The exponential rise in the need for better, more efficient power sources has sparked an incredible amount of research into batteries. A primary focus of research has been increasing the energy density of batteries, as it allows for lighter, more portable storage of energy. Lithium-ion batteries, for example, have a much higher energy density than conventional lead-acid batteries and can be used for various purposes, such as in electric vehicles.

This article collection provides a comprehensive list of references for new methods and technologies for increasing the energy density of batteries.
Dual-Function Near-Infrared Emitting Aerogel-Based Device for Detection and Sunlight-Driven Photodegradation of Antibiotics: Realizing the Processability of Silsesquioxane-Based Fluorescent Porous Materials

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It is highly desirable to develop facile methods to improve the processability of porous materials for industrial applications. Herein, the preparation of a novel near-infrared emitting hybrid aerogel (PCS-CA) is reported by physically blending a porous material with chitosan. The applied porous material (PCS-CZ-O-DCM) is obtained from a near-infrared emission semiconductor compound (CZ-O-DCM) and octavinylsilsesquioxane (OVS). PCS-CZ-O-DCM can detect tetracycline hydrochloride selectively and rapidly in various solution with an extremely low detection limit of 0.29 μM for fluorescence quenching. It also exhibits an outstanding sunlight-driven photodegradation activity for antibiotics even in the absence of additional oxidation agents or pH control. PCS-CA also performs better than PCS-CZ-O-DCM powder. A PCS-CA-based glass device is further fabricated, which enables a larger amount of water purification of antibiotics by a continuous flow-through system by light-driven degradation. By blending with a soft polymer matrix, improved processability can be applied to insoluble porous materials. As a result, a novel functional devices can be realized which provides a new way to apply insoluble porous materials.

1. Introduction

Cage silsesquioxane-based hybrid polymers (PCSs) have attracted growing attention recently because of their large surface areas with abundant pores that provide sufficient binding sites and good transport channels.[1–3] However, most of these materials are highly cross-linked insoluble powders. As a result, it is difficult to apply them into large-sized devices, and their industrial applications was limited. In order to improve their processability, four strategies have been applied: i) long alkyl chains were introduced to improve polymer solubility; ii) reduce cross-linking to make polymers soluble; iii) apply mini-emulsion polymerization to realize dispersible polymers in solutions; and iv) porous films were prepared at the liquid-electrode interface.[4–10] However, reduction of the porosity was observed in the first two strategies, while (iii) and (iv) require specific synthetic methods. In addition, large-scale fabrication of insoluble porous materials is also an important issue. Therefore, processability is still a great challenge for most porous materials. Aerogels are ultra-light materials with 3D porous network. Many unique physical properties, such as high porosity and low density, high surface area, and high mechanical properties are endowed by nanoporous structure.[11,12] In particular, according to the specific requirements of the devices, their continuous structure can be fabricated and applied in various fields. Chitosan (CS), as a natural linear polysaccharide, has outstanding properties, such as being non-toxic, non-irritant, biocompatible, anti-bacterial, hydrophilic, etc.[13–15] Due to its unique properties, CS is a good matrix for the preparation of aerogels. To address the processability problems, the loading of powder nanoparticles into hydrogels–aerogels has received much attention.[16,17] This strategy overcomes the...
processing difficulty of power nanoparticles and allows the advantages of individual components to be integrated. As a result, new versatile materials with enhanced properties can be obtained that are hardly realizable simply by the individual components on their own.\textsuperscript{[16,17]}

In recent years, the environmental impact of emerging contaminants has attracted extensive attention.\textsuperscript{[18–20]} Many of them, such as endocrine disrupting chemicals, pharmaceuti- cals, personal care products, and other persistent organic compounds show biological toxicity, environmental persistence, and bioaccumulation.\textsuperscript{[21]} Tetracycline hydrochloride (TC) is one of the most common broad-spectrum antibiotics widely used in medicine, animal husbandry, aquaculture, and agricultural production due to its inactivation of various pathogenic bacteria and harmful microorganisms.\textsuperscript{[22–26]} However, most antibiotics are difficult to be fully digested and absorbed by humans and animals, and $>80\%$ are excreted in the form of feces and urine, accumulating in the ecosystem.\textsuperscript{[27]} Antibiotics can disrupt the balance of microbial populations in the environment and even induce the development of resistance genes, causing irreversible harm to humans.\textsuperscript{[28]} Therefore, it is crucial to develop green, environmentally friendly, low-toxicity, and efficient materials for detection and removal of antibiotics. Membrane filtration, biodegradation, adsorption, or ozonation have been applied for the removal of the residual antibiotics.\textsuperscript{[29–32]} In order to achieve high efficiency, mild reaction condition, low cost, and no secondary pollution, photocatalytic degradation is regarded as the most favorable.\textsuperscript{[33,34]} In chemical sensing, fluorescence detection is more sensitive and quick compared to traditional detection methods.\textsuperscript{[35]} The large surface area and rich pores in fluorescent PCSs allow the analyte to freely pass through and fully bind to the recognition site, thus improving the fluorescence detection sensitivity.\textsuperscript{[36]} Thus, design and fabrication of a device based on fluorescent PCSs capable of simultaneous antibiotics detection and photodegradation are particularly fascinating.

