Full Length Article

Promotion of phenol photodecomposition and the corresponding decomposition mechanism over g-C$_3$N$_4$/TiO$_2$ nanocomposites

Xueqin Wang[a,1], Fang Wang[a,1], Bo Chen[b], Kai Cheng[a], Junlei Wang[a], Jiaojing Zhang[a], Hua Song[a,c,*]

[a] College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, China
[b] School of Mechanical Science & Engineering, Northeast Petroleum University, Daqing 163318, Heilongjiang, China
[c] Provincial Key Laboratory of Oil & Gas Chemical Technology, Northeast Petroleum University, Daqing 163318, China

ABSTRACT

Composite photocatalysts containing TiO$_2$ nanoparticles grown on nanosheet-structured graphitic carbon nitride (g-C$_3$N$_4$) were synthesized using a facile calcination approach. A series of g-C$_3$N$_4$/TiO$_2$ nanocomposites was prepared by varying the amount of the urea precursor from 1 g to 5 g. The as-prepared catalysts were characterized by X-ray diffraction; scanning electron microscopy; N$_2$ adsorption-desorption isotherm analysis; and Fourier transform infrared, X-ray photoelectron, and UV–Vis spectroscopies. The results revealed that small TiO$_2$ particles were well dispersed on the surface of the g-C$_3$N$_4$ nanosheets. Compared with pure TiO$_2$ nanoparticles, the obtained g-C$_3$N$_4$/TiO$_2$ nanocomposites showed enhanced photocatalytic activity toward the degradation of phenol as a result of improved separation of photogenerated electrons and holes derived from the synergistic interaction of TiO$_2$ and g-C$_3$N$_4$. The g-C$_3$N$_4$/TiO$_2$ composite prepared with 4 g of urea precursor showed the best photocatalytic performance toward phenol decomposition with a degradation rate of 99.4%. It was found that during the degradation process, p-benzoquinone, catechol, and hydroquinone were generated; hydroquinone was identified as the main intermediate product. Furthermore, mechanisms were proposed to explain the electron-hole separation and transport over the g-C$_3$N$_4$/TiO$_2$ photocatalyst as well as phenol degradation under ultraviolet light irradiation.

1. Introduction

The ever-increasing environmental pollution over the past decades has become a major concern in modern society [1,2]. Specifically, while numerous methods have been applied to resolve the issue of phenol contamination, phenol is a pollutant that is not readily susceptible to degradation. From this point of view, photocatalysis has emerged as an ideal alternative wastewater treatment method owing to the high selectivity, nontoxicity, and long-term stability of many of the catalysts utilized for this purpose [3,4]. It has been found that among the different oxide semiconductor photocatalysts [5–7], titanium dioxide (TiO$_2$) is an appropriate candidate for the photocatalytic degradation of organic compounds and water splitting. It has also been pointed out that TiO$_2$ maintains its high catalytic activity and strong oxidizing properties during operation, and exhibits excellent chemical stability and non-toxicity [8]. Furthermore, several studies have reported that TiO$_2$ can decompose a variety of organic pollutants into CO$_2$ or other small molecules in the presence of H$_2$O, O$_2$, and UV/Vis light. However, pure TiO$_2$ shows a wide band gap of about 3.2 eV, rendering it ineffective in the visible light region as it only absorbs UV light, which comprises 4% of the solar radiation spectrum. Meanwhile, the high recombination rate of photogenerated electron-hole pairs further restricts the photocatalytic applications of TiO$_2$. Therefore, considerable efforts have been made to improve the photocatalytic performance of TiO$_2$, including doping/co-doping with metals [9], non-metals [10], and noble metal ions [11]; hybridization with other semiconductors [12]; and surface sensitization with dyes and metal complexes.

