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Polyurethane-Supported Graphene Oxide Foam Functionalized with Carbon Dots and TiO₂ Particles for Photocatalytic Degradation of Dyes

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Featured Application: The CQDs/TiO₂/GO foam reported in this paper has the advantages of convenient recovery, remarkable effect, and degradation under visible light. It has great potential to be used in the treatment of wastewater containing organic dyes in actual industrial production.

Abstract: The design and optimal synthesis of functional nanomaterials can meet the requirements of energy and environmental science. As a typical photocatalyst, TiO₂ can be used to degrade dyes into non-toxic substances. In this work, we demonstrated the in-situ hydrothermal synthesis of carbon quantum dots (CQDs)-modified TiO₂ (CQDs/TiO₂) particles, and the subsequent fabrication of three-dimensional (3D) graphene oxide (GO) foam doped with CQDs/TiO₂ via a facile strategy. By making full use of the up-conversion characteristics of CQDs, the synthesized CQDs/TiO₂ exhibited high catalytic activity under visible light. In order to recover the photocatalyst conveniently, CQDs/TiO₂ and GO were mixed by ultrasound and loaded on 3D polyurethane foam (PUF) by the multiple impregnation method. It was found that GO, CQDs/TiO₂, and PUF reveal synergistic effects on the dye adsorption and photocatalytic degradation processes. The fabricated 3D CQDs/TiO₂/GO foam system with a stable structure can maintain a high photocatalytic degradation efficiency after using at least five times. It is expected that the fabricated 3D materials will have potential applications in the fields of oil water separation, the removal of oils, and the photothermal desalination of seawater.

Keywords: graphene oxide; carbon quantum dots; TiO₂; photocatalysis; water purification

1. Introduction

Due to increasing environmental problems currently, a lot of studies have been performed to develop new materials to control environmental pollution, especially the high performance purification of polluted water and air [1–5]. It is well known that the removal of pollutants from water and air systems could be achieved by several physical and chemical processes including physical adsorption, chemical oxidation, electrocatalysis, and photocatalysis [6–8], among these methods, the photocatalysis strategy shows high potential due to its advantages, such as pollution-free, clean, safe, economic, and high-efficient properties. Therefore, the environmental treatment through photocatalysis degradation of pollutants has attracted more and more interests in recent years.

Titanium dioxide (TiO_2) has been widely used as a photocatalyst due to its strong, light-based oxidizing abilities [9,10], while the wide bandgap (>3.2 eV) of TiO_2 limits its applications in the visible region and in the fast electron-hole recombination related to the enhanced catalytic activity [11–13]. Several previous studies proved that the photocatalytic efficiency of TiO_2 can be greatly improved by introducing other light-sensitive nanomaterials (such as quantum dots) with TiO_2 [13–16]. The advantage of dimensional quantization is that the visible light response range can be adjusted by controlling the particle size. Meanwhile, a single photon in a quantum dot (QD) can generate multiple charge carriers. Thus, the energy of the photon is much higher than the band gap, generating multiple excitation electrons and increased photocurrent signal [16].

Carbon quantum dots (CQDs) have exhibited wide applications in the field of photocatalysis due to their high fluorescent quantum effect, low toxicity, and facile preparation [13,15–17]. CQDs can be used as a place to store electrons of TiO_2 under ultraviolet light and play an important role in electron-hole separation. When irradiated by visible light, CQDs, as a photosensitizer, can produce excited electrons to make TiO_2 sensitized. For instance, it has been found that the hydrogen evolution rate of TiO_2 doped by CQDs can be significantly increased under visible light (>450 nm) [18]. In another case, Zhang and co-workers conjugated N-doped CQDs with rutile TiO_2 to create a novel hybrid rod structure, which exhibited an enhanced photocatalytic ability towards the degradation of rhodamine dye [19].