In this report, we present a novel approach to improve processability of PCS materials by physically blending chitosan to prepare a near-infrared emitting hybrid aerogel capable of simultaneous detection and photodegradation of antibiotics. First, we synthesized a new donor–acceptor–donor (D–A–D) emitter, 2-(2,6-bis((E)-2-(5-(9H-carbazol-9-yl)furan-2-yl)vinyl)-4H-pyran-4-ylidene)malononitrile (CZ-O-DCM) (Figure S1, Supporting Information). CZ-O-DCM was optimized at the B3LYP/6-311+G** level. The optical properties of CZ-O-DCM in N,N-Dimethylformamide (DMF) solution were investigated by UV–vis and fluorescence (FL) spectroscopies. The maximum absorbance and FL peaks were measured at 463 and 625 nm, respectively, with the tail emission extended to 800 nm (Figure 2a). The emission wavelengths of CZ-O-DCM in different polarity solvents was investigated. As the solvent polarity gradually increased, FL peak intensity first increases and then decreases, and the maximum emission peak showed a red-shifted trend (Figure 2b). The emission profile of CZ-O-DCM (10 $\mu$M) was further investigated in tetrahydrofuran (THF) solution with different water fractions ($f_w$). In pure THF, CZ-O-DCM emitted a strong fluorescence at 640 nm (Figure 2c). The emission of CZ-O-DCM was gradually quenched when the $f_w$ in the

2. Results and Discussion

2.1. Fabrication and Characterization

The fabrication of NIR-emitting material (PCS-CZ-O-DCM) and PCS-CZ-O-DCM@Chitosan aerogel (PCS-CA) is illustrated in Scheme 1. Three main steps are included: 1) synthesis of 2-(2,6-bis((E)-2-(5-(9H-carbazol-9-yl)furan-2-yl)vinyl)-4H-pyran-4-ylidene)malononitrile (CZ-O-DCM) (Figure S1, Supporting Information); 2) preparation of NIR-emitting material of PCS-CZ-O-DCM from CZ-O-DCM with OVS (Scheme 1a); 3) chitosan was combined with the PCS-CZ-O-DCM powder to prepare the PCS-CA with a designable shape (Scheme 1b).

The structural characterizations of CZ-O-DCM were conducted by $^1$H NMR, $^{13}$C NMR, and high-resolution mass spectrometry (Figures S3–S5, Supporting Information). Single crystals of CZ-O-DCM suitable for X-ray analysis were obtained by slow evaporation from a mixture of dichloromethane and hexane at room temperature (Figure 1a). The unit cell of CZ-O-DCM was monoclinic with space group C2/c with $Z = 4$ (Figure 1b and Table S1, Supporting Information). As revealed by the crystal structure of CZ-O-DCM, the dihedral angle between the central 4H-pyran ring and the furan ring was 12.2°. That between the furan ring and the ethylene unit was 6.2°. In addition, the dihedral angle was recorded to be 23.1° at the N position of the carbazole group. To better illustrate the relationship between the photophysical properties, the CZ-O-DCM was further investigated by density functional theory (DFT) calculations. The geometry of CZ-O-DCM was optimized at the B3LYP/6-311+G** level. The highest occupied molecular orbital (HOMO) of CZ-O-DCM is mainly located in the carbazole and furan fraction, while the lowest unoccupied molecular orbital (LUMO) is mainly contributed by the orbitals of the electron-withdrawing DCM fraction. Such electron separation of the HOMO and LUMO indicates a $\pi$–$\pi*$ transition with a charge transfer character. The CZ-O-DCMs were packed parallel to each other along the b-axis direction, while the furan-bridged carbazole units were arranged alternately at the periphery of the column (Figure 1c). The close face-to-face stacking ensures effective $\pi$–$\pi*$ interactions, and quenched red-shifted emissions in the aggregated state was observed (Figure 1d). The closest distance between N atom in C$\equiv$N group and H atom in ethylene moiety is 2.632 Å, which is caused by contact bonding in the aggregated state (Figure 1e). The dipole-dipole interactions lead to red-shifted emissions in a solid state. The optical properties of CZ-O-DCM in N,N-Dimethylformamide (DMF) solution were investigated by UV–vis and fluorescence (FL) spectroscopies. The maximum absorbance and FL peaks were measured at 463 and 625 nm, respectively, with the tail emission extended to 800 nm (Figure 2a). The emission wavelengths of CZ-O-DCM in different polarity solvents was investigated. As the solvent polarity gradually increased, FL peak intensity first increases and then decreases, and the maximum emission peak showed a red-shifted trend (Figure 2b). The emission profile of CZ-O-DCM (10 $\mu$M) was further investigated in tetrahydrofuran (THF) solution with different water fractions ($f_w$). In pure THF, CZ-O-DCM emitted a strong fluorescence at 640 nm (Figure 2c). The emission of CZ-O-DCM was gradually quenched when the $f_w$ in the
THF/water mixtures was 10–90 vol.%, while the emission was slightly red-shifted (Figure 2d). This is due to the large planar conjugated structure of CZ-O-DCM, where the strong \( \pi \rightarrow \pi \) stacking between molecules leads to emission quenching at high concentrations, which is consistent with the results of single-crystal validation.\[38\] This further proves that CZ-O-DCM is a typical ACQ active molecule.

