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Novel alginate immobilized TiO₂ reusable functional hydrogel beads with high photocatalytic removal of dye pollutions

Abstract: TiO₂ semiconductor photocatalysis is an effective technology for the treatment of wastewater containing organic dye pollutants, which has been received extensive focus. However, the problems in the recovery and reutilization process impede the large-scale applications of particulate photocatalytic materials. Herein, a macro sized hydrogel bead loaded with nano TiO₂ powder was successfully prepared by taking advantage of the cross-linking and gel property of alginate salt, which could form egg-box structure naturally when Na⁺ ions in sodium alginate (SA) were replaced by divalent ions such as Cu²⁺, Co²⁺, and Sr²⁺ ions. The photocatalytic degradation rate of methyl orange (MO) solution in the presence of the hydrogel beads reaches 99% within 60 min under the ultraviolet light irradiation, which is competitive with that of TiO₂ nano powder. Furthermore, the hydrogel beads prepared by this strategy maintain over 95% photocatalytic degradation rate after 10 cycles of degradation process. The results indicate that the network structure of alginate could immobilize and disperse TiO₂ particle effectively, and it is readily for the spherical beads to contact and harvest the light, making the alginate beads have excellent photocatalytic functions. Also, the alginate based beads integrate good performance with high stability and excellent recyclability perfectly.

Keywords: alginate; hydrogel beads; photocatalysis; TiO₂.

1 Introduction

In recent years, semiconductor photocatalysis technology has shown great advantages as a solution for the light energy utilization, wastewater treatment and other environmental problems [1, 2]. Many nanostructured photocatalysts such as g-C₃N₄, ZnO, and perovskite materials have shown superior electrocatalytic and photocatalytic activity for hydrogen storage and water treatment [3–5]. Among which, nano TiO₂ with moderate price, high chemical stability, photostability, nontoxicity, and water-insoluble under most environmental conditions has been proved as one of the most of widely studied and promising semiconductor photocatalysts in oxidative degradation of organic dyes, water purification and environmental wastewater treatment fields [6–8]. The photogenerated carriers generated by TiO₂ under the excitation of ultraviolet (UV) light undergo redox reaction with the pollutant molecules adsorbed on their surface, thus realizing the catalytic degradation of water pollutants [9–11]. Since TiO₂ often exists in the form of suspended particles in water during the photocatalytic process, separation and recovery of the photocatalyst particles from the purified liquid requires time-consuming and expensive post-process, which brings additional cost and limits their further practical applications [12–14]. Some researchers have prepared nanocomposites containing magnetic particles to reduce the weight loss of the particulate photocatalysts during the cyclic photocatalytic degradation process. The maintained photocatalytic degradation capacity of the materials is not more than 85% after multiple cycles [15–17]. Therefore, it is an urgent topic to obtain photocatalysts with good reusability and high photocatalytic efficiency retention. Another way to improve the recycling performance is to provide bulk carriers for TiO₂ nanoparticles with more practical and safe macroscopic structures, such as glass, fiber, or zeolite substrate [18–20]. However, compared with pure TiO₂ nano-powder material, the decreased specific surface area of bulk material, poor compatibility between carrier materials, and TiO₂ have become factors that reduce their photocatalytic performance [21].
Alginates are a natural polysaccharide polymer extracted from the cell wall of brown algae, which is composed of β-D-mannuronic acid (m) and α-l-guluronic acid (g) [22–24]. Na+ ions in the soluble sodium alginate (SA) can be substituted by divalent or multivalent cations such as Cu2+, Sr2+, and Co2+ ions in palaeuronic acid, and then they join these palaeuronic acid groups together to form egg-box structured insoluble alginate gels [25–27]. The porous three-dimensional structure and polar functional groups endorse hydrogel outstanding performance on scavenging heavy metal ions from wastewater or adsorbing many kinds of liquid pollutants [28–30]. Alginate gel materials demonstrate good characters of nontoxicity [31], simple production [32], biodegradability [33], biocompatibility [34] and so on, they have been innovatively applied to immobilize some adsorbents (such as activated carbon) to help remove dyes, pigments or heavy metals from aqueous solutions. However, the main drawback of the gels based on SA is the weak strength and stability due to the macroporous structure in the gel network [35, 36]. Although the access of the nanograins in SA matrix could give it definite functionality, how to keep the good photocatalytic performance without losing the stability and recycling ability of the SA based gels is worthy of further study.

