The g-C3N4/TiO2 nanocomposites for photoelectrochemical performance under UV light illumination

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Abstract

the $g\text{-}C_3N_4/TiO_2$ nanocomposite materials were synthesized by sol-gel method With Tetrabutyl titanate as precursor and urea as N source. The as-obtained materials were characterized by X-ray diffraction. The performance of coatings were measured by electrochemical techniques. The result of XRD show that g- C_3N_4 can influence the growth of TiO_2 crystal grain. Under UV irradiation, the interfacial heterojunction between g- C_3N_4 and TiO_2 can provide an efficient channel for the transfer of charge and suppress the direct recombination of photogenerated e--h+pairs, leading to the strengthened photocatalysis .

Keywords

$g\text{-}C_3N_4$, TiO_2, photoelectricity.

1. Introduction

It is extensive studied due to the optical and electronic properties, long-term stability, low cost , and nontoxicity of TiO_2 [1]. However, the photocatalysis of TiO_2 is limited by its energy band structure, and high recombination rate of photogenerated electron-hole pairs is another main factor [2]. Therefore, optimizing energy band structure of TiO_2 or improving separation rate of photogenerated e^--h^+ pairs is the main way to enhance photocatalytic and photoelectric properties of TiO_2.

Currently, $g\text{-}C_3N_4$ has been widely investigated by researchers as a photocatalytic organic Semiconductor [3,8], which possess a layered structure very similar to graphene . Due to its outstanding characteristics, such as thermostability, chemical stability [4,9] and low cost, it become the top research spot in photocatalytic materials. It is reported that the band position of $g\text{-}C_3N_4$ can well match with that of TiO_2 and can improve the separation rate of photogenerated e^--h^+ pairs. Yan et al. [1] successfully synthesized $TiO_2\text{-}g\text{-}C_3N_4$, and proved H_2 evolution rate was remarkably enhanced by coupling TiO_2 with C_3N_4. Li et al. [5] reported that $g\text{-}C_3N_4/TiO_2$ nanocomposites show much better photocatalytic activity than pure TiO_2 and C_3N_4 in terms of the degradation of MO under visible light. The $g\text{-}C_3N_4/TiO_2$ synthesized by Wang et al. [6] shows high photoelectrocatalytic activity towards degradation of rhodamine B.

In this study, $g\text{-}C_3N_4$ was synthesized by thermal decomposition of urea firstly, then using sol-gel method to synthesize $g\text{-}C_3N_4/TiO_2$ nanocomposite.

2. Experimental detail

2.1 Materials

Tetrabutyl titanate was purchased from Qingdao Jingke Instruments and reagents Co., Ltd. Glacial acetic acid, ethanol, distilled water and urea were also purchased from Qingdao Jingke instruments and reagents Co., Ltd. All the reagents used in this study were analytical grade and were used directly without any further processing.

2.2 Preparation of g-C3N4

The $g\text{-}C_3N_4$ was synthesized by a frequently-used heating method and using urea as precursor. In detail, 25.0g urea was placed into a 50ml alumina crucible with a cover, which was then put into a programmable furnace and heated at 500℃ for 4 hours with a heating rate of 10℃/min. after cooling to ambient temperature. The resultant yellow products in bulk form were ground into power for further use.

2.3 Synthesis of g-C3N4/TiO2 composites

The g-C_3N_4/TiO_2 nanocomposites were prepared by typical sol-gel method. The detailed steps as follows: 1ml distilled water,1.5ml glacial acetic acid, 6ml ethanol and g-C_3N_4 with different mass ratio (g-C_3N_4/TiO_2=0, 0.1,0.3,0.5) were mixed in a 50ml beaker, which was called A solution. Then keeping A solution by ultrasonic treatment for 30 minutes. 5 ml ethanol was put into another 50ml beaker, then tetrabutyl titanate was added slowly to the ethanol solution under magnetic stirring , and keeping stirring for 10 minutes, which was called B solution. At last, B solution was added into A solution drop by drop under magnetic stirring for 24 hours. When the obtained sol turned into gel, putting them into a drying oven for 10 hours. The dried gel was ground into powder, then placed into an uncovered alumina crucible and heated at 500℃ for 2 hours with a heating rate of 4℃/min. the obtained materials were ground into fine powder for further use.

3. Results and discussion

3.1 XRD

The XRD patterns for g-C_3N_4, pure TiO_2, and g-C_3N_4/TiO_2 are shown in figure 1. For g-C_3N_4, two apparently diffraction peaks were found at about 13.0 °and 27.4 °,which correspond to the (002) and (100) plane diffraction of g-C_3N_4 [7], respectively. The mixed phase of anatase and rutile can be found for bare TiO_2. There is only one peak at 27.4 °for rutile phase, indexed as the (100) crystal plane. And the peak of rutile phase is little change when the mass ratio of g-C_3N_4 is 0.1, but it is almost disappeared with other g-C_3N_4 loading. As can be seen in table 1. With the increasing of g-C_3N_4, the size of TiO_2 nanocomposite particles gradually decreased [5]. Which is ascribed to the layered structure of g-C_3N_4 that could restrain the TiO_2 particles from aggregation during calcination [12]. No typical peaks of g-C_3N_4 are found from the diffraction patterns of g-C_3N_4/TiO_2 nanocomposite, attributing to its poor crystallization.

