Article

Strainer-Separable TiO\textsubscript{2} on Halloysite Nanocomposite-Embedded Alginate Capsules with Enhanced Photocatalytic Activity for Degradation of Organic Dyes

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Abstract: Photocatalysis driven by natural sunlight is an attractive approach to removing pollutants from wastewater. Although TiO\textsubscript{2}-based photocatalysts using various support nano-materials with high catalytic activity and reusability have been developed for purifying wastewater, the centrifugal separation methods used for the nanocatalysts limit their use for treating large amounts of water. Here, we prepared a TiO\textsubscript{2} nano-catalyst supported on a halloysite nanotube (HNT)-encapsulated alginate capsule (TiO\textsubscript{2}@HNT/Alcap) to recapture the catalysts rapidly without centrifugation. The structure of TiO\textsubscript{2}@HNT/Alcaps was characterized by X-ray diffraction, SEM, and TGA. In our system, the combination of HNTs and alginate capsules (Alcaps) improved the efficiency of adsorption of organic pollutants to TiO\textsubscript{2}, and their millimeter-scale structure allowed ultra-fast filtering using a strainer. The TiO\textsubscript{2}@HNT/Alcaps showed ~1.7 times higher adsorption of rhodamine B compared to empty alginate capsules and also showed ~10 and ~6 times higher degradation rate compared to the HNT/Alcaps and TiO\textsubscript{2}/Alcaps, respectively.

Keywords: photocatalyst; halloysite nanotubes; titanium oxide; alginate capsule; strainer separation; photocatalytic effect; degradation; organic dyes

1. Introduction

Photocatalysis driven by inexhaustible solar energy may be well-suited to the issue of wastewater purification in the textile industry through an eco-friendly and efficient method \cite{1,2}. As a photocatalyst, anatase TiO\textsubscript{2} nanoparticles have shown high activity for the degradation of organic dyes and toxic molecules in the aquatic environment \cite{3–5}. However, their innate toxicity incurs other burdens for environmental health and safety and limits their large-scale use. Thus, to minimize environmental burden and optimize function, both the TiO\textsubscript{2} catalyst retrieval strategy and catalytic activity need improvement for practical use.

For enhancing TiO\textsubscript{2} catalytic activity, catalyst immobilization on supporting materials has been applied to prevent aggregation and sustain activity. Among the many support materials available, halloysite nanotubes (HNTs) that consist of aluminosilicate clay minerals with a tubular bilayer structure have contributed to the enhanced catalytic activity...
of TiO$_2$ [6–9]. Additionally, it is spotlighted as a naturally occurring porous material for activity enhancement through the adsorption of contaminants induced by electric charges on the surface and inside of HNTs. The negatively charged Si-O-Si surface structure and positively charged Al-OH internal structure can adsorb cationic dyes (methylene blue, neutral red, crystal violet, and malachite green) and anionic dyes (congo red and methyl orange), respectively. [10–16] Although several TiO$_2$@HNTs composites have shown enhanced activity in photocatalytic degradation of organic pollutants [17–23], their nanosize still requires complicated separation processes, hindering the catalysts’ retrieval.

From the perspective of reuse and easy separation, alginate has been employed as a supporting material. Alginate, a component extracted from natural algae, is a linear copolymer composed of (1,4) linked $\alpha$-L-guluronic acid and $\beta$-D-mannuronic acid [24]. In previous research, alginate has adsorbed dyes and heavy metals, purifying the wastewater [25,26]. For usability, gelated alginate particles have been prepared by combining alginate polymers via cations [27]. By adding the catalysts during the gel formation, TiO$_2$ nanoparticles can be encapsulated on the gelated particle. These alginate capsules containing TiO$_2$ improved the degradation efficiency of methylene blue and methyl orange under UV conditions and could be easily separated by strainer [28,29] in a short time. Despite the easy separation resulting from the regulated millimeter size of alginate gel, their low activity requires the use of a large amount of catalyst, decreasing the purifying efficiency. For practical use of the photocatalyst, both the enhancement of catalytic activity and the feature of high reusability are required.

