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New g-C_3N_4 based photocatalytic cement with enhanced visible-light photocatalytic activity by constructing muscovite sheet/SnO_2 structures

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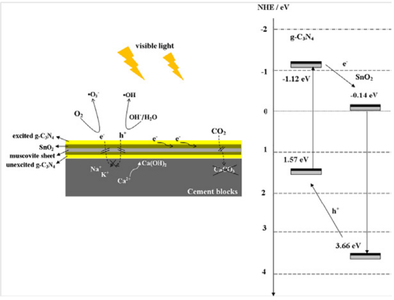
HIGHLIGHTS

- We explored stable and active photocatalytic cement based on the g-C_3N_4 for the first time.
- The construction of muscovite sheets can improve the stability of photocatalytic cement.
- The photocatalytic cement can degrade volatile isopropyl alcohol or Rhodamine B stains on its surface tempestuously.

GRAPHICAL ABSTRACT



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ABSTRACT

An imperative new trend of the green construction industry is to integrate photocatalytic technology with building materials. Here, novel g-C_3N_4 based photocatalytic cement has been designed for the first time, which mainly integrates three functional modules, i.e. g-C_3N_4 photocatalytic layer, SnO_2 electronic acceptor layer and muscovite sheet protective layer, with the aim to purify the surrounding environment. The construction of muscovite sheets into photocatalytic cement can keep the photogenerated carriers from the alkali ionic species in cement, reducing the recombination probability. What's more, the muscovite sheet layer can also prevent the products of the photocatalytic reaction from accelerating the carbonation of cement. Hence, the presence of muscovite sheets helps to solve the stubborn problems of traditional photocatalytic cement, improving the stability of photocatalytic cement. Moreover, due to the suitable bandgap position, the SnO_2/g-C_3N_4 heterostructures have been devised to enhance electron-hole separation and interfacial charge transfer. By degrading Rhodamine B stains and volatile isopropyl alcohol, it has been found that the visible-light photocatalytic activity can be improved dramatically because of the functional modules. Consequently, this design provides promising outdoor use and will be of important significances to the development of green construction industry.

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1. Introduction

In decades, due to industrial waste and automobile exhaust, water and air pollution is becoming more and more serious, and even threatens the human's health [1,2]. Facing these problems, photocatalysis technique, as one of the most promising methods of easing environmental pollution, has got wide attention from home and abroad [3–5]. For the convenience of practical application, it has been proposed that the photocatalysis technique should be combined with building materials, such as cement mortar [6–9]. Based on the building materials, it is convenient for the photocatalyst to be excited by the energy from solar light and degrade pollutants in the surroundings [7,10–12], offering a simple way to purify the environment. So far, many efforts have been paid to combine TiO_2 photocatalyst with cement for the photocatalytic oxidation ability [12–15], self-cleaning and anti-bacterial effect [16–18]. With deeper study, some problems are emerging [13–15,19,20]: (1) the alkali ionic species in cement, such as K^+, Na^+, Ca^{2+}, would cause the electron-hole recombination, reducing the photocatalytic performance; (2) the products of the photocatalytic reaction would damage the surface structure of cement, accelerating the carbonation of cement, which will affect the durability of cement and even decay the buildings, bring incalculable loss. Conversely, calcium carbonate produced during the carbonization process will also reduce the activity of the photocatalyst [21]; (3) TiO_2 with a wide bandgap (3.2 eV) cannot use the visible light, which occupies a large part of the solar light. Therefore, a new type of visible-light photocatalytic cement with stable structures should be designed to solve the above problems.

Recently, a kind of hydrous layered silicate, the muscovite, has brought our attention, because of its good chemical stability, thermostability, insulativity and low cost [22]. Besides, as layered silicates, the muscovite can be easily stripped into two-dimensional sheets [23]. Due to these characteristics, the muscovite sheets can be used as stable interlayers to avoid direct contact of excited photocatalysts and cement blocks. This can help to get rid of the interactive influence between photocatalytic reactions and cement blocks, and then improve the stability of photocatalytic cement. Thus, the strategy will be an ideal solution to the above first two problems.