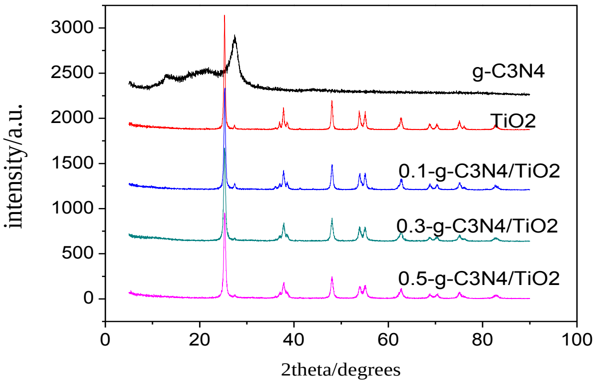

Fig. 1 XRD patterns of pure g-C3N4, TiO2, g-C3N4/TiO2 composites. The mass ratios of g-C3N4 and TiO2 are 0.1, 0.3, 0.5.

3.2 Photocurrent

Photoelectrochemical performance is an effective approach to examine the separation rate of photogenerated electron-hole pairs for photocatalyst. The photocurrent of pure TiO_2/ITO, g-C_3N_4/TiO_2/ITO are shown in figure 4. Under UV light irradiation, the photocurrent density of all specimens have a sharp increase as compared with the absence of light, and the photocurrent density of samples back to their original state when turning off the lights. It also can be seen that the increase of 0.1-g-C_3N_4/TiO_2/ITO (the mass ratio of g-C_3N_4 and TiO_2 is 0.1) is especially obvious. Which is ascribed to the function of g-C_3N_4 coupling. Since the energy levels of HOMO (1.57eV) and LUMO (-1.12eV) of g-C_3N_4 [10] match well with that of VB (2.91eV) and CB (-0.29eV) of TiO_2 [11], respectively. The excited electrons in the LUMO of g-C_3N_4 can easily migrate to the CB of TiO_2, and the holes in the VB of TiO_2 could easily transfer to the HOMO of g-C_3N_4 via interfacial interaction. Therefore the separation rate of photogenerated e^{-}-h^{+} pairs is greatly improved, and g-C_3N_4/TiO_2/ITO shows more enhanced photocurrent density. But the photocurrent density of 0.5g-C_3N_4/TiO_2/ITO has little change as compared with that of pure TiO_2/ITO, that's because that the surface of TiO_2 particles could be covered by the excess g-C_3N_4, which could stop partial absorption of ultraviolet light, leading to the obvious decrease of photoeletrochemical performance of hybrids.

Table 1 the size of particles for all samples

Sample	TiO_2	0.1-g-C_3N_4/TiO_2	0.3-g-C_3N_4/TiO_2	0.5-g-C_3N_4/TiO_2
XS (nm)	30.4	25.7	20.3	17.6

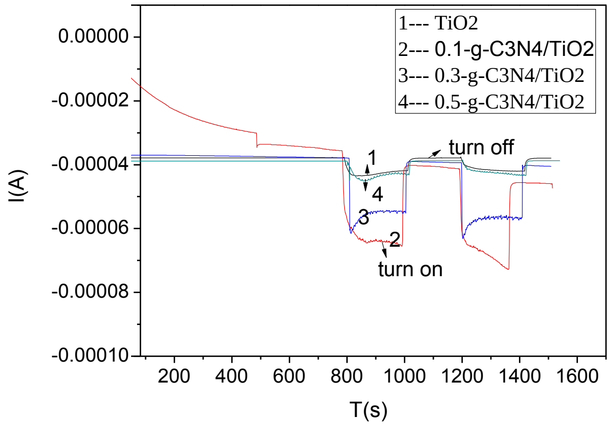

Fig. 4 photocurrent-time curves of pure TiO2, g-C3N4/TiO2 hybrids.

4. Conclusion

The g-C_3N_4/TiO_2 nanocomposites with different g-C_3N_4 loading are synthesized via sol-gel method. Under UV light irradiation, the nanocomposites exhibit wonderful photoelectrochemical performance due to the synergistic heterojuction formed at the interface between TiO_2 and g-C_3N_4, which could greatly suppress the recombination of photogenerated e^{-}-h^{+} pairs. The result of the analysis for XRD demonstrates that the adding of g-C_3N_4 result in decrease in the size of TiO_2 particles.

Acknowledgements

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