In this study, we prepared an alginate capsule including TiO$_2$ nanoparticles on HNTs (TiO$_2$@HNTs/Alcaps) to achieve both improved photocatalytic activity and ultra-fast catalyst separation (Figure 1). There are different chemical methods used for the synthesis of uniform micro- and nano-particles and their composites: for example, the micro-emulsion method [30], co-precipitation method [31], sol-gel method [32], and solvothermal/hydrothermal method with different surfactant and caping agents [33]. In this work, a TiO$_2$ on HNTs (TiO$_2$@HNTs) composite was synthesized by a simple sol-gel method using titanium(IV) isopropoxide (TTIP). The mixed solution of alginate and TiO$_2$@HNTs was added dropwise to the CaCl$_2$ solution, forming millimeter-sized capsules by crosslinking. Our capsules can be rapidly separated from the reaction mixture by a strainer with a sub-millimeter mesh size. Since the centrifugation of a large amount of wastewater would require huge equipment and energy in quantity, the nano-catalysts needed for separation processes including centrifugation offer limited use in large-scale processing. However, our catalysts of millimeter size can be easily separated from the wastewater without centrifugation, so that they can be applied for practical use regardless of the scale of operation. Additionally, comparing to the other catalysts of millimeter size, our catalysts showed much higher photocatalytic activity, allowing for the use of smaller quantities of catalyst. The dye adsorption efficiency improved by 1.7 times through the encapsulation of TiO$_2$@HNTs compared to the alginate gel. The combination of TiO$_2$ nanoparticles, HNTs, and encapsulation in alginate gel promoted photocatalytic activity up to ~10 and ~6 times compared to HNT/Alcaps and TiO$_2$/Alcaps, respectively, due to their synergistic effect.
Figure 1. Design of TiO$_2$@HNTs/Alcaps and graphical scheme of their easy separation. The combination of TiO$_2$ nanoparticles, HNTs, and encapsulation in alginate gel improves the photocatalytic activity through enhanced adsorption efficiency and high reusability through the easy separation using a strainer.

2. Materials and Methods

2.1. Preparation of TiO$_2$@HNTs Composite

TiO$_2$ nanoparticles on the HNT surface were synthesized by the sol-gel method [19,34] (Figure 2a). In brief, 5 mL of TTIP was dissolved in 24 mL of isopropanol. To the 16 mL of mixture, 16 mL of water was added. Then, 16 mL of isopropanol and 0.2 mL of nitric acid were added dropwise to the round-bottom flask containing the reaction mixture, with vigorous stirring. After 2 h stirring, 1.3 g of HNT was added, with 2 h stirring. Through 1-day aging at room temperature, the TiO$_2$@HNTs were formed. Through centrifugation (8000 rpm for 10 min) and several washing steps with ethanol/water mixture (1:1), the TiO$_2$@HNTs were purified. To gain the powder form of catalysts, the samples were dried in a vacuum oven at 85 °C for 12 h and then were ground and calcined at 350 °C for 2 h (2 °C/min rates) under ambient conditions. The synthesized catalysts were analyzed by high-resolution TEM (Figure S1) and showed successful immobilization and the characteristic anatase structure of TiO$_2$. From the XRD spectrum of TiO$_2$ nanoparticles, HNT, and TiO$_2$@HNT, we could also confirm the adsorption of TiO$_2$ nanoparticles on the HNTs (Figure S2). In the spectrum of TiO$_2$@HNT, the typical peaks of HNT and TiO$_2$ crystal structure were observed.