To verify the structure of PCS-CZ-O-DCM and PCS-CA, FT-IR characterizations were carried out. As shown in Figure 3a, peaks according to Si–O–Si and C≡N were observed at 1123 and 2212 cm\(^{-1}\), respectively, indicating the PCS-CZ-O-DCM was successfully fabricated.\[36\] The \( \nu \)(O–H) and \( \nu \)(N–H) peaks on the glucosamine unit of PCS-CA at 3434 cm\(^{-1}\) are superimposed to form a broad peak.\[14\] Meanwhile, the characteristic peak at 1123 cm\(^{-1}\) associated with Si–O–Si appeared, signifying that PCS-CZ-O-DCM was successfully doped into the CS matrix. The silicon resonance in \( ^{29}\)Si CP/MAS NMR spectra showed that PCS-CZ-O-DCM contains T silicon unit \([T: \text{CSi-(OSi)}_3]\) (−66.8 ppm) and Si–CH=CH\(_2\) (−80 ppm) species (Figure 3b). According to the integration ratio, it was shown that \( \approx 93\% \) of the vinyl groups were consumed in the reaction.\[36\] Solid-state \( ^{13}\)C CP/MAS NMR was also used to confirm the formation of PCS-CZ-O-DCM (Figure S6, Supporting Information). All major peaks were in the range of 111.3–158.2 ppm, corresponding to the aromatic moieties of CZ-O-DCM monomer and unreacted vinyl groups, suggesting the polymer with OVS and CZ-O-DCM as skeletons is successfully prepared.\[36\] Peaks in aliphatic carbon regions (5–60 ppm) were assigned to Si–CH\(_2\)–CH\(_2\)–CZ-O-DCM or Si–CH(CH\(_3\))–CZ-O-DCM.

The porosity of the PCS-CZ-O-DCM was explored by N\(_2\) adsorption–desorption isotherm at 77 K. The typical type IV isotherm and corresponding pore size distribution in Figure 3c,d indicate that pores in the PCS-CZ-O-DCM were mainly micropores (1.4–1.6 nm) and partial mesopores (>2.7 nm), reflecting the hierarchically porous structure.\[2\] The surface area of PCS-CZ-O-DCM was calculated to be 842 m\(^2\) g\(^{-1}\) based on the Brunauer–Emmett–Teller method (Table S2, Supporting Information). Characteristic thermal behaviors of OVS, CZ-O-DCM, PCS-CZ-O-DCM, and PCS-CA were investigated by TGA, and the results are depicted in Figure S7 (Supporting Information). PCS-CZ-O-DCM has high thermal stability, maintaining polymer mass >95% in N\(_2\) at 400 °C. The initial weight loss from 30 to 210 °C was 8.5 wt.% for PCS-CA, which can be attributed to the evaporation of the absorbed water, including free water and bound water. The mass loss at 220–500 °C was mainly due to the disintegration of the aerogel skeletal structure and the decomposition of organic components. The subsequent 8.6 wt.% weight lost between 510 and 700 °C is mainly attributed to the decomposition of PCS-CZ-O-DCM.

Figure 3e shows the solid-state emission spectra of CZ-O-DCM and PCS-CZ-O-DCM. Compared with CZ-O-DCM monomer, the emission spectrum of PCS-CZ-O-DCM is red-shifted by \( \approx 45\) nm, which is due to the longer conjugation length of the highly cross-linked network.\[36\] The quantum yields of CZ-O-DCM and
Figure 1. a) Structures, dihedral angles, and HOMO-LUMO distributions by DFT calculations of CZ-O-DCM. b) Crystal cell for CZ-O-DCM in \( \alpha \)-axis direction. c) Molecular packing motif of CZ-O-DCM in \( b \)-axis direction. d,e) Intermolecular interactions of CZ-O-DCM.
Figure 2. a) The absorption and FL spectra of CZ-O-DCM in DMF ([CZ-O-DCM] = 10^{-6} M). b) Solvent effect of CZ-O-DCM ([CZ-O-DCM] = 10^{-6} M). c) The emission spectra of CZ-O-DCM in THF/water mixtures with different f_w ([CZ-O-DCM] = 10^{-5} M). d) Plot of fluorescence intensity versus f_w.