For the facile fabrication of TiO_2 -based three-dimensional (3D) materials, other supporting materials like polymer foam or graphene are needed [20–22]. It has been found that graphene oxide (GO) reveals enhanced functions by combining with a lot of polymers [23–26]. In particular, the combination between GO and polyurethane foam (PUF) made it possible to fabricate novel 3D structured materials for various applications [25,27,28]. For example, Ji et al. have immersed melamine foams in the reduced GO solution to prepare super hydrophobic composites for oil adsorption [27]. In another case, Nguyen and co-workers have applied the dipping method to load GO onto the melamine foam framework, and then used polydimethylsiloxane to form the superhydrophobic foam [28]. It has been found that the as-synthesized foam can absorb oil and organic solvent that are over 165 times its weight with good recyclability. Inspired by these studies, we propose novel 3D PUF-supported GO foams that doped with CQDs-modified TiO_2 particles (the process is shown in Scheme 1), which enable the as-prepared GO or TiO_2 foams with improved photocatalytic efficiency.

Scheme 1. Schematic presentation on the fabrication of polyurethane foam (PUF)-supported graphene oxide (GO) foam that doped with carbon quantum dots (CQDs)/ TiO_2 particles for adsorption and photocatalytic degradation of dyes.

To achieve our aim, we first synthesized CQDs/ TiO_2 particles via an in-situ hydrothermal method, which were then mixed with GO and loaded onto 3D PUF for final fabrication of 3D GO foam doped with CQDs/ TiO_2 particles (CQDs/ TiO_2 /GO). The in-situ synthesis of CQDs/ TiO_2 particles allows the binding of CQDs on the surface of TiO_2 particles, and the chemical bonds make them bind very tightly. In addition, CQDs/ TiO_2 particles were firmly loaded onto the PUF framework after combining with GO via multiple immersion drying, which can enhance both the mechanical strength and stability

of the PUF-based 3D materials in this work. The fabricated 3D CQDs/TiO₂/GO exhibited a high performance for the adsorption and photocatalytic degradation of dyes, proving high potentials in photocatalytic water decomposition, photothermal heating desalination and the development of inorganic photoelectric materials.

2. Materials and Methods

2.1. Regents and Materials

Natural graphite flake (99.8% purity) was purchased from Sigma–Aldrich (Shanghai, China). Furfural (C₅H₄O₂, ≥99% purity) was purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Titanium tetrabutanol (C₁₆H₃₆O₄Ti, CP), titanium dioxide (TiO₂, P25, CP), phosphoric acid (H₃PO₄, CP), sulfuric acid (H₂SO₄, CP), hydrochloric acid (HCl, CP), potassium permanganate (KMnO₄, CP), methylene blue (C₁₆H₁₈ClN₃S, MB, CP) and rhodamine B (C₂₈H₃₁ClN₂O₃, RB, CP) were purchased from J&K (Beijing, China). Ethanol (C₂H₆O > 99.7% purity), aether (C₄H₁₀O) and hydrogen peroxide (H₂O₂, 30%) were purchased from Beijing Chemicals Co., Ltd. (Beijing, China). Polyurethane foam (PUF, 1m × 1m) purchased from BASF SE (Shanghai, China). All the chemicals used were directly used without additional purification. GO was synthesized with the typical Hummers' method with suitable modifications [29,30]. The water purified through a Millipore system (Beijing Shengsheng Technology Development Co., Ltd., Beijing, China) (18.2 MΩ·cm) was used throughout. Cu grids for transmission electron microscopy (TEM) characterization were purchased from Plano GmbH (Wetzlar, Germany).

2.2. Preparation of CQDs/TiO₂ Particles

CQDs/TiO₂ particles were synthesized through a hydrothermal method. First, 18 mL ethanol was added into a 50 mL breaker, followed by a slow drip of 0.9 g aether. Under gentle stirring, the two chemicals were completely soluble. After that, 1 g C₁₆H₃₆O₄Ti was added into the above solution under stirring. The dark yellow mixed solution was then transferred to a reactor and reacted for 10, 12, and 14 h at 180 °C, respectively. Finally, the supernatant was collected, and the brown precipitate was washed with ethanol and centrifuged 3 times. The product of CQDs/TiO₂ was collected and dried overnight in an oven under 60 °C for next characterizations.

