratio of g-C$_3$N$_4$ and TiO$_2$. As Fig. 8 shows, the mass fraction of final remaining material to total quality in TiO$_2$/g-C$_3$N$_4$ (1.5) was 11.2 %, that was to say the content of TiO$_2$ in TiO$_2$/g-C$_3$N$_4$ was 11.2 % and the quality ratio of g-C$_3$N$_4$ and TiO$_2$ was about 8:1. Therefore, we prepared the sample by mechanical grinding according to the ratio and labelled it as g-C$_3$N$_4$+TiO$_2$ (8:1). The photocatalytic result was also presented in Fig. 7. From Fig. 7a we can see that the phenol was degraded completely in 70 min, which is better than the pure g-C$_3$N$_4$ or pure TiO$_2$ but weaker than the in-situ prepared TiO$_2$/g-C$_3$N$_4$ (1.5). And the degradation constant rate of TiO$_2$/g-C$_3$N$_4$(1.5) is about 1.4 times that of g-C$_3$N$_4$+TiO$_2$ (8:1) (Fig. 7b), indicating the in situ method is favourable for the enhancement of photocatalytic activity, which results from the uniform and close contact between g-C$_3$N$_4$ and TiO$_2$ through the in situ growth.

To further investigate the mechanism for the enhancement of the photocatalytic activity by growing TiO$_2$ nanocrystals on g-C$_3$N$_4$, photoluminescence (PL) spectra were measured. Fig. 9a was the results of PL spectra of pure g-C$_3$N$_4$, TiO$_2$/g-C$_3$N$_4$ (1.5) and g-C$_3$N$_4$+TiO$_2$ (8:1) under the excitation wavelength of 365 nm. PL emission measurement has been widely used to investigate the fate of electron-hole pairs in semiconductor particles because PL emission is known to result from the recombination of excited electrons and holes for some semiconductors. The higher the PL emission intensity is, the higher the recombination efficiency of the photogenerated carriers is. As evident in Fig.9, the g-C$_3$N$_4$ sample exhibits strong photoluminescence at room temperature centered
at 450 nm. In comparison, the intensity of this emission band drops significantly for TiO$_2$/g-C$_3$N$_4$ (1.5). This indicates the growth of TiO$_2$ nanocrystals on g-C$_3$N$_4$ can inhibit the annihilation of the photogenerated electron–hole pairs and improve their separation efficiency. In addition, the TiO$_2$/g-C$_3$N$_4$ (1.5) sample has lower PL intensity than g-C$_3$N$_4$+TiO$_2$ (8:1), implying the in situ growth method can promote the charge separation more effectively, which is consistent with the photocatalytic activity of the samples. The electrochemical impedance spectroscopy (EIS) measurement reveals an analogous trend with respect to the PL spectra and photocatalytic activity. As can be seen from Fig. 9b, the EIS result reflects that the impedance arc radius of TiO$_2$/g-C$_3$N$_4$ (1.5) is smaller than that of pure g-C$_3$N$_4$ and g-C$_3$N$_4$+TiO$_2$ (8:1) under simulated sunlight irradiation, indicating that TiO$_2$/g-C$_3$N$_4$ composite demonstrates enhanced separation efficiency of the photo-excited charge carriers compared with that of pure g-C$_3$N$_4$ and g-C$_3$N$_4$+TiO$_2$ (8:1)$^{56,57}$. 

On the basis of the above experimental results, we believe that the enhanced photocatalytic activity induced by the in situ growth of TiO$_2$ is attributed to the effectively separation of photogenerated electron-hole pairs. Fig. 10 schematically shows the proposed mechanism for the promotion of the photocatalytic phenol degradation performance of TiO$_2$/g-C$_3$N$_4$. With the irradiation of simulated sunlight, both TiO$_2$ and g-C$_3$N$_4$ can absorb light to produce photo-induced electron-hole pairs. As the band positions of the g-C$_3$N$_4$ and TiO$_2$ match very well, the photogenerated electrons of g-C$_3$N$_4$ readily transfer to the conduction band (CB) of TiO$_2$, while the holes migrate from the valence band (VB) of TiO$_2$ to the VB of g-C$_3$N$_4$. In addition, the uniform and close contact between TiO$_2$ and g-C$_3$N$_4$ resulted from the in situ growth of highly dispersed TiO$_2$ nanocrystals promoted this interfacial transfer of photo-generated electrons and holes, as demonstrated by the photocatalytic result discussed above. Thus the recombination of photogenerated electrons and holes is sufficiently inhibited, leaving more electrons in the CB of TiO$_2$ and more holes in the VB of g-C$_3$N$_4$. Therefore, an effective charge separation can be achieved, resulting in longer lifetime of the photo-generated electrons and holes for enhanced photocatalytic activity. The photogenerated electrons in VB of TiO$_2$ could be used to catalyze a series of reduction reactions, and the photogenerated holes in CB of g-C$_3$N$_4$ could be used to catalyze series of oxidation reactions. All of these made the scope of application of this composite catalyst greatly broadened.

**Conclusions**

In this study, a simple solvothermal method has been developed for the in situ growth of TiO$_2$ nanocrystals on g-C$_3$N$_4$. The TiO$_2$ nanocrystals could achieve high dispersion on the surface of g-C$_3$N$_4$ and composed by only one nanocrystalline of anatase. In addition, there were some high energy (001) facets exposed. The photocatalytic activities of the composited catalysts were far greater than the pure catalysts (g-C$_3$N$_4$ or TiO$_2$) or the mechanically mixed catalyst, which was confirmed by the photocatalytic degradation experiments of phenol. The enhanced photocatalytic performance can be attributed to the increased charge separation in the composited catalysts derived from the well-constructed nano-architectures and well matched energy level between the TiO$_2$
and g-C3N4. This simple solvothermal method is quite hopeful to be extended for the synthesis of other semiconductor composites g-C3N4 in the applications of photocatalysis and other fields.

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References

Highly dispersed TiO$_2$ nanocrystals with (001) facet were successfully grown in-situ on g-C$_3$N$_4$ through a facial method. The resultant composite exhibits remarkably enhanced photocatalysis comparing to pure TiO$_2$ or g-C$_3$N$_4$ or mechanically mixed TiO$_2$/g-C$_3$N$_4$. 