PCS-CZ-O-DCM were 26.5% and 4.0% at room temperature, respectively (Figure 3g). In addition, the corresponding mean lifetimes (τ) of CZ-O-DCM and PCS-CZ-O-DCM were also determined. One can see in Figure 3f, the mean lifetime (τ) value (1.7 ns) of CZ-O-DCM is higher than PCS-CZ-O-DCM (1.4 ns). As shown in Figure 3h, the CIE coordinates of CZ-O-DCM and PCS-CZ-O-DCM are calculated to be (0.676, 0.323) and (0.725, 0.275), respectively. The chromaticity revealed their pure red and NIR emission properties. Figure S8 (Supporting Information) also indicates that PCS-CZ-O-DCM offers excellent and stable fluorescence signals in different solvent systems.

The detailed morphology and microstructure of PCS-CZ-O-DCM and PCS-CA were investigated by field emission scanning electron microscopy (FE-SEM). FE-SEM images showed that PCS-CZ-O-DCM were composed of agglomerated particles (Figure S9a,b, Supporting Information). The EDS mapping of O, N, and Si elements was uniformly distributed in the particles (Figure S9c, Supporting Information). As shown in Figure 4a, the aerogel possesses interconnected well-organized honeycomb-like structures and oriented channels, and inhomogeneous pores were observed. This architecture contributed to ultra-light while strong mechanical strength, and it can work as an ideal fluid channel to allow rapid diffusion of contaminant solutions.\(^{[16]}\) As the high-magnification images shown in Figure 4b,c, the surfaces of the aerogel channel became rough, indicating that PCS-CZ-O-DCM was encapsulated in the CS matrix rather than simply attached to the surface. Evidently, the addition of PCS-CZ-O-DCM powder destroyed the aerogel structure, but it was uniformly dispersed by the porous framework, which greatly reduced the agglomeration and loss. The EDS mapping of O, N, and Si elements was uniformly distributed in PCS-CA, which also proved that the PCS-CZ-O-DCM powder was uniformly doped in the chitosan aerogel (Figure 4d). To further investigate the morphology and structure message of PCS-CA aerogel, HR-TEM measurement was executed. Importantly, HR-TEM image (Figure S10, Supporting Information) clearly reveals that the PCS-CZ-O-DCM nanoparticles (black stuff) are fully encapsulated into the CS aerogel (a large semitransparent smooth plane), reflecting the anchoring of PCS-CZ-O-DCM on CS aerogel, further confirming the successful construction of PCS-CA aerogel. The
Figure 3. a) FT-IR spectra. b) $^{29}$Si CP/MAS NMR spectra. c) $N_2$ adsorption–desorption isotherm. d) The pore size distribution curve calculated by NL-DFT. e) FL spectra in solid-state. f) The absolute quantum yields. g) Fluorescence transient decays curves. h) CIE properties.

PCS-CZ-O-DCM polymer shows agglomeration to some extent, which is probably due to the POSS moieties tend to aggregate in a more compact fashion. The chemical composition of the material was studied using TEM-EDS, and the results for PCS-CA is shown in Figure S11 and Table S4 (Supporting Information). All the characteristic elements, such as C, O, N, and Si were detected in the PCS-CA aerogel, which also confirms that the composite is successfully prepared. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images in Figure 4e,f confirm the presence of a hierarchically porous structure of PCS-CZ-O-DCM with wide micropores and mesopores distribution (as shown in the red circle in image), which agrees with the result of the NL-DFT method. As shown in Figure S12, Tables S3, and S4 (Supporting Information), Elemental analysis and TEM-EDS analysis confirms the presence of C, N, O, and Si in PCS-CZ-O-DCM, proving its successful formation. Due to the non-planar structure of CZ-O-DCM and OVS, PCS-CZ-O-DCM lack crystallization, and thus the skeleton structures of PCS-CZ-O-DCM could not be verified (Figure S13, Supporting Information). In addition, outstanding superhydrophilicity is a key property for wastewater treatment. Then, the dynamic contact angle (CA) was measured to evaluate the hydrophobic/hydrophilic properties of the material. Interestingly, PCS-CZ-O-DCM showed surface hydrophobicity with CA of 137° (Figure S14a, Supporting Information). Nevertheless, as shown in Figure S14b (Supporting Information), the water droplets penetrated the aerogel rapidly within 0.05s, further demonstrating its superhydrophilicity. As a result, the introduction of PCSs did not reduce the wettability, and the rapid penetration of pollutants into the aerogel was possible.