2.3. Fabrication of 3D GO and CQDs/TiO₂/GO Foams

The fabrication of 3D CQDs/TiO₂/GO foams is based on the binding of CQDs/TiO₂ and GO with PUF. In brief, CQDs/TiO₂ particles with different amounts (10, 20, and 30 mg) were first added into 20 mL GO solution (2 mg/mL), which were treated with ultrasonic for 30 min to create uniform mixing. Next, PUFs were cut into cubes with a side length of about 1 cm and soaked in GO and CQDs/TiO₂/GO solutions. The formed PUF-supported GO and CQDs/TiO₂/GO foams were then put in an oven at 60 °C for 1 h until the color of foam turned brown. The final 3D GO and CQDs/TiO₂/GO foams were fabricated by repeating these steps 3 times.

2.4. Adsorption and Photocatalytic Degradation and Dyes

To determinate the standard adsorption curve of dyes, the UV-vis absorption spectra of both MB and rhodamine solutions with various concentrations of 40, 60, 80, 100, 120 and 120 μM/mL were determined, respectively. According to the relationship between concentration and absorbance, the slope of the molar absorption coefficient was obtained.

To test the photocatalytic degradation of materials (TiO₂, CQDs/TiO₂, and 3D CQDs/TiO₂/GO foams), 30 mg TiO₂, 30 mg CQDs/TiO₂, and 3D CQDs/TiO₂/GO foams with different loading amount of CQDs/TiO₂ (10, 20, and 30 mg) were put into MB solution (100 μM/mL), and then the dye solution with various materials were irradiated under 350 W xenon lamp. The dye solution was taken

every hour and characterized with a UV-vis spectrometer. The experiment was repeated several times to test the reusability of the materials.

2.5. Characterization Techniques

All scanning electron microscope (SEM) images were obtained by JSM-6700F scanning electron microscope (JEOL, Tokyo, Japan), and the elements analysis of surface micro-area composition was carried out by energy dispersive spectrometer (EDS). Transmission electron microscope (TEM) images were got by JEM-2100 transmission electron microscope with a voltage of 200 kV (JEOL, Tokyo, Japan). Atomic force microscope (AFM) images were obtained by using a Bruker MultiMode 8 atomic force microscope (Bruker, Germany). These methods were used to characterize the surface and internal morphologies of the prepared composites. An Ultima IV X-ray diffractometer (Japan science. Co., Ltd., Japan) has been used to identify phase and lattice structure. For the X-ray photoelectron spectroscopy (XPS) we used an ESCALAB 250 X-ray photoelectron spectroscopy (Thermo Scientific, Massachustees, M.A., USA) to detect the elements and determine the valence states of elements. Fourier transform infrared spectroscopy (FT-IR, Nicolet NEXUS) was used to detect the types and contents of functional groups in substances. UV-vis absorption spectroscopy combined with fluorescence spectroscopy was used to detect the composition and purity of substances

3. Results and Discussion

3.1. Morphological Characterizations of CQDs/TiO₂ Particles

The synthesized CQDs/TiO₂ particles were first characterized with morphological (SEM and TEM) techniques.

Figure 1. Scanning electron microscope (SEM) images and particle-size distribution diagrams of carbon quantum dots(CQDs)/TiO₂ particles obtained at different hydrothermal reaction periods: (a–c) 10 h; (d–f) 12 h; (g–h) 14 h; and (i) SEM image of CQDs/TiO₂ particles surface.

