Water-mediated modulation of TiO2 decorated with graphene for photocatalytic degradation of trichloroethylene

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Abstract

The improvement of photocatalytic properties of TiO2 was achieved by using water-mediated TiO2 decorated with graphene (WTiO2-d-graphene) composites. This work describes the photocatalytic degradation of trichloroethylene (TCE) in the presence of WTiO2-d-graphene composites. WTiO2-d-graphene composite photocatalysts, containing different amounts of graphene, were prepared by facile ultrasonic assisted techniques and thermal reaction. The surface properties of these WTiO2-d-graphene composites were characterized by X-ray photoelectron spectroscopy (XPS). Peaks attributable to C\textsubscript{1s} (284.4 eV), denoted as the C1s spectrum, and C=O bonds (288.6 eV) appeared simultaneously in the XPS spectrum. It was inferred that this was due to the presence of Ti=O=C bonds. The photocatalytic properties were determined by monitoring the degradation of TCE in the headspace of the vial at different times using gas chromatography. From the results, it was apparent that the photocatalytic activities of WTiO2-d-graphene composites were higher than that of pure TiO2. This can be attributed to their ability to absorb light over a wider range of wavelengths.

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1. Introduction

In recent years, issues such as environmental pollution arising from scientific developments and rapid industrial growth, abnormal climate caused by depleting water resources and global warming, increased water scarcity and unreliable underground water have already caused our country to be designated as a water-stressed country. The combined effect of the aforementioned problems is such that the situation cannot be resolved by natural water cycle replenishment [1–3]. While water demand continues to increase, water supply, which depends mostly on rainfall, is rapidly diminishing due to worsening environmental issues. This has aggravated the situation by decreasing the amount of clean water available for human consumption. Therefore, as part of a combined effort towards addressing the clean water crisis, eco-friendly water treatment technologies are required in order to adequately process polluted water resources. To this end, the study and development of suitable photocatalysts that can decompose organic pollutants in water resources has become an urgent necessity and is currently being intensively pursued by the research community [4–7].

A photocatalyst is a substance that generates electrons and holes when it absorbs energy greater than the bandgap energy, and decomposes contaminants when the hole reacts with the hydroxyl ion in water. Titanium dioxide (TiO2), one of the widely used and well-studied photocatalysts, has excellent catalytic and economic efficiency, chemical stability, as well as eco-friendly characteristics [8,9].

TiO2 is non-toxic as a photocatalyst, and its use is far more economical than the currently used chlorination method to clean water. This is because it is cheap and convenient to store owing to its insolubility in water. A TiO2 photocatalyst has very strong oxidizing power and has been certified as one of the most appropriate processing technologies to decompose non-degradable material, including COD (Chemical Oxygen Demand) [10–13].

Recently, interest in graphene has increased due to its unique characteristics and its utility in several applications. There are several known synthetic methods for the manufacture of graphene [14]. The method that is considered most effective is the deoxidation of exfoliated graphene oxide. This method is cheap and can be carried out on a large scale [15–18]. Furthermore, interest in the synergistic effect of graphene-applied composites has recently been increasing. Graphene, a two dimensional carbonaceous

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material with atoms adapted in a honeycomb structure, has recently garnered much interest in the field of photocatalysis. The favorable energy levels of the photocatalyst and the intensive interface hybrid effect that appears within this material leads to a rapid charge separation. Recently, attempts have been made to tailor the electronic properties of the delocalized conjugated graphene in order to open up further possibilities of new graphene chemistry [19–21]. In recent years, TiO₂/carbon composites photocatalysts have attracted significant attention for their enhanced photocatalytic performance. When combining graphene with TiO₂ particles, the plethora of delocalized electrons in the π-conjugated electronic structure of graphene endows it with outstanding electronic conductivity [22].

The purpose of this study was to investigate the improvement in graphene-based TiO₂ photocatalysts and the photocatalytic decomposition of trichloroethylene (TCE). The study also seeks to determine the photocatalytic effect, if any, of graphene content on the photocatalytic degradation process. The graphene composites used were manufactured by deoxidating exfoliated graphene oxide in a process with water-mediated TiO₂, photocatalyst through ultrasonication and thermal reaction.