As for the third defect, although a sea of methods were reported to extend the spectral response range of photocatalysts [2,24–26], the visible-light photocatalytic cement hasn't been reported till now. This might result from their low activity and poor stability. However, the combination of building materials and visible-light photocatalytic technology will be an irreversible new requirement in the construction industry. Fortunately, graphitic carbon nitride ($g\text{-}C_3N_4$) has appeared as a robust visible-light photocatalyst since 2008 [27]. Due to its narrow bandgap of 2.7 eV, the $g\text{-}C_3N_4$ can make full use of visible light for photocatalytic water splitting [28–30], organics degradation and outdoor pollution control [31–33]. Contrary to traditional visible-light photocatalysts, $g\text{-}C_3N_4$ is a graphene-like polymeric semiconductor, and has good chemical and thermal stability [34,35]. Besides, because of this chiffon-like nanostructure, $g\text{-}C_3N_4$ can be combined with building materials more easily and stably than conventional semiconductor, and does not rely on complicated device manufacturing [27].

Nevertheless, the $g\text{-}C_3N_4$ has an obvious inherent shortcoming that it is easy for the photogenerated carriers to get recombined, which may significantly decrease the photocatalytic activity [36,37]. A series of studies have been reported to reduce the probability of electron-hole recombination [11,38,39], such as the deposition of noble metal particles [38], the combination with carbon based materials or other semiconductors [40]. Among these, coupling $g\text{-}C_3N_4$ with other semiconductors is acknowledged as one of the most effective methods, and is more adaptable to industrial production because of its low cost [35], such as $TiO_2/g\text{-}C_3N_4$ and $ZnO/g\text{-}C_3N_4$ [37,41]. Lately, some studies show that tin oxide (SnO_2) is better than TiO_2 and ZnO when used as an electronic acceptor [35,42]. Some SnO_2/photocatalysts systems have been developed for better charge separation [43]. For $g\text{-}C_3N_4$, its valence band (VB) is about 1.57 eV and conduction band (CB) is about -1.12 eV respectively, while the VB of SnO_2 is about 3.66 eV and its CB is about -0.14 eV respectively [35]. Consequently, $SnO_2/g\text{-}C_3N_4$ composites can be constructed for better charge separation, enhancing the visible-light photocatalytic activity.

Here, through a coating method, we design novel visible-light photocatalytic cement (muscovite sheet/$SnO_2/g\text{-}C_3N_4$ cement) with three functional modules to settle the above problems. As Fig. 1 shows, the $g\text{-}C_3N_4$ on the surface of the photocatalytic cement can be excited to degrade pollutants under visible light irradiation; the muscovite sheet will be used as a protective layer, which can avoid the mutual influence between cement blocks and excited photocatalysts, improving the stability of photocatalysts and the durability of cement; besides, SnO_2 layer, as the electronic acceptor, will be coupled with $g\text{-}C_3N_4$, which can benefit the charge transfer and separation. This new structural strategy will promote the development of photocatalyst in construction industry. Yet, until now no report has studied the $g\text{-}C_3N_4$ based materials in cement system.

2. Materials and methods

2.1. Materials

Deionized water was employed throughout the whole experiment. All the commercial reagents were of analytical grade and were used as received without further purification. The raw materials are listed in the Table 1.

2.2. Preparation of muscovite sheet/SnO_2 (MS) powders

Two-dimensional muscovite sheet was prepared by liquid-phase exfoliation. Typically, the muscovite powders (5 g) were added into ethanol solution (200 mL), and then the mixture solution was stirred for two hours. After this, the prepared suspension was put into a biomixer, using sonication (400 W) to strip muscovite powders for 4 h. Then water and ethanol were used to wash the product. Finally, by dry at 60 °C for 12 h, the two-dimensional muscovite sheet was obtained.

The as-obtained muscovite sheets (5 g) were added into hydrochloric solution (200 mL) with a pH of 2. Afterwards, stannic chloride (5 g) was added into the above solution. Then put the solution into a thermostatic bath at 70 °C for 3 h. After that, products were washed and then dried at 60 °C. Through annealing at 600 °C for 2 h, muscovite sheets coated with SnO_2 layer were obtained successfully, and named as MS powders.

2.3. Preparation of muscovite sheet/$SnO_2/g\text{-}C_3N_4$ (MS/CN) photocatalyst powders

Urea was mixed with MS powers by mechanical stirring. Then the mixture was heated at a ramp of 25 °C/min and keep 520 °C for 4 h. By annealing, faint yellow powders were obtained. The names of prepared powders are listed in the Table 2.

The M3/CN powders were prepared with urea (20 g) and muscovite sheet (0.6 g) instead of MS powers.