Figure 1 shows the typical SEM images and size analysis of the synthesized CQDs/TiO₂ particles with different reaction periods. Nano-titanium and nano-carbon, obtained by titanium sources and furfural, were fused together due to functional groups on the TiO₂ surface and grew to form a core-shell structure. It can be seen that the obtained CQDs/TiO₂ particles show uniform spheres with an average diameter of 0.91 μm after 10 h reaction (Figure 1a–c). When the reaction time was increased to 12 h, the formed CQDs/TiO₂ particles remained in a spherical shape, however, their average size increased to about 1.41 μm , as shown in Figure 1d–f. It is clear that CQDs/TiO₂ particles continue to grow with the increasing reaction period. By comparing the SEM images of Figure 1b and 1e, it can be found that the size of the particles with a 12 h reaction are more uniform than that with a 10 h reaction. When the reaction time continued to increase to 14 h, besides spherical particles, some rod-like substances were produced, as shown in Figure 1g and h. The thickness of the rods was measured to be about 0.5 μm . Therefore, we suggest that the synthesized CQDs/TiO₂ was not a solid sphere with uniform density and composition, but a multilayer core-shell cladding structure. Furthermore, it can be observed from Figure 1b and e that the surface of the particles became smoother with the increasing reaction time. The higher resolution image of CQDs/TiO₂ particles shows that a lot of nanoparticles with a size of 10 nm were created on the surface of particles.

To further prove the formation of CQDs on TiO₂ surface, TEM and related EDS elemental analysis were utilized.

The formation process of CQDs/TiO₂ particles can be further explained through Figure 2a,b. Titanium sources were first hydrolyzed in ethanol to generate nanoscale TiO₂. Due to abundant functional groups on the TiO₂ surface, furfural was carbonized and deposited on TiO₂. Therefore, a large number of particles grew up and form microspheres. In this process, some particles first come into contact to form a thin shell, and the particles inside the thin shell formed the core. Figure 2c–e present the element analysis of the obtained CQDs/TiO₂ particles that are shown in Figure 2a, and it can be clearly found that the elements of Ti, O, and C (Figure 2c–e) are dominant in the tested materials. The EDS analysis (Figure 2f) further proves the existence of Ti, O, and C elements.

Figure 2. (a–b) TEM images of CQDs/TiO₂ particles; (c–e) Distribution images of CQDs/TiO₂ particles Ti, O and C; (f) EDS analysis results of CQDs/TiO₂ particles.

3.2. Spectrum Characterizations of CQDs/TiO₂ Particles

The synthesized CQDs/TiO₂ particles were characterized with spectrum techniques to understand their structural and optical properties.

Figure 3a shows the XRD spectra of the synthesized CQD/TiO₂ particles under different reaction periods from 10 to 12, and 14 h. All of the peaks in the XRD spectra could be seen on the standard card of anatase [31], which confirms that the prepared CQDs/TiO₂ is an anatase type. Anatase is more favorable for the photocatalytic reaction due to more defects in the crystal lattice to improve the separate of electrons and holes. As the reaction time increases, the intensity of each crystal plane diffraction peak gradually increases and the peak width at half height becomes narrower. Moreover, the high-energy crystal plane of TiO₂ can promote the catalytic effect of TiO₂ [32]. With more exposure of the high energy crystal plane, better photocatalytic effect can be obtained. The percentages of the high-energy lattice plane with different reaction times were calculated and shown in Table 1, the equation is displayed in Supplementary Information. It can be found that the crystallinity of TiO₂ is poor and the exposure fraction of high energy crystal plane is low when the reaction time is too short (for instance 10 h). However, a too long reaction time (for instance 14 h) will lead to the breakage of particles and agglomeration of CQDs deposition, thus losing the characteristics of CQDs.

Figure 3. (a) X-ray diffraction (XRD) patterns and (b) Fourier transform infrared spectroscopy (FTIR) spectra of CQDs/TiO₂ particles that synthesized with different hydrothermal reaction periods of 10, 12, and 14 h.

Table 1. Different sizes of carbon quantum dots (CQDs)/TiO₂ synthesized by hydrothermal method.

Samples	Average Thickness/nm	Average Length /nm	Percentage of High-Energy Lattice Plane
10 h CQDs /TiO ₂	5.3	6.1	22%
12 h CQDs /TiO ₂	6.5	9.5	30%
14 h CQDs /TiO ₂	5.8	9.1	32%

Figure 3b gives the FTIR spectra of the obtained CQDs/TiO₂ particles, which reveal the composition and functional group information of the tested materials. The peak at 565 cm⁻¹ generated by the role of Ti-O in TiO₂, which confirms the existence of TiO₂ in the CQDs/TiO₂ composites [31,33]. The corresponding peak of 1400 cm⁻¹ is assigned to the C-O bond, and the vibration peak at 1625 cm⁻¹ is ascribed to the unsaturated C = C bond. The peak at 2925 cm⁻¹ is related to the absorption peak of C-H in aldehyde group, indicating some oxygen-containing functional groups were carried on CQDs/TiO₂. Moreover, the absorption peaks of CQDs/TiO₂ with 12 h reaction show highest intensity strongest among the reaction time of these different lengths.