In recent years, two-dimensional materials such as graphene and g-C$_3$N$_4$, which possess extraordinary electron transfer properties, have attracted significant attention for the modification of photocatalysts [13,14]. In 2009, Wang et al. [15] found that the H$_2$ production rates increased substantially when Pt was coupled with g-C$_3$N$_4$ as a cocatalyst. Consequently, g-C$_3$N$_4$-based nanostructures have generated a lot of interest owing to their potential as photocatalysts for energy and

environmental applications [16–19] such as photocatalytic water reduction and oxidation, degradation of pollutants, and carbon dioxide reduction. Furthermore, the metal-free polymer and n-type semiconductor g-C$_3$N$_4$ possesses a medium band gap of 2.7 eV, high thermal and chemical stability, an appropriate electronic structure, is nitrogen-rich, and can be synthesized via uncomplicated preparation methods. Among the various preparation strategies, the thermal condensation method has become very popular because of its simplicity and widely available raw materials, in addition to the complete crystalline structure and large surface area of the final g-C$_3$N$_4$ product. It has been reported that the heterojunction between g-C$_3$N$_4$ and TiO$_2$ efficiently reduces the recombination of photogenerated electrons and holes, thus improving the photocatalytic performance [20]. Wei et al. [21] prepared a TiO$_2$/g-C$_3$N$_4$ thin film electrode material by surface hybridization and dip-coating and applied it as photocatalyst for the degradation of phenol. Their experimental results revealed that the photocatalytic performance of this composite material was improved by the surface hybridization method. Although, the total decomposition efficiency of phenol was demonstrated to have been improved by combination of g-C$_3$N$_4$ and TiO$_2$, to the best of our knowledge, there are very few studies that have discussed the mechanism of photodegradation of phenol over g-C$_3$N$_4$/TiO$_2$ nanocomposites.

Herein, we report a two-step method to synthesize g-C$_3$N$_4$/TiO$_2$ nanocomposites containing different amounts of g-C$_3$N$_4$ nanosheets. Therein, amorphous TiO$_2$ nanoparticles were synthesized by the direct hydrolysis of tetrabutyltitanate. As the precursor of g-C$_3$N$_4$, urea was homogeneously mixed with the as-prepared TiO$_2$ nanoparticles to form a tightly coupled composite. The morphology, structure, and optical properties of the various g-C$_3$N$_4$/TiO$_2$ nanocomposites were systematically determined. Their photocatalytic performances were evaluated based on the degradation of phenol and the concentrations of the intermediate degradation products were closely monitored. The mechanism of the degradation process and the synergistic effect between TiO$_2$ and g-C$_3$N$_4$ have also been discussed.

2. Experimental

2.1. Raw materials

All chemicals and solvents, namely, urea (CO(NH$_2$)$_2$), absolute ethanol (C$_2$H$_5$OH), tetrabutyltitanate (Ti(OBu)$_4$), methanol (CH$_3$OH), isopropyl alcohol ((CH$_3$)$_2$CHOH), p-benzoquinone (C$_6$H$_4$O$_2$), and ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$), were of analytical grade, procured from Sigma-Aldrich, and used without further purification.

2.2. Synthesis of TiO$_2$ nanoparticles

TiO$_2$ powder was synthesized by hydrolysis using Ti(OBu)$_4$ as precursor. In detail, 0.9 mL of distilled water was mixed with 10 mL of absolute ethanol and 1.5 mL of tetrabutyltitanate (TBOT) was added dropwise to the ethanol solution under vigorous stirring at room temperature. A white gel was formed immediately and was left to age for 4 h under gentle stirring at 45 °C. Subsequently, the milky white precipitate was collected by centrifugation and washed several times with ethanol to remove residual organic compounds. The product was dried in an oven at 60 °C overnight.

2.3. Synthesis of g-C$_3$N$_4$/TiO$_2$ nanocomposites

As previously described in the literature, the simple calcination of pure urea [22], melamine [21], or dicyandiamide [23], leads to the formation of g-C$_3$N$_4$ directly and no further purification is necessary. Different g-C$_3$N$_4$/TiO$_2$ nanocomposites were synthesized by heating mixtures of urea and TiO$_2$ nanoparticles to form a heterojunction structure between g-C$_3$N$_4$ and TiO$_2$. First, varying amounts of urea powder (1 g, 2 g, 3 g, 4 g, and 5 g) were dissolved in 20 mL of methanol