2.2. Detection of Antibiotics

The superior fluorescence property, high porosity, long-term chemical stability, and abundant electron-donating unit indicate that PCS-CZ-O-DCM is a potential sensor for detecting antibiotics. Selectivity is a fundamental performance for assessing the quality of fluorescent sensors. Therefore, to evaluate the selectivity of PCS-CZ-O-DCM for trace amounts of antibiotics, fluorescence-quenching titration experiments were performed by sequential addition of antibiotic solution to the PCS-CZ-O-DCM suspensions. Here, three different antibiotics, including Tetracycline hydrochloride (TC), Ceftazidime (CTD),...
and Mafenide Hydrochloride (MH), were detected. As seen in Figure 5a, only TC quenched the fluorescence of PCS-CZ-O-DCM, i.e., the bright red-light emission turned to dark quickly, while almost no reduction in fluorescence intensity was observed with high concentration of other antibiotics, indicating an excellent selectivity of the PCS-CZ-O-DCM probe system. As seen in Figure 5b, the emission intensity of PCS-CZ-O-DCM decreases completely and monotonically as the TC concentration increases from 0 to 500 μM, indicating a “turn-off” fluorescence detection. The highest quenching efficiency of PCS-CZ-O-DCM for TC was 93%. The $K_{SV}$ and LOD of the PCS-CZ-O-DCM toward TC were calculated to be 26630 M$^{-1}$ and 0.29 μM, respectively (Figure S15, Supporting Information).

To investigate the applicability of using PCS-CZ-O-DCM fluorescent probe in a practical environment, TC aqueous solution was added to artificial urine, bovine serum albumin (BSA), and egg albumin samples (Figure 5c). It was observed that artificial urine and protein samples without TC addition did not affect the fluorescence intensity of PCS-CZ-O-DCM. This result indicated that PCS-CZ-O-DCM could quench fluorescence only in the presence of TC, whereas artificial urine, BSA, and egg albumin solutions had no obvious matrix effect and fluorescence signal difference for TC detection. Additionally, pH is a critical element for assessing the practicability of sensors for fluorescence detection applications. Consequently, we investigated the pH dependence of the PCS-CZ-O-DCM response to TC. As shown in Figure 5d, the sensor PCS-CZ-O-DCM is stable, and the fluorescence intensity is constant over the range of pH 2–12. As a result, PCS-CZ-O-DCM showed good efficiency in detection for antibiotics in various solutions.

We further investigated the sensing test of PCS-CA to TC aqueous solution. As shown in Figure 5e, PCS-CA was cut into two
portions: one was used as the blank control, and the other was put into TC aqueous solution with a concentration of 50 μM, and then its fluorescence intensity was measured. It is very clearly observed that the fluorescence of PCS-CA immersed in the TC aqueous solution is significantly reduced compared to the fluorescence of the blank fraction (FL intensity from 6164 to 2442 a.u.). Judging from the above results, the PCS composite aerogel exhibited great significance in the use of a specific sensor for the antibiotic of TC. Considering that PCS-CZ-O-DCM is tightly loaded on the aerogel, the aerogel sensor has the potential to be recycled, so its reusability was investigated. The aerogel sensor was first immersed in TC aqueous solution (50 μM) and the fluorescence intensity was recorded. Then, the quenched aerogel was immersed in the ethanol for 10 min to wash away the residual TC. The fluorescence of the aerogel sensor can be completely recovered by removing the residual TC. PCS-CA aerogel sensor does not demonstrate a loss of fluorescence sensitivity up to the 11th cycle, displaying excellent reusability (Figure S16, Supporting Information).

To explore the possible quenching mechanism, the optical properties of antibiotics and PCS-CZ-O-DCM were examined (Figure 5f). In the UV–vis absorption spectra of TC, two peaks centered at 275 and 355 nm were observed, respectively. Among them, the peak at 355 nm overlaps well with the excitation spectra of PCS-CZ-O-DCM, while no overlap occurs with the UV absorption spectra of CTD and MH, suggesting that the significant fluorescence quenching of PCS-CZ-O-DCM on TC is caused by the inner filter effect (IFE).[39–41]