Figure 4a shows the AFM image of the supernatant solution of CQDs/TiO₂, in which some of the CQDs are not deposited on the surface of TiO₂ and can therefore be measured with AFM. The size of the CQDs was about 4 nm. According to the section analysis in the graph (Figure 4b), the synthesized CQDs are roughly homogeneous in sphere-shape.

Figure 4. (a) The AFM image of CQDs/TiO₂ and (b) height distribution; (c) UV-vis spectra of CQDs and CQDs/TiO₂; (d) fluorescence spectra of CQDs/TiO₂ with different excitation.

To further prove the formation of CQDs/TiO₂ composites, UV-vis (Figure 4c) and fluorescence (Figure 4d) spectroscopy were used to characterize the supernatant of CQDs/TiO₂. There is a peak at 320 nm for the UV-vis spectrum of CQDs/TiO₂, which is absent for the spectrum of CQDs. It is clear that the peaks of 290 and 320 nm are ascribed to the characteristic peaks of TiO₂ and CQDs [34], respectively, and therefore the UV-vis result elaborates the formation of CQDs/TiO₂.

The fluorescence spectra of CQDs/TiO₂ with different excitations are shown in Figure 4d. Under the excitation of 280 nm and 320 nm, CQDs form emission peaks at 370 nm and 430 nm, respectively. As the excitation wavelength increases, the emission peak of CQDs/TiO₂ shows a significant red shift with enhanced fluorescence intensity.

Based on the above spectrum characterizations, the optimal synthesis of CQDs/TiO₂ with the desired structures and properties are achieved.

3.3. Characterization of 3D CQDs/TiO₂/GO Foams

CQDs/TiO₂ particles can bind with GO through hydrogen bonding or π - π interaction due to the existence of a large number of oxygen-containing functional groups in the composites. Compared to bare PUF, the surface of the PUF loaded with CQDs/TiO₂/GO is very rough, as shown in SEM images (Figure 5a–c). Some smaller holes in bare PUF were filled by GO nanosheets, which are sought to be useful for increasing the load capacity of CQDs/TiO₂/GO and the surface area of materials for enhanced catalytic and adsorption performance. In addition, compare to the smooth surface of pure PUF (Figure 5d), a lot of tiny particles were formed on the surface of PUF-based CQDs/TiO₂/GO foam with high density (Figure 5b), which is ascribed to the dispersion of CQDs/TiO₂ particles by GO nanosheets. It should be noted that the color of PUF foam has changed dramatically (see inset optical images in Figure 5a–c), and the mechanical properties have also been enhanced due to the loading of CQDs/TiO₂/GO composites.

Figure 5. SEM images of (a,b) polyurethane foam (PUF)-supported GO/CQDs/TiO₂ foam with 12 h reaction, and (c,d) PUF foam.

3.4. Adsorption and Photocatalytic Degradation of Dyes

The as-prepared 3D CQDs/TiO₂/GO foams with different loading amount of CQDs/TiO₂ particles (10, 20, and 30 mg) were used to adsorb and photocatalytic degrade dyes, MB and rhodamine by using a 350 W xenon lamp as the source of visible light. Under the irradiation condition, the electrons in the valence band (VB) of TiO₂ were stimulated to transit to the conduction band (CB) and release photoelectrons. Hydroxyl radicals and oxygen radicals were produced by the interaction of water and oxygen with electrons and photons. These two radicals can degrade dyes into H₂O and CO₂ (Figure S2). The CQDs with an up-conversion performance can convert visible light into ultraviolet light at 300–400 nm, which stimulates the generation of electrons and holes in TiO₂. The result of our experiment (Figure S3) exhibits an up-conversion at 300–400 nm, which is consistent with Reference [35]. Then the pairs of electron and hole can migrate to the surface of particles to initiate the generation of oxygen-free radicals, which can degrade the dyes. At the same time, the GO network can conduct the electrons, put off the recombination of electron holes, and provide more active sites for photocatalysis.