2.2. Preparation of TiO$_2$@HNTs/Alcaps Composite

TiO$_2$@HNTs were readily immobilized in calcium alginate capsules (~2.5 ± 0.2 mm) using a simple dropping technique with a syringe [28,35] (Figure 2b). A 2.0 g portion of the TiO$_2$@HNTs was dispersed in DI-water (~100 mL) to attain a 2% solution (w/w). The solution was heated to 60 °C, with stirring for 30 min. A 2 g portion of sodium alginate was dissolved in the solution to result in the mass ratio between alginate and TiO$_2$@HNTs being 1:1. Using a syringe, we dropped the polymer solution into a 0.1 M CaCl$_2$ solution during gentle stirring at room temperature. After aging for several hours, the obtained capsules were washed with DI-water and dried in an oven at 60 °C for 12 h.
Figure 2. Synthesis processes of TiO$_2$@HNTs nanocomposites and TiO$_2$@HNTs/Alcaps: (a) TiO$_2$ nanoparticles on the HNT surface were synthesized using the sol-gel method. (b) The alginate capsules were prepared by dropping the mixture of alginate-TiO$_2$@HNTs to CaCl$_2$ solution. The calcium ions binding to alginate polymer chain form the cross-linked gel. (c) Photos of 1: alginate gel; 2: HNT/Alcap; 3: TiO$_2$/Alcap; and 4: TiO$_2$@HNT/Alcap.

2.3. Structural Analysis of TiO$_2$@HNT/Alcaps

The morphology of capsules was analyzed using a scanning field emission electron microscope (FE-SEM, Hitachi, s-4800 instrument). For the measurement, the TiO$_2$@HNT/Alcap sample was freeze-dried and then coated with platinum. To examine thermal degradation characteristics of alginate gel and TiO$_2$@HNTs/Alcaps, thermogravimetric analysis (TGA) was performed using the SDT Q600, TA Instruments (Heating: 10 °C/min, $N_2$ = 100 mL/min, 800 °C). UV-vis measurements were performed with Evolution 60S (Thermo Fisher Scientific: Waltham, MA, USA).

2.4. Measurement of Rhodamine B Adsorption

The dye adsorption experiments were evaluated by adding 0.1 g of alginate, HNTs/Alcap, TiO$_2$/Alcaps, and TiO$_2$@HNTs/Alcaps to 20 mL of 5.0 mg/L rhodamine B solution. The absorbance at 554 nm of the rhodamine B solution was monitored under stirring (800 rpm) conditions for 1 h. To calculate the removal efficiency (%), $q_t$ (the rhodamine B adsorption capacity, unit: mg/g), $q_e$ (the rhodamine B adsorption capacity at equilibrium, unit: mg/g), and $k_2$ (rate constant, unit: g/mg min), we used the following the equations [36].

\[
\text{Removal efficiency} \% = \frac{C_0 - C_e}{C_0} \times 100
\]

\[
q_e \text{ (mg/g)} = \frac{(C_0 - C_e)V}{m}
\]

\[
q_t \text{ (mg/g)} = \frac{(C_0 - C_t)V}{m}
\]
\[
t = \frac{1}{q_{	ext{t}}} = \frac{1}{k_2 q_e^2 + q_e} t \quad (4)
\]

where \(C_0\) and \(C_t\) are the concentrations of dye at initial and \(t\) time (unit: mg/L), respectively; \(m\) and \(V\) are the weight of catalyst (unit: g) and the volume of dye solution (unit: L), respectively.

2.5. Photodegradation of Rhodamine B Using the Capsules

For the photocatalytic dye degradation of rhodamine B, 0.1 g of alginate, HNTs/Alcaps, TiO\(_2\)/Alcaps, and TiO\(_2\)@HNT/Alcaps were added to 20 mL of 5.0 mg/L rhodamine B solution, respectively. The solutions were stirred in the dark for 1 h. Then, we applied UV light (250 W, 356 nm) using a lamp (Ushio-SP9) to monitor the change of absorbance induced by the dye degradation. The dye degradation efficiency (%) and the rate constant were obtained using the equations below [37].

\[
\text{Degradation efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (5)
\]

\[
\ln \frac{C_0}{C} = k_1 t \quad (6)
\]

where \(C_0\) and \(C\) are the dye concentrations at initial and final times (unit: mg/L) and \(k_1\) is the rate constant of the pseudo first order (unit: min\(^{-1}\)).