2.3. Degradation of Antibiotics

The photocatalytic performances of PCS-CZ-O-DCM and PCS-CA were investigated by the degradation experiments of antibiotics under UV light irradiation. Commercial antibiotic pharmaceuticals, such as Tetracycline hydrochloride (TC) were used as pollutant models. The amount of catalyst in the photocatalytic experiment was 3 mg, and the original concentration of the TC solution is 50 mg L\(^{-1}\). Figure 6a shows the removal efficiency by absorbance change in the dark for 60 min and following photodegradation under UV light for 70 min. TC hardly degrades in the absence of catalyst, indicating that TC was quite stable under illumination. After dark adsorption for 70 min, the removal efficiency of TC by PCS-CZ-O-DCM and PCS-CA was \(\approx 20\%\). In contrast, prominent increase under UV light irradiation was observed showing the photocatalytic degradation efficiency. The photocatalytic degradation efficiency of TC with PCS-CA aerogel was significantly higher (100%) in 70 min when compared with PCS-CZ-O-DCM powder (90%). The higher photocatalytic ability of the aerogel than powder form can be attributed to the structural features of the aerogel, including porous structure, hydrophilicity, and swelling behavior, which facilitate rapid
Figure 6. a) Photocatalytic time curves of TC by PCS-CA and PCS-CZ-O-DCM. b) Reusability of PCS-CA aerogel for TC degradation. c) The photograph of photocatalytic device outdoors. d) Degradation efficiency of PCS-CA and PCS-CZ-O-DCM for different concentrations (1–200 mg L\(^{-1}\)) of TC under natural sunlight.

penetration of contaminants into the active sites of the aerogel.\(^{[42-44]}\) It can be seen from Figure S17 (Supporting Information) that the kinetic curves of different samples. The pseudo-first-order kinetic constants \(k_{obs}\) of PCS-CA and PCS-CZ-O-DCM were 0.0446 and 0.0314 min\(^{-1}\), respectively. In addition, the photocatalytic performances of PCS-CA and PCS-CZ-O-DCM were compared with the reported catalysts as shown in Table S5 (Supporting Information). Remarkably, with the diverse light sources, removal efficiency and \(k_{obs}\) of PCS-CA and PCS-CZ-O-DCM were higher than that of the related catalysts.\(^{[45-50]}\)

Reusability is an important factor for photocatalysts.\(^{[51]}\) Therefore, we investigated the stability of PCS-CA and PCS-CZ-O-DCM by recycling experiments (Figure 6b; Figure S18, Supporting Information). We can see that the degradation efficiency of PCS-CA aerogel and PCS-CZ-O-DCM photocatalysts in the fifth cycle was hardly reduced compared with the first one. The property of PCS-CZ-O-DCM was essentially unchanged by photocatalytic cycling tests, and this was also confirmed by the comparison of FT-IR and UV–vis spectra (Figure S19, Supporting Information).

Harnessing unlimited solar energy for the solution of the problem of energy scarcity and environmental pollution has always been the most appealing field for scientists.\(^{[52,53]}\) The UV–vis absorption spectrum of PCS-CZ-O-DCM was found to cover the range of natural sunlight, which indicates that it is capable of directly absorbing cheap and renewable solar energy. This inspired
us to investigate the ability of PCS-CA and PCS-CZ-O-DCM to degrade antibiotics under natural sunlight. TC, the most common antibiotic class of drugs, is found in hospital and pharmaceutical industry wastewater at extremely high residual concentrations of 1–1100 mg L$^{-1}$. In order to be closer to the concentration level of TC in the real wastewater, this experiment not only set up a low concentration of TC solution (1 mg L$^{-1}$), but also increased the concentration of TC to 200 mg L$^{-1}$. Figure 6c shows the photo of a practical device for photocatalytic degradation reactions under natural sunlight. The relation of TC initial concentration and its degradation in PCS-CA and PCS-CZ-O-DCM systems is shown in Figure 6d. The catalytic removal efficiency of TC was reduced from 100% to 96.8% and 100% to 86.5% for PCS-CA and PCS-CZ-O-DCM, respectively, when the initial contaminant concentration was changed from 1 to 200 mg L$^{-1}$. At low contaminant concentrations, TC molecules can fully interact with the oxidizing species, therefore the degradation efficiencies are very high. The number of TC molecules covering surfaces of PCS-CZ-O-DCM and PCS-CA increases with growing pollutant concentrations, which may conceal active sites and thus hinder the redox-active centers on PCS-CZ-O-DCM and PCS-CA surfaces. In addition, at high pollutant concentrations, the competitive effect of pollutant molecules and intermediates for limited free radicals may intensify. As well as in the case of an elevated TC concentration, most of the photon influx is absorbed in the surface of TC molecules, rather than in the active surface sites. As a result, less electron-hole pair generated and thus decontamination efficiency was reduced.

In order to disclose the degradation pathway and realize effective TC degradation, it is important to identify the degradation by-products. TC solutions with different reaction time were analyzed by linear ion trap high-resolution LC-MS, and possible degradation pathways were proposed based on MS spectra (Figure 7; Figure S20, Supporting Information). Owing to the low binding energy of N–C bonds, it was easily attacked in photocatalytic oxidation. Subsequently, the bond of the CO group was broken and a product A (m/z 430) was got. The removal of the N–CH$_3$ from the product A forms product B (m/z 318). The product C (m/z 274) was formed due to the ring-rupturing reactions and the loss of functional groups. After a sequential redox reaction, the six-membered ring structure is opened. The product D (m/z 204) was produced by further catalyzed through a demethylation reaction. Finally, the intermediate products were completely decomposed by ring-rupturing reactions to achieve the mineralization of TC, and inorganic products, such as CO$_2$, H$_2$O were generated.

