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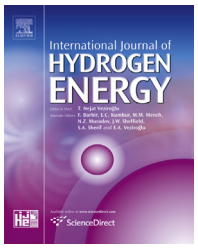

Ternary composites of TiO_2 nanotubes with reduced graphene oxide (rGO) and meso-tetra (4-carboxyphenyl) porphyrin for enhanced visible light photocatalysis

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ABSTRACT

Meso-tetra (4-carboxyphenyl) porphyrin (H_2TCPP) loaded on the surface of TiO_2 nanotubes (TNTs) by modification of reduced graphene oxide (rGO) nanostructures has been successfully performed through improved hydrothermal and heating reflux composite technology. The influence of rGO and H_2TCPP on the co-photocatalytic behavior of TNT during the degradation of Methylene blue (MB) were studied. The novel photocatalysts have been characterized and analyzed by high-resolution transmission electron microscopy (TEM), elemental mapping by energy-dispersive X-ray spectroscopy (EDX), powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, ultraviolet–visible diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy (PL) and electron paramagnetic resonance (EPR). The results from these investigations provide a deeper insight into the materials chemistry of H_2TCPP/rGO-TNT nanocomposites. Additionally, the photocatalytic activity was evaluated by the photodegradation of MB under irradiation with visible light. The degradation results showed a purification of more than 92% MB in wastewater, which is about 4.3 times higher than that of the pure TNT. The results confirm that the prepared H_2TCPP/rGO-TNT nanocomposites possess superior absorption and co-photocatalytic activities. First, graphene works as the adsorbent, electron acceptor and transporter to efficiently increase the separation of the electron–hole pairs. Then it can accelerate the decomposition of organic pollutants. Second, the H_2TCPP plays a critical role in capturing photons and expands the absorption wavelength to the visible light region when dealing with water resource.

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Introduction

Semiconductor photocatalysis is a talented strategy to solve the serious problems, including energy production and environmental protection [1]. The nanosized TiO_2 semiconductor photocatalyst has been attracting significant attention because of its physical and chemical properties, especially the excellent photocatalytic activity [1,2]. That's because it can be used for fulfilling the tasks of energy production and environmental protection. Owing to the rapid advancements both in industry and economy in China, the increasing environmental problems have become topics of great global concern. Nanosized TiO_2 has been regarded as a promising photocatalyst which can be employed to aid with these two major problems [1,3]. For example, nanosized TiO_2 was regarded as one of the most suitable materials for photocatalysis for the purification of water resource. It is also considered as one of the most promising electrode materials for application in the energy storage and conversion field [3–5]. However, there are still some problems regarding this novel photocatalytic material [5,6], such as its 3.2 eV band gap. In addition, the sensitivity was limited to only the UV light region. The photocatalytic activity of TiO_2 can be modified by different types of carbon-rich materials, such as carbon nanotubes, activated carbon and graphene [7–10]. Graphene (GR) is a honeycomb-like, one atom thick sheet of carbon that exhibits a number of unique physical and chemical properties [11]. Graphene has the advantage of high specific surface area, which is beneficial for the adsorption of organic pollutants for water treatment. Graphene also possesses other advantages, such as no gap between its valence and conduction bands, high light transmittance, high chemical stability, and high conductivity. Thus, it is an excellent candidate as an electron acceptor material. Furthermore, GR can also improve the adsorption performance of TiO_2 through chemical adsorption, which enhances electron transfer between these materials [12]. Hence, GR-TiO_2 composites increase the photocatalytic activity, improve photoinduced heterogeneous interfacial charge transfer and reduce the recombination of electron–hole pairs. Therefore, GR-TiO_2 composites are excellent candidates as catalytic materials [13–19]. Many efficient methods have been reported to ameliorate the catalytic performance of the GR-TiO_2 composites, such as hybridization with carbon fiber or carbon nanotubes, depositing Pt on its surface [20–22] and others [23–25]. However, as electron acceptors, graphene possesses a good ability for accepting long-distance transporting electrons, which will be favorable for separating electron–hole pairs during catalysis.

All of these findings encouraged us to probe the potential materials that could 1) act as excellent electron donors, resulting in the effective separation of electron–hole pairs, and 2) broaden the absorption wavelength for enhancing the co-photocatalytic activity, enabling the organic pollutants to be degraded efficiently with the aid of visible light irradiation. As a potential compound, meso-tetra (4-carboxyphenyl) porphyrin (H_2TCPP) was chosen as a suitable electron donor in the novel donor-acceptor system. Owing to its delocalization system of conjugate macrocyclic π-electrons, the energy bands between HOMO and LUMO can be decreased [21,22,26]. However, the carboxy and phenyl groups in the H_2TCPP molecule are electron-withdrawing, which will improve the separation of the excited electron–hole pairs. Therefore, H_2TCPP possesses a larger spectral response and higher quantum yields, even in the visible light region [20–23,26]. Connecting graphene with porphyrins through covalent and non-covalent bonds can result in effective heterogeneous interfacial electron transfer and long-distance transport, which will reduce the recombination of electron–hole pairs within the whole catalytic system. Therefore, this will encourage broad application prospects for use as photoelectric material or environmental protection material [24–26].

Therefore, the aim of this study was to synthesize TNTs decorated onto the surface of rGO followed by co-modification of H_2TCPP (H_2TCPP/rGO-TNTs) through an easy and novel method, as shown in Scheme 1. Visible light-assisted co-photocatalytic oxidation of organic pollutants by reduced graphene oxide (rGO)-TiO_2 nanosized composites modified by H_2TCPP has not been reported before. The ternary complex displays a higher photocatalytic performance for organic pollutants, such as MB, compared with pure TNTs or rGO-TNTs. In this photocatalysis, H_2TCPP was used as the light antenna, and it was also an excellent electron donor. However, rGO was the photogenerated electron acceptor, which could accept electrons from H_2TCPP or TNT. The recombination of electron–hole pairs among the whole catalytic system will be reduced, owing to the efficient heterogeneous interface charge transfer among them. Interestingly, the photocatalytic activity and re-usability of H_2TCPP/rGO-TNTs could be distinctly improved with the assistance of visible light irradiation. Both rGO and H_2TCPP play a crucial role in contributing to the enhanced catalytic performance and the recycling of the catalyst. The present work might provide a new paradigm for developing efficient yet long-term recyclable catalysts for environmental protection with the assistance of visible light irradiation. It could be applied to energy production and environmental protection in the future.

Experimental

Materials

H_2TCPP sensitizer was purchased from J&K Scientific Ltd. TiO_2 nanoparticles (P25, d = ca. 25 nm) were supplied by Evonik-Degussa Co., Ltd., Germany. N,N-Dimethylformamide (DMF) and MB, both of analytical reagent grade quality, were purchased from Beijing Entrepreneur Science & Trading Co., China, and used without further purification. Natural graphite, sodium nitrate ($NaNO_3$, 99%), potassium permanganate ($KMnO_4$, 99%), hydrogen peroxide aqueous solution (H_2O_2, 35%), concentrated sulfuric acid (H_2SO_4, 98%) and other chemicals were analytical or reagent-grade products. They were also used without further purification. All of the solutions were prepared with high-purity deionized (DI) water.

Preparation of graphene oxide (GO)

GO was prepared through a modified Hummers' method [26,27]. 1.0 g of natural graphite and 1.0 g of $NaNO_3$ dissolved in 46 mL of 18.4 M H_2SO_4 were stirred evenly in an ice bath for 10 min. Then, 8.0 g of $KMnO_4$ was slowly added in an ice bath to yield a purple-green hybrid solution with stirring for another 20 min. This