3. Results and Discussion

3.1. Morphology of TiO\(_2\)@HNT/Alcaps Capsule

To confirm the encapsulation of TiO\(_2\)@HNTs in the alginate gel, we observed their morphology using FE-SEM. In the images of TiO\(_2\)@HNT/Alcaps, the smallest capsule size was \(~2.5 \pm 0.2\) mm (Figure 3a). Although the TiO\(_2\)@HNTs catalysts were barely seen on the capsule surface (Figure 3b,c), a large number of catalysts were observed in the inside of the capsule (Figure 3d–f). TiO\(_2\)@HNTs with lengths of 200–500 nm were observed and TiO\(_2\) nanoparticles existed on the HNTs’ surface. We assumed that this morphology of TiO\(_2\)@HNT/Alcaps could prevent the sweep of photocatalysts from the capsules. The TEM images of the TiO\(_2\)@HNT clearly show the immobilization of TiO\(_2\) nanoparticles on the HNTs and the crystal structure of TiO\(_2\) nanoparticles (Figure S1). In the image, \(~10\) nm–sized TiO\(_2\) nanoparticles were immobilized on the surface of HNTs, and the crystal structure of the nanoparticles showed the (101) phase, typical anatase TiO\(_2\) structure.

![Figure 3. Scanning electron microscopy images of TiO\(_2\)@HNT/Alcaps. Surficial morphology (a–c) and the interior structure of TiO\(_2\)@HNT/Alcaps (d–f) were visualized.](image-url)
3.2. Thermogravimetric Analysis of TiO$_2$@HNT/Alcaps

The thermal degradation characteristics of TiO$_2$@HNT/Alcaps and pure alginate gel as controls were measured through TGA analysis (Figure 4). In the range of 0 to 200 $^\circ$C, the alginate gel and TiO$_2$@HNT/Alcaps showed decompositions of 9.83% and 5.65%, respectively, indicating the evaporation of water adsorbed in the alginate capsule [38]. We observed decompositions of 34.59% of alginate gel and 17.20% of TiO$_2$@HNT/Alcaps in the range of 200 to 300 $^\circ$C. This decomposition results from the decarboxylation in the glycoside chain of alginate [39]. In the range of 450–550 $^\circ$C and the resultant dihydroxylation, 5.86% of alginate gel and 5.07% of TiO$_2$@HNT/Alcaps were decomposed [40,41]. We assumed that the reason for the higher decomposition of alginate gel is that the pure alginate gel possesses more alginate monomer including hydroxyl groups than TiO$_2$@HNT/Alcaps at the same weight. The remaining amounts were 33.3% for alginate gel and 59.5% for TiO$_2$@HNT/Alcaps. From the 26.2% difference between residues, we estimated the weight % of TiO$_2$@HNTs in TiO$_2$@HNT/Alcaps. Based on the peak intensity of the XRD spectrum of TiO$_2$, HNTs, and TiO$_2$@HNTs, we could roughly confirm that our TiO$_2$@HNT/Alcaps consisted of 9% HNTs, 17% TiO$_2$, and 74% alginate gel.

3.3. Adsorption and Kinetic Studies of Rhodamine B Using TiO$_2$@HNT/Alcaps

After material characterizations, we probed the rhodamine B adsorption and decomposition kinetics of the pure alginate gel, HNTs/Alcap, TiO$_2$/Alcap, and TiO$_2$@HNT/Alcap under dark conditions to prevent the photodegradation of dyes (Figure 5a). In the adsorption curve of rhodamine B for each sample, the adsorption amount increased significantly up to 10 min and stabilized after 30 min. For all samples, the rate of rhodamine B removal rapidly increased initially but steadily decreased as it reached an equilibrium state. In the early stage, a large amount of rhodamine B was adsorbed promptly because of the sufficient availability of adsorption sites on the alginate gels and HNT surface. Table 1 summarizes the adsorption amount and rate constants. The adsorption curve of the dye mainly follows pseudo-second-order kinetics (Figure 5b) [42]. The adsorption amount of rhodamine B for two hours showed that the $q_e$ of TiO$_2$@HNT/Alcap was 0.1704, which was about 1.7 times higher than that of the bare alginate capsules ($q_e$ 0.1026). This result indicated that TiO$_2$@HNT/Alcap was 0.1704, which was about 1.7 times higher than that of the bare alginate capsules ($q_e$ 0.1026). This result indicated that the TiO$_2$@HNTs inside
the alginate gel could expand the surface area to bind the dye molecules, enhancing the adsorption ability.