A series of free radical trapping experiments were conducted to explore the photoinduced species generated during PCS-CZ-O-DCM photocatalysis (Figure 8a). Three radical scavengers, p-benzoquinone (p-BQ), isopropyl alcohol (IPA), and EDTA-2Na (EDTA) were used for peroxide radicals (•O$_2^−$), hydroxyl radicals (•OH), and holes (•h$^+$), respectively. IPA had almost no inhibitory effect, which indicated that PCS-CZ-O-DCM could not produce •OH under light conditions or •OH did not contribute significantly to the degradation process. In contrast, the efficiency of photocatalytic degradation of TC was significantly reduced when p-BQ and EDTA were added; these findings clearly proved that •O$_2^−$ and •h$^+$ radicals were the predominant active species in the degradation of TC. To confirm the production of free radicals, the electron spin resonance (ESR) spectra of PCS-CZ-O-DCM were recorded. As shown in Figure 8b, the characteristic peaks of •O$_2^−$ were observed under visible light irradiation, but cannot be detected under dark. The peaks of DMPO-•OH were not detected under neither UV irradiation nor dark conditions, which agreed with a previous prediction (Figure S21, Supporting Information).

In addition, photoelectrochemical tests were conducted to investigate the charge transfer and separation in the bulk. The electrochemical impedance spectroscopy (EIS) in Figure 8c showed that CZ-O-DCM had a much smaller arc radius of Nyquist plot than that of PCS-CZ-O-DCM and PCS-CA, reflecting lower electric resistance for charge transfer. Figure 8d, recorded the photocurrent response density spectra of CZ-O-DCM, PCS-CZ-O-DCM, and PCS-CA during the successive visible-light on and off cycles at 50 s intervals. Obviously, under the identical condition, CZ-O-DCM presented much higher photocurrent density than that of the PCS-CZ-O-DCM and PCS-CA. These observations indicate that CZ-O-DCM has a higher capability to realize the separation.
of photogenerated charge carriers. The reason is that the chromophore contents in PCS-CZ-O-DCM and PCS-CA are much lower than CZ-O-DCM. Therefore, the electron mobility and photogenerated charge carrier separation ability can be controlled by changing the chromophore content in this study.

The UV–vis DRS spectrum shown in Figure 8e indicates that PCS-CZ-O-DCM possesses a strong UV and visible light harvesting capacity. According to the corresponding Tauc’s plots (Figure 8f), bandgap energy ($E_g$) of PCS-CZ-O-DCM (1.65 eV) was calculated. The valence band maximum ($E_{VB}$) of PCS-CZ-O-DCM was 0.79 eV as determined based on the valence band-XPS scan spectrum (Figure 8g), equaling to 0.77 (vs NHE) on the calculation formula ($E_{NHE} = \Phi + E_{VB}$). Furthermore, according to the formula ($E_{VB} = E_{CB} + E_{CB}$), the conduction band potential ($E_{CB}$) was calculated to be −0.88 eV (vs NHE).

As depicted in Figure 8f, the band structure was performed in detail and combined with the free radicals. In the catalytic systems, $h^+$ and $^{•}O_2^{-}$ are the main active species. In addition, the CB potential (−0.88 V vs NHE) is lower than the standard reduction potential of $O_2$ ($E^0(O_2/^{•}O_2^{-}) = −0.33$ V vs NHE), $^{•}O_2^{-}$ can be generated via $O_2 + e^− →^{•}O_2^{-}$ reaction. However, the VB potential of PCS-CZ-O-DCM is located above the redox potential of $H_2O/^{•}OH(2.38$ eV vs NHE) and this reaction could not be initiated. This is fully consistent with the degradation mechanism we proposed earlier, i.e., the active substances are $^{•}O_2^{-}$ and $h^+$ radicals.