Previous study [37] in our group has shown that the calcium alginate (CA) hydrogel beads prepared by crosslinking process have an egg-box structure, where the super hydrophilic group exists inside the gel, and the surface is super hydrophobic. In the meantime, the ultra-high water content and surface hydrophobicity makes it easy to exist in a spherical hydrogel shape. The higher transparency greatly increases the contact area between the beads and dyes or external light sources. By designing the porous microstructure of macro scaled beads and adjusting the loading of photocatalytic powder, the high recovery efficiency and photocatalytic performance of photocatalytic materials are achieved simultaneously.

Inspired by the above research, in this work, the commercialized TiO2 (P25) materials were utilized as photocatalytic powders and loaded among the alginate salt networks which were crosslinked in to spherical beads by different divalent ions. During the gelatin process, TiO2 particles could be immobilized and dispersed effectively in the network structure of alginate, and the spherical shape leads to a good contact between the beads and the dyes or light sources. The adsorption ability and photocatalytic degradation ability of the hydrogel beads were further explored, which indicates good cyclic performance and potential applications in the wastewater treatment fields.

## 2 Materials and methods

### 2.1 Materials

Commercial TiO2 (Macklin Company, P25, Degussa, 20 nm) and other raw materials such as analytically pure sodium alginate (SA), CaCl2, Sr(NO3)2, CuCl2 (Tianjin Guangfu Fine Chemicals Co., LTD) and de-ionized water were purchased and used without further purification.

### 2.2 Preparation of TiO2-SA beads

TiO2 powders were introduced into SA hydrogels by sol–gel process. Typically, P25 typed TiO2 (1.2 g) powders were firstly dispersed in de-ionized water (60 mL) to form a homogeneous suspension under magnetically stirring and the further ultrasonic treatment. The concentration of TiO2 is of 2 wt%. Then, 1.2 g of SA powder was added into the suspension (2 wt%) under continuous stirring. The viscous mixture drops were injected into 50 mL of aqueous solution of CaCl2, CoCl2, and Sr(NO3)2 by using a plastic syringe, respectively. These TiO2-SA hydrogel beads were formed quickly and then aged overnight. The obtained hydrogel beads in CuCl2, CoCl2, and Sr(NO3)2 solutions are named as Cu-TiO2, Co-TiO2, and Sr-TiO2, respectively. The beads without TiO2 correspondingly are named as Cu-SA, Co-SA and Sr-SA, respectively.

### 2.3 Characterization

The optical images of hydrogel beads were recorded by the ultra depth of field optical microscope (Keyence, VH-Z500R). The crystal phase of the as-prepared product was detected by X-ray diffractometer (XRD, Rigaku/MAX2500) using CuKα radiation (λ = 0.154059 nm), and the scanning rate is 8°/min. Morphological observations were carried out with a scanning electron microscope (SEM, JSM-7800F). An ultraviolet–visible spectrophotometer (UV–Vis, T6, Beijing General Instrument Company) was used to determine the light response range of the as-obtained samples. FTIR (IvS, Thermo Fisher Nicolet) was used to detect the presence of functional groups and chemical bonds.

### 2.4 Photocatalytic performance of the hydrogel beads

The photocatalytic activity was evaluated by the degradation of methyl orange (MO) using a xenon lamp (300 W, MC-PF300B) as the UV light source. 2 g of Cu-TiO2 (Co-TiO2, Sr-TiO2) hydrogel beads were dispersed in 50 mL of MO aqueous solution (5 mg/L). Before illumination, the solution was stirred slowly under dark conditions for 30 min to establish the adsorption–desorption equilibrium. After the illumination, 3 mL of the MO solution was extracted at certain time intervals, and the absorbance of it was recorded by a visible spectrophotometer when it is exposed to a single light with the wavelength of 485 nm. The degradation rate of MO was calculated as \( \frac{C_t}{C_0} \), where it equals the absorbance ratio of MO at the reaction time of \( t \) min and 0 min, respectively.
3 Results and discussion

The photos of hydrogel beads without/with TiO₂ loading are shown in Figure 1. It can be seen that the beads demonstrate different colors as the cross-linked divalent ions vary accordingly. As shown in Figure 1A, blue Cu-SA dydrogel beads are transparent in whole and show good sphericity, the diameter is about 3.2 mm. Figure 1B are TiO₂ loaded Cu-SA hydrogel beads, which appears as light blue color with a larger diameter of approximately 3.5 mm. Sr-SA and Co-SA beads in Figure 1C and D are white and pink color with the diameter of about 3.4 and 3.7 mm, respectively. All beads loaded with TiO₂ powder are opaque and show good sphericity.