Figure 6a,b presents the degradation effect of MB and rhodamine versus time with different catalytic agents. Due to the foams being porous, they have a high adsorption effects on dyes. To make it clearer for the adsorption and degradation effects of 3D CQDs/TiO₂/GO foams, the bare PUF foam, GO foam, and CQD/GO foam were used as a control material for the photocatalytic experiments to exclude the effect of adsorption on this experiment. It is clear that the use of larger amounts of CQDs/TiO₂ particles for the GO foam could cause a quicker degradation of both dyes. For instance, when the foam was loaded with 30 mg CQDs/TiO₂, it is about 2 h faster than GO alone for the degradation of MB, and 1 h faster for the degradation of rhodamine, which indicated the superiority of CQDs/TiO₂/GO foam for photocatalysis. In order to exclude the effect of adsorption, dark field experiments were carried out in order to study the photocatalytic mechanism, as shown in Figure S4. It could be summarized that the photocatalytic degradation has an important effect on removal of dyes. Foams cannot get rid of all the dyes for 6 h at dark while the dyes could be completely removed with irradiation, which showed that the main mechanism of dye removal in this experiment is the photocatalytic degradation.

Figure 6. Photocatalytic degradation of (a) methylene blue (MB) (b) rhodamine with the loaded capacity of 10 mg (TiO₂(1)), 20 mg (TiO₂(2)), and 30 mg (TiO₂(3)) CQDs/TiO₂ particles, respectively. (c) Comparison of the photocatalytic degradation ability of P25-TiO₂ and CQDs/TiO₂ nanoparticles in one hour to degrade MB. (d) Recycling capability test of CQDs/TiO₂/GO foam of MB.

To further illustrate the advance of the CQDs/TiO₂ nanoparticle for the photocatalysis of dyes, the light-based degradation efficiency between P25-TiO₂ and CQDs/TiO₂ nanoparticles was compared after one hour of light irradiation (Figure 6c). In this test, 30mg P25-TiO₂ and 30mg CQDs/TiO₂ were used to degrade MB under xenon lamp with stirring. The time of the photocatalytic degradation greatly reduced due to the fuller contact of nanoparticles with dyes. It is found that the degradation effect of dyes was remarkably improved by using CQDs/TiO₂ nanoparticles.

The reusability test of the fabricated CQDs/TiO₂/GO foam is shown in Figure 6d. The recycling experiment was tested five times, each experiment was illuminated for three hours and the foam was washed several times by deionized water and ethanol, and then dried for use. The used foam kept a high photocatalytic ability for dyes, indicating that the photocatalyst and the framework are relatively strong, and the catalytic performance would not reduce obviously after dye degradation.

4. Conclusions

In summary, CQDs/TiO₂ microspheres were synthesized by the in-situ hydrothermal synthesis, which were further utilized with GO for the fabrication of PUF-supported 3D CQDs/TiO₂/GO foams. The as-prepared CQDs/TiO₂ composite could expose more than 30% of high-energy crystal planes and exhibited an enhanced photocatalytic property. The addition of GO to this hybrid foam system had positive impacts on the transition of electrons and holes. These effects improved the photocatalytic activity of the fabricated CQDs/TiO₂/GO foams. The adsorption and photocatalytic degradation experiments indicated that the fabricated CQDs/TiO₂/GO foams exhibited a high efficiency, stability, and reusability for the decomposition of both MB and rhodamine dyes, revealing high potentials for the oil water separation, removal of oils, and the photothermal desalination of seawater.

Supplementary Materials: Experimental details and additional figures are provided that include the calculation of the percentage of the high energy lattice plane, XPS analysis, electronic band diagram of CQDs/TiO₂/GO, up-conversion fluorescence test, and the UV–vis absorbance spectrum at dark.

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