![Graph showing adsorption and kinetic studies](image)

**Figure 5.** (a) Adsorption of rhodamine B onto alginate gel, HNT/Alcap, TiO$_2$/Alcap, and TiO$_2$@HNT/Alcaps. (b) Pseudo-second-order kinetics for rhodamine B adsorption on the catalysts.

| Sample          | $q_e$ (mg/g) | $k_2$ (g/mg min) | $R^2$  |
|-----------------|-------------|------------------|--------|
| Alginate        | 0.1026      | 1.9690           | 0.9967 |
| HNT/Alcap       | 0.1191      | 1.2501           | 0.9961 |
| TiO$_2$/Alcap   | 0.1420      | 0.7619           | 0.9948 |
| TiO$_2$@HNT/Alcap | 0.1704  | 0.5635           | 0.9932 |

### 3.4. Photocatalytic Degradation of Rhodamine B Using TiO$_2$@HNT/Alcaps

After confirmation of enhanced adsorption of the catalysts, we monitored the photocatalytic degradation of the rhodamine B under UV conditions (Figure 6a). The solution of rhodamine B and the catalysts became transparent, indicating the photolysis of dyes after 2 h. The TiO$_2$@HNT/Alcaps showed a 97.65% decomposition of rhodamine B for 120 min, while the alginate gel, HNT/Alcap, and TiO$_2$/Alcap showed only a maximum of 50% degradation. Since the HNT/Alcaps can adsorb the dye molecules but are unable to decompose the dye due to the lack of photocatalysts, only adsorption occurred, without photolysis. Although the TiO$_2$/Alcaps showed higher degradation efficiency than the HNT/Alcaps, they showed only 50% photocatalytic efficiency compared to the TiO$_2$@HNT/Alcaps. From this result, we assumed that the alginate gels provide a supporting site facilitating the prevented aggregation of TiO$_2$ nanoparticles but that they cannot offer the effect of enhanced catalytic activity, unlike the HNTs. In the case of the TiO$_2$@HNT/Alcaps, the alginate gel provides a millimeter-sized structure for easy separation; the HNTs offer enhanced adsorption efficiency, inducing the improved photocatalytic activity, and the TiO$_2$ nanoparticles as photocatalysts take charge of photolysis. This hierarchical structure based on their function allowed the TiO$_2$@HNT/Alcaps to boost photocatalytic activity.
Figure 5. (a) Adsorption of rhodamine B onto alginate gel, HNT/Alcap, TiO$_2$/Alcap, and TiO$_2$@HNT/Alcap. (b) Pseudo-second-order kinetics for rhodamine B adsorption on the catalysts.

Table 1. Pseudo-second-order kinetic model parameters of rhodamine B adsorption by catalyst composite capsules.

| Sample          | $q_e$ (mg/g) | $k_2$ (g/mg min) | $R^2$   |
|-----------------|-------------|------------------|---------|
| Adsorption      |             |                  |         |
| Alginate gel    | 0.1026      | 1.9690           | 0.9967  |
| HNT/Alcap       | 0.1191      | 1.2501           | 0.9961  |
| TiO$_2$/Alcap   | 0.1420      | 0.7619           | 0.9948  |
| TiO$_2$@HNT/Alcap | 0.1704    | 0.5635           | 0.9932  |

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Figure 6. (a) Photocatalytic degradation of rhodamine B with various alginate/catalyst hybrid capsules under UV light. (b) Pseudo-first-order kinetic curves of photocatalytic degradation of rhodamine B, depending on catalysts.

From kinetic analysis, we could confirm that the catalysis followed the pseudo-first-order kinetics. (Figure 6b and Table 2) [43]. The rate constant $k_1$ of TiO$_2$@HNT/Alcap was 10 times and 6 times higher than that of HNT/Alcap and TiO$_2$/Alcap, respectively, showing improved degradation efficiency.