From XRD patterns of SA powder and dried Cu-SA gel powder in Figure 2, we cannot observed any diffraction peaks, indicating that they are existing in amorphous forms. Other loaded TiO₂ samples show the same patterns with bare TiO₂ powder, the corresponding diffraction peaks of (101), (103), (004), (200), (105), (211), and (204) belong to the anatase phase, which conforms to the tetragonal crystal system of TiO₂ with space group of I41/amd (JCPDS NO. 21-1272), The other diffraction peaks match the characteristics of the standard rutile TiO₂ phase (JCPDS NO. 21-1276). According to Scherrer equation, the average crystalline size of the TiO₂ powder is 23.51 nm, which is consistent with the data provided by the manufacturer. The average crystal sizes of Co-TiO₂, Sr-TiO₂, and Cu-TiO₂ are calculated as 23.49, 23.61, and 23.64 nm respectively, which means TiO₂ crystals are distributed in hydrogel network with unchanged size.

The functional groups of the samples are shown in Figure 3. It can be seen from the FTIR spectra that all the samples have –OH stretching vibrations at 3355 cm⁻¹. Co-TiO₂, Cu-TiO₂, Sr-TiO₂, and Co-SA hydrogel beads are similarly shown COO⁻ symmetric and antisymmetric stretching vibrations at 1400 and 1600 cm⁻¹, respectively, which are the characteristic peaks of alginate. In addition, both of the hydrogel samples loaded with TiO₂ and the pristine TiO₂ powder have wide vibrations at 580 cm⁻¹, indicating the existence of Ti–O bonds. The characteristic peaks of alginate and TiO₂ indicate that the hydrogel beads have composite structure of alginate and TiO₂.
The optical picture of different hydrogel beads is shown in Figure 4. It is clearly seen that Cu-SA hydrogel bead presents transparent state, smooth surface, good spherical shape, and homogenously color (Figure 4A), which is consist with that in Figure 1A. Figure 4B–D indicate the surface of TiO₂ loaded hydrogel bead appears small granular morphology, it is concluded the structure of all hydrogel beads became more dense and uniform after the loading of TiO₂ powder. The uniform sectional morphology of the beads indicates that TiO₂ is well combined with the network structure of alginate. Interestingly, the size of crosslinking network formed by different ions substituting Na⁺ in sodium alginate is different. It can be seen from Figure 4D that Co-TiO₂ hydrogel bead has the largest particle size.

Figure 5 indicates much clear internal structure of the as-obtained beads after the drying treatment, all figures have the same scale. As shown in Figure 5A–C, the gel samples without loading TiO₂ powder show smooth cross-sectional SEM morphologies. Some cracks appear in the image are due to the fast drying and dehydration process. It can be seen from Figure 5D–E, there is absent dry cracks but evenly grain particles distributed across the section network of the composite gels, which indicates that TiO₂ loading is helpful to the stability of the whole structure of the beads.

MO solution is utilized as the simulated pollutants to evaluate the photocatalytic properties of each hydrogel bead. In order to eliminate the influence of the self-degradation of blank dyes or alginate hydrogel beads on the photocatalytic performance, the UV light irradiated photocatalytic degradation effect on the MO solution in the presence of hydrogel beads with/without TiO₂ loading, pure TiO₂ powder and blank dyes are all executed under the same conditions. As shown in Figure 6, under the UV light irradiation, the degradation efficiency of MO is not significant, which shows no difference from that of hydrogel beads, indicating that neither bare dyes nor SA based hydrogel beads have photocatalytic properties. After loading TiO₂ powder, however, the hydrogel beads show enhanced photocatalytic effect. In particular, Sr-TiO₂ hydrogel beads can decolorize 99% of MO solution within 60 min, which is the best one that can be competitive with the same weight of TiO₂ powder (it needs 30 min).

Figure 4: Optical microscopic images of different hydrogel beads: (A) Cu-SA, (B) Cu-TiO₂, (C) Sr-TiO₂, and (D) Co-TiO₂.