The manufacture of plasticity devices based on PCSs is crucial for practical applications. To achieve scaled-up photodegradable wastewater treatment, PCS-CA aerogel was filled and fixed inside a transparent glass tube to form a continuous flow-through device (Figure 9a). For the photodegradation experiments, TC-contaminated water (200 mL, 100 mg L$^{-1}$ initial concentration) was passed through PCS-CA aerogel device upon UV irradiation at a flow rate of 50 mLmin$^{-1}$. The TC content continually decreased as the operating time of the device increased. After 70 min of continuous circulation, 99.8% of TC degraded, and the effluent in the container became clean water. In contrast, only 20% of TC was removed by chitosan aerogel column. The recycle and reuse potential of PCS-CA aerogel device as a photocatalyst in TC degradation reactions were investigated in
continuous operation using the same aerogel samples. As shown in Figure 9c, the degradation efficiency of the PCS-CA device for TC was still >96% after five consecutive runs. In addition, the effect of the initial concentration of TC on the photodegradation device was also investigated (Figure 9d). At antibiotic concentrations of <10 mg L\(^{-1}\), \(\approx\)100% of the pollutant molecules were removed after 70 min of the photodegradation device operation. When the TC concentration was further increased to the range of 80 to 200 mg L\(^{-1}\), the efficiency of the photocatalytic device was reduced, but the photodegradation efficiency could still reach 97%. Therefore, we can conclude that this multifunctional NIR emitting PCS-CA aerogel is a promising hybrid material for facile wastewater treatment with high water flux, excellent fluorescence property, and longstanding durability.

To further explore the application value of degrading antibiotics in real samples, PCS-CA aerogel device was applied in four different types of water (tap water, seawater, lake water of Daming Lake, and spring water from Black Tiger Spring) to perform experiments on the degradation of antibiotics. The real samples were spiked with known amounts of antibiotic. For the photodegradation experiments, TC-contaminated real wastewater was passed through PCS-CA aerogel device upon UV irradiation at a flow rate of 50 mLmin\(^{-1}\). The results are shown in Table S7 (Supporting Information). PCS-CA aerogel device has a slightly lower degradation efficiency for antibiotic than corresponding value under the same conditions in the deionized water. This may be related to the natural organic matter (NOM) that has similar structure to antibiotic pollutants in actual water.
samples, which may have effects on the degradation performance for the antibiotic pollutants.\textsuperscript{[14]} Despite the decrease, a relatively high removal efficiency was still achieved (>91% in both tap water, seawater, lake water of Daming Lake, and spring water from Black Tiger Spring), reflecting the PCS-CA aerogel device has good applicability in various water bodies.

3. Conclusion

In summary, we successfully synthesized a highly efficient dual-function porous material (PCS-CZ-O-DCM) by bonding a novel near-infrared emission organic (CZ-O-DCM) with octavinyl-silsesquioxane (OVS). Importantly, the hybrid material shows great potential as both a promising fluorescence nanoprobe for the detection of Tc antibiotic and a visible-light-driven photocatalyst for the degradation of Tc antibiotic, providing a unique platform to easily address the issue of antibiotic wastewater treatment. This study offers a new perspective on the development of wastewater treatment technology for simultaneous analysis and photocatalytic treatment of actual sewage. Finally, we have fabricated a hybrid aerogel-based device through a templated freeze-drying approach on PCS-CZ-O-DCM and low-cost chitosan, and the scaled-up wastewater treatment was successfully realized. This research significantly enriches silsesquioxane-based multifunctional NIR porous materials, but also provides an approach to hybrid aerogel for practical applications.

4. Experimental Section

Fabrication of PCS-CZ-O-DCM: In an inert atmosphere, CZ-O-DCM (0.396 g, 0.6 mmol) was placed in a three-necked flask, and dry 1,2-dichloroethane (12.5 mL) was added by a syringe. To this, OVS (0.560 g, 0.396 g, 0.6 mmol) was placed in a three-necked flask, and dry 1,2-dichloroethane (10.0 mL) was added dropwise. The solution was stirred for 0.5 h at room temperature, and anhydrous AlCl$_3$ (0.534 g, 4.0 mmol) was added, then heated at 85 °C for 24 h. The mixture was cooled to room temperature, generated precipitate was filtered and washed with anhydrous CH$_3$OH (200 mL), THF (200 mL), CHCl$_3$ (200 mL), and acetone (200 mL) to remove starting compounds and catalyst residue. The PCS-CZ-O-DCM was further purified in a Soxhlet extractor with CH$_3$OH and CH$_2$Cl$_2$ for 24 h, and dried in a vacuum under 100 °C to afford a red powder in 99% yield.

Preparation of PCS-CZ-O-DCM-Chitosan Aerogel (PCS-CA): Chitosan powder (200 mg) and PCS-CZ-O-DCM (20 mg) were added to an agate mortar and ground for 15 min to mix thoroughly. Then, deionized water (10 mL) was added and stirred for 30 min. After the mixture became viscous liquid, 60 μL of acetic acid was added and the mixture was stirred for 60 min. Subsequently, 1.4-butandiol diglycidyl ether (240 μL) was added and stirred for 60 min. The composite solution was transferred to the mold and left for 12 h until a stable hydrogel was formed. The hydrogel was placed in a refrigerator for 12 h to form crystals. Finally, the compound was freeze-dried at −50 °C for 1 d to afford different shapes of PCS-CZ-O-DCM@chitosan aerogels.

CCDC 2209833 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

antibiotics, near-infrared emission aerogels, photocatalysts, processability, sensors

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