2. Experimental

2.1. Preparation of WTiO₂-d-graphene composites

The TiO₂ (P25) powder was purchased from Degussa Inc., while graphene oxide (GO) was manufactured from natural graphite powder using the Hummers method [23]. A highly efficacious photocatalyst was prepared by chemical reduction between water-treated TiO₂ and GO, followed by thermal treatment. Fig. 1 shows a schematic illustration of the synthetic route for WTiO₂-d-graphene composites. TiO₂ (0.4 g) was dispersed in 200 mL of distilled water by ultrasonication for 1 h. The water treatment increases the zeta potential, providing evidence for the formation of a positive charge on the TiO₂ surface [24]. The results of the zeta-potential (Nanotrac wave Q, Microtrac Co.) of the samples are listed in Table 1. Different amounts of the negatively charged GO suspension (5 mL, 0.1 mg/mL) were added to the positively charged water-mediated TiO₂ (WTiO₂) dispersion to obtain varying weight ratios of GO to WTiO₂ (0:1, 0.00125:1, 0.0025:1, 0.005:1, 0.01:1). The precipitate was obtained by using a centrifugal separator. The WTiO₂-d-graphene composite powders were acquired by calcinating the obtained precipitate in a high-temperature electric furnace at 400 °C under nitrogen gas for 2 h. The acquired WTiO₂-d-graphene composites were named TiO₂, WTiO₂-d-graphene-5, WTiO₂-d-graphene-10, WTiO₂-d-graphene-20, and WTiO₂-d-graphene-40.

2.2. Characterization

The change in the structure of each sample was examined by X-ray diffraction (XRD, Bruker D2 PHASER), while the morphology was checked using a scanning electron microscope (SEM, Hitachi SU8010). Information on chemical bond energy was obtained using X-ray photoelectron spectroscopy (XPS, VG Scientific Co. ESCA LAB MK-II).

2.3. Photocatalytic properties

The photocatalytic properties of each sample were investigated by monitoring the decomposition reaction of an aqueous solution.
of TCE (500 ppm, 99.99% purity, Sigma Aldrich) as the pollutant. After stirring the mixture of the WTiO2-d-graphene composite powder (8 mg) and TCE solution (100 mL) for 30 min in a dark room, a solar simulator (ABET Technology, USA) was used as the light source to irradiate the samples; the intensity of irradiation was 500 W/m². Wavelengths shorter than 440 nm were excluded using a glass filter. Analysis was carried out after 15, 30, 45 and 60 min of exposure to ultraviolet rays. To confirm photocatalytic degradation of TCE, the samples were analyzed by gas chromatography (DANI, Master GC).

3. Results and discussion

3.1. Characterization of WTiO2-d-graphene composites

Fig. 2 illustrates the XRD results of the manufactured WTiO2-d-graphene composites and TiO2. As shown in Fig. 2, the TiO2 and WTiO2-d-graphene composites are similar in their XRD patterns, implying a similarity in their crystal structures. Also, compared to graphene oxide, complete disappearance of the graphene oxide peak in all composites indicates successful conversion of graphene oxide to reduced graphene in the WTiO2-d-graphene composites. Fig. 3 illustrates a SEM image of the WTiO2-d-graphene composite. Fig. 3(a) shows the structure of the TiO2 nanoparticle; after thermal treatment for the reduction GO and the WTiO2, a TiO2 nanoparticle attached to the graphene table can be seen in Fig. 3(b). The XPS spectra of the WTiO2-d-graphene composites, used to determine the organizing element of WTiO2-d-graphene composites, bond status, and energy levels, are shown in Fig. 4(a). As can be seen in Fig. 4(a), the peaks corresponding to Ti2p, O1s, and C1s appeared around 480, 520, and 280 eV, respectively. Fig. 4(b) indicates that the intrinsic peak of C–C (284.4 eV) denoted as the C1s spectrum and C–O (288.6 eV) could be observed simultaneously. It can be inferred that these observations are due to the presence of Ti–O–C bonds [25,26]. As this phenomenon, below numeric structure exists in the atom of carbon inherently and it is judged due to the effect of Ti–O–C bonds which appears newly. Fig. 5 shows the diffuse reflectance spectrum of the TiO2 and WTiO2-d-graphene composites. The graphene attachment onto surface of TiO2 allows the energy state change of conduction band by the interaction between unpaired π electrons and Ti atoms, resulting in the shift of the band-edge and the considerable bandgap reduction of WTiO2-d-graphene composites. Thus, it can be observed that TiO2 absorbs UV light, whereas the WTiO2-d-graphene composites absorb over a wide wavelength range, including visible light. Fig. 7 illustrates plots of the Kubelka–Munk remission function corresponding to the spectrum [27,28]. While the bandgap of TiO2 (P25), as determined from the spectrum, was 3.25 eV, the bandgap for both WTiO2-d-graphene-20 and WTiO2-d-graphene-40 was significantly reduced to 2.59 eV.