under constant stirring for ~30 min. Then, 100 mg of as-prepared TiO$_2$ nanoparticles were added to the above solution and the mixture was stirred for another 30 min. Subsequently, the suspension was dried in an oven at 80 °C until the product was completely dry. Finally, these TiO$_2$/urea products were transferred to an alumina crucible with a cover and heated up to 550 °C at a heating rate of 2.3 °C min^{-1}, and maintained at 550 °C for 4 h, resulting in g-C$_3$N$_4$/TiO$_2$ nanocomposites. The as-prepared samples have been denoted as g-C$_3$N$_4$/TiO$_2$-1, g-C$_3$N$_4$/TiO$_2$-2, g-C$_3$N$_4$/TiO$_2$-3, g-C$_3$N$_4$/TiO$_2$-4, and g-C$_3$N$_4$/TiO$_2$-5, respectively, based on the amount of used urea (1–5 g). For comparison, pure TiO$_2$ nanoparticles and urea were separately calcined under the same conditions to obtain the crystalline TiO$_2$ and g-C$_3$N$_4$ photocatalysts, respectively.

2.4. Physicochemical properties

The crystalline phase of the samples was identified by X-ray diffraction (XRD, D8 Discover, Bruker, USA) using Cu Kα radiation at 40 kV and 30 mA between 10 and 80° at a scan rate of 10° min^{-1}. The morphology of the samples was examined using scanning electron microscopy (SEM, NOVA600, FEI, USA). Fourier transform infrared spectroscopy (FT-IR) measurements of the samples were carried out on a Bruker Tensor 27 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALab250 XPS system (Thermo Fisher, USA) with an Al Kα source and a charge neutralizer, and all binding energies were referenced to the C 1s peak at 284.8 eV originating from the adventitious carbon layer. The Brunauer-Emmett-Teller (BET) surface area of the samples was determined using a NOVA2000e (Quantachrome Instruments, USA) apparatus based on N$_2$ adsorption-desorption isotherm measurements at 77 K. UV–Vis absorption spectra were obtained using a UV–Vis spectrophotometer (UV-2550, Shimadzu, Japan). BaSO$_4$ was used as reflectance standard in a UV–Vis diffuse reflectance experiment. High-resolution transmission electron microscopy (HRTEM) images of the samples were obtained (TEM, JEM-2100). Photoluminescence spectra (PL) of the samples were acquired using a Perkin Elmer LS55 fluorescence spectrophotometer at 293 K.

2.5. Photocatalytic activity

The photoinduced decomposition of phenol was monitored under ambient conditions and irradiation of a high-pressure mercury lamp (300 W) to evaluate the photocatalytic performance of the catalysts. The suspensions of the catalysts and phenol were kept in the dark for 40 min before testing to ensure adsorption-desorption equilibrium. After a certain duration of irradiation time, 4 mL aliquots of the suspension were collected and centrifuged. The supernatant liquid was analyzed using a UV–Vis spectrophotometer (UV1900/UV1901PCS, Shanghai Yoke Instrument Co., China). The concentration of residual phenol and the reaction intermediates, like catechol, benzoquinone and hydroquinone were calculated using methods reported elsewhere [24]. The trapping experiments for photogenerated radicals and holes were performed using a similar procedure as described above, except for the addition of isopropyl alcohol (IPA, hydroxyl radical scavenger), ammonium oxalate (AO, hole scavenger), or p-benzoquinone (BQ, superoxide radical scavenger), respectively, for the three intermediates.

3. Results and discussion

3.1. Structure of g-C$_3$N$_4$/TiO$_2$ nanocomposites

XRD measurements were conducted to determine the composition and crystal phase of pure TiO$_2$, g-C$_3$N$_4$ nanosheets, and g-C$_3$N$_4$/TiO$_2$ nanocomposites. As can be seen in Fig. 1, pure TiO$_2$ and the g-C$_3$N$_4$/TiO$_2$ nanocomposites showed strong diffraction peaks at 2θ = 25.34°, 37.78°, 48.02°, 53.92°, and 55.08°, which could be assigned to the