Table 2. Pseudo-first-order kinetic parameters of photocatalytic degradation of rhodamine B by catalyst composite capsules.

| Sample          | Dye removal % | $k_1$ (min$^{-1}$) | $R^2$   |
|-----------------|---------------|-------------------|---------|
| UV irradiation  |               |                   |         |
| Dye             | 9.980         | 0.0007            | 0.9918  |
| Alginate gel    | 20.30         | 0.0017            | 0.9963  |
| HNT/Alcap       | 38.01         | 0.0031            | 0.9943  |
| TiO$_2$/Alcap   | 51.32         | 0.0052            | 0.9933  |
| TiO$_2$@HNT/Alcap | 97.65      | 0.0312            | 0.9939  |

3.5. Catalyst Recycling for Photocatalytic Degradation

In the catalyst recycling experiment, our catalysts were separated using a strainer after photodegradation under UV conditions. The catalysts’ separation time from the reaction mixture was only one minute using a strainer (mesh size: 1 mm). The separation time can be shortened by increasing the water flow rate and broadening the mesh size of the strainer. Although the TiO$_2$@HNT/Alcap had lower photocatalytic activity ($k_1$: 0.0321 min$^{-1}$) compared to the nanocatalysts (TiO$_2$@HNTs, $k_1$: 0.1206 min$^{-1}$) [19], our catalysts possess economic benefits for the treatment of a large amount of wastewater, considering that the centrifugation of a large amount of wastewater would require huge equipment and energy. Without the centrifugal separation process, the TiO$_2$@HNT/Alcap could maintain their photocatalytic activity at under 10% loss in five cycle reuses, showing the potential of reusable catalysts for industrial use (Figures 7 and S3).
In this work, we encapsulated the TiO$_2$@HNTs catalysts into alginate gel for fast separation. The hybrid capsule was analyzed by FE-SEM to confirm the alginate surface morphology and the encapsulation of TiO$_2$@HNTs inside the gels. The thermal decomposition properties and the composition ratio of the capsule were confirmed by TGA analysis. The adsorption of rhodamine B using TiO$_2$/HNT@Alcaps increased by 1.7 times over that of the alginate gel, indicating the expansion of the surface area to which the dye can bind. The photocatalytic activity of TiO$_2$/HNT@Alcaps under UV conditions was improved by six times compared to that of TiO$_2$/Alcaps. The retrieval strategy was demonstrated by easy and fast separation of our catalyst in five recycling tests with a 1 min separation time using a strainer. The stability of the catalyst was demonstrated through its high removal efficiency, with under 10% loss of function over five times of recycled use. This designed catalyst with retrieval capacity and catalytic efficiency can be applied to purify an aquatic environment contaminated with organic pollutants for the textile industry.

4. Conclusions

In this work, we encapsulated the TiO$_2$@HNTs catalysts into alginate gel for fast separation. The hybrid capsule was analyzed by FE-SEM to confirm the alginate surface morphology and the encapsulation of TiO$_2$@HNTs inside the gels. The thermal decomposition properties and the composition ratio of the capsule were confirmed by TGA analysis. The adsorption of rhodamine B using TiO$_2$/HNT@Alcaps increased by 1.7 times over that of the alginate gel, indicating the expansion of the surface area to which the dye can bind. The photocatalytic activity of TiO$_2$/HNT@Alcaps under UV conditions was improved by six times compared to that of TiO$_2$/Alcaps. The retrieval strategy was demonstrated by easy and fast separation of our catalyst in five recycling tests with a 1 min separation time using a strainer. The stability of the catalyst was demonstrated through its high removal efficiency, with under 10% loss of function over five times of recycled use. This designed catalyst with retrieval capacity and catalytic efficiency can be applied to purify an aquatic environment contaminated with organic pollutants for the textile industry.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12142361/s1, Figure S1: High-resolution TEM images of TiO$_2$@HNT nanocomposites, Figure S2: The XRD patterns of TiO$_2$, HNTs, and TiO$_2$@HNTs, Figure S3: Catalytically recyclable degradation of dye with the TiO$_2$@HNTs/Alcaps; Table S1: Pseudo-second-order kinetic model parameters of rhodamine B adsorption by catalyst composite capsules; Table S2: Pseudo-first-order kinetic parameters of photocatalytic degradation of rhodamine B by catalyst composite capsules.

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