3.2. Degradation of TCE

The photocatalytic properties of the WTiO2-d-graphene composites were analyzed by observing the removal of TCE from the reaction medium using gas chromatography. Each sample was added to a 500 ppm TCE solution, and the resultant mixture was irradiated with light. The photocatalytic reaction of TiO2 proceeds via the generation of electrons and positive holes in TiO2 particles that have been irradiated with light. The chemical processes that take place are represented by Equations (1)–(5) [29,30].

\[ \text{TiO}_2 + \text{Solar light} \rightarrow \text{TiO}_2 + \left( e_{CB}^+ + h_{VB}^- \right) \]  

\[ \text{TiO}_2 \left( e_{CB}^+ + h_{VB}^- \right) \rightarrow \text{heat} \quad \text{(recombination)} \]  

\[ \text{TiO}_2 \left( h_{VB}^+ \right) + \text{OH}^- \rightarrow \text{OH}^- \]  

\[ \text{TiO}_2 \left( e_{CB}^- \right) + \text{O}_2 \rightarrow \text{O}_2^- \]  

\[ \text{TCE} + \text{OH}^- \quad \text{or} \quad \text{O}_2^- \rightarrow \text{CO}_2 + \text{HCl} \quad \text{(Mineralization)} \]
During the initial stage of photolysis, electrons and positive holes are generated in light-irradiated TiO$_2$ particles according to the reaction in Equation (1). In the next step, TiO$_2$ particles are bonded with release of heat as shown in Equation (2). However, if there is any dissolved oxygen or an electron donor, a hydroxyl radical (OH$^\cdot$) is generated by the reaction of the positive holes ($h^+$) in the valence bands with the active hydroxyl groups (OH) on the surface or of H$_2$O, as in Equation (3). During the next stage, as shown in Equation (4), electrons ($e^-$) are generated in the conduction bands by the photolysis reaction, and superoxide (O$_2^-$) is formed in a reaction with dissolved oxygen. Their (OH$^\cdot$ or O$_2^-$) radical can sustain the mineralization process in Equation (5).

Fig. 6 shows the change in TCE concentration with respect to reaction time for comparison of photocatalytic efficiency. Fig. 7 shows the graph used to calculate the specific reaction rate in order to compare photocatalytic efficiency quantitatively. As can be seen, WTiO$_2$-d-graphene-20 showed a TCE removal efficiency of about 75%. Removal of TCE by WTiO$_2$-d-graphene composite samples under visible light is known to follow the Langmuir–Hinshelwood rate Equation (6) [31,32]. The rate constant was determined from the graph in Fig. 7 using the TCE photolysis rate equation. The terms $C_0$ and $C$ refer to the initial TCE concentration and TCE concentration after a radiation time ($t$), respectively. $K_{app}$ is...
the pseudo first order rate constant \( (\text{min}^{-1}) \). This rate constant is dependent on reaction conditions such as temperature, wavelength of irradiated light, and pH; i.e., the larger these values are, the higher the reactivity is. The pseudo first order rate constant for the efficient removal of TCE, determined from Fig. 7, were observed to be \( K_{\text{app}} \) (P25) = 0.0068/min, \( K_{\text{app}} \) (WTiO\(_2\)-d-graphene-5) = 0.0154/min, \( K_{\text{app}} \) (WTiO\(_2\)-d-graphene-10) = 0.0162/min, \( K_{\text{app}} \) (WTiO\(_2\)-d-graphene-20) = 0.0225/min, and \( K_{\text{app}} \) (WTiO\(_2\)-d-graphene-40) = 0.018/min. As can be seen, WTiO\(_2\)-d-graphene-20 exhibited the highest rate constant. The rate constants and regression coefficients of the samples are listed in Table 2.

\[
\ln \frac{C}{C_0} = -K_{\text{app}} t
\]  

(6)

From the results, it is apparent that the amount of degraded TCE follows the order TiO\(_2\) (30%), WTiO\(_2\)-d-graphene-5 (60%), WTiO\(_2\)-d-graphene-10 (62%), WT- WTiO\(_2\)-d-graphene-20 (75%), and WTiO\(_2\)-d-graphene-40 (65%). From the experimental results, it can be concluded that the new Ti–O–C bond formed through the complexion of TiO\(_2\) and graphene leads to a decrease in the bandgap, and the subsequent expansion in the range of absorbed wavelengths increases the photocatalytic efficiency.

4. Conclusions

A facile synthesis of WTiO\(_2\)-d-graphene composites was accomplished via a thermal reaction using commercially available TiO\(_2\) nanoparticles (P25), and their photocatalytic activity in terms of volatile organic compound (VOC) degradation was measured under visible light irradiation. We found that WTiO\(_2\)-d-graphene-20, synthesized from a 0.005:1 weight ratio of GO to WTiO\(_2\), demonstrates excellent photocatalytic activity under visible light for the degradation of TCE, with a rate constant much higher than that of P25. The photocatalytic activity of WTiO\(_2\)-d-graphene-20 was the highest of all samples. The high VOC degradation efficiency of WTiO\(_2\)-d-graphene-20 can be attributed to its ability to absorb a wider range of wavelengths, including visible light, and its low bandgap. Although WTiO\(_2\)-d-graphene-40 also had Ti–O–C bonds and low bandgap characteristics, its VOC degradation activity was lower than anticipated due to its lower rate constant caused by the increased graphene content. This results in increased light reaping competition between TiO\(_2\) and graphene. It can be concluded, therefore, that the low bandgap and suitable graphene content in the WTiO\(_2\)-d-graphene-20 sample had the most favorable effect on photocatalytic degradation properties.

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