Figure 5: SEM images of (A) Cu-SA, (B) Co-SA, (C) Sr-SA, (D) Cu-TiO₂, (E) Co-TiO₂, and (F) Sr-TiO₂.
Co-TiO₂ and Cu-TiO₂ hydrogel beads need 120 and 135 min, respectively, indicating that the composite hydrogel beads prepared by the proposed scheme have good photocatalytic activity. In order to investigate the rate of photocatalytic degradation of MO by hydrogel beads, we analyzed the first order kinetic equations of hydrogel beads crosslinked by different ions. The equations are as follows:

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

where \(C_0\) and \(C\) are the degradation rate of MO aqueous solution at times of 0 and \(t\), respectively. \(k\) is the first-order rate constant given by the slope of the graph of \(\ln(C_0/C)\) versus \(t\). It can be observed that the \(k\) value of the TiO₂, Sr-TiO₂, Cu-TiO₂, and Co-TiO₂ is approximately 0.10, 0.05, 0.02, and 0.03 min⁻¹, respectively. The \(R^2\) values support the pseudo-first order kinetic mechanism for the photo-degradation process of as-obtained samples, which is about 0.9 on average. The photocatalytic performance indicates that the degradation rate of Sr-TiO₂ hydrogel beads is reduced slightly compared to that of TiO₂ powder with the same weight.

We conducted UV–Vis absorption test on hydrogel beads formed by crosslinked Cu²⁺, Co²⁺ and Sr²⁺ ions and their corresponding blank SA hydrogel beads, which is shown in Figure 7 comparing to the UV–Vis absorption spectra of blank SA hydrogel beads, the influence of color (introduced by different divalent ions) on the light absorption and transmittance of the transparent hydrogel beads is not significant, while the absorbance range of the three hydrogel beads supported by TiO₂ powder enlarges.

From the cyclic photocatalytic degradation data in Figure 8, we are surprised to find that the Sr-TiO₂ hydrogel beads show excellent photocatalytic performance through ten degraded cycles, indicating a good stability. In the first cycle, it takes 60 min to decolorize MO solution completely, and that is only 45 min in the fourth cycle. The possible reason for the acceleration is that with the increase of UV irradiation time, SA is gradually decomposed and the new surface of hydrogel is continuously exposed. The internal TiO₂ powder is gradually exposed to light, so as to improve the photocatalytic performance.

Sr-TiO₂ hydrogel beads could be used to degrade MO dyes for many times, which is much superior to that of powder materials. The morphology of Sr-TiO₂ hydrogel beads...
Figure 8: Cyclic photodegradation rate of MO solutions in the presence of Sr-TiO$_2$ hydrogel beads.

Figure 9: Photos of Sr-TiO$_2$ hydrogel beads after (A$_1$) first cyclic and (A$_2$) tenth cyclic degradation process, and the corresponding (B) diameter, and (C) mass change after the cyclic process.
beads maintains very well after ten times of photocatalytic degradation process, indicating a strong stability (see Figure 9A). The diameter of beads measured by particle size distribution meter (Figure 9B) and the mass data of beads after multiple degradation process show that the beads stay well after each accomplishment during the multiple cyclic degradation experiments.

Based on these results, we proposed a photocatalytic mechanism for TiO$_2$ based hydrogel beads. Firstly, sodium alginate hydrogels were formed with divalent ions cross-linked, whose egg box structure can effectively immobilize and disperse TiO$_2$ powder. Due to the spherical shape, the beads can make TiO$_2$ contact with MO molecules and light more easily. When the beads are exposed to the UV light, electron–hole pairs are generated inside of TiO$_2$ semiconductors. Due to the movement of holes in the valence band of TiO$_2$ photocatalyst to the surface, redox reaction occurs to degrade MO pollutants. Moreover, the loading of TiO$_2$ powder would also help to improve the stability of the beads, providing the possibility of recycling and reusing the hydrogel beads for many times, allowing the catalyst to have good performance in cyclic photocatalysis.

4 Conclusions

In summary, a facile alginate crosslinking technique are introduced to produce macroscopically colorful TiO$_2$ hydrogel beads, which can absorb light to a greater extent and degrade MO dye pollutants under UV light excitation. Among them, the photocatalytic degradation efficiency of white Sr-TiO$_2$ beads is competitive to the corresponding TiO$_2$ powders, and they still remain excellent reusable activity after many repeated cyclic photocatalytic degradation tests, which provides a good way for the recycling of particle photocatalytic materials.


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