

Hydrophobic Porous Polymer Films for the Degradation of Poorly Water-Soluble Dyes by Immobilization of Visible-Light- Responsive Photocatalysts

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Abstract

Hydrophobic porous polymer films immobilized with visible-light-responsive photocatalyst, namely a ZnSe/ZnTe hybrid, were successfully fabricated using a modified breath figure method to build a reusable environmental platform. Due to the hydrophobic property, the fabricated polymeric matrix attracts and gathers poorly water-soluble dye molecules inside the pores, which significantly accelerates the interfacial photocatalytic degradation process. To demonstrate the real degradation performance without any confusion from initial dye trapping, the efficiency was evaluated strictly after the film reached a complete adsorption equilibrium under dark conditions. In practical tests using alizarin as a model poorly water-soluble dye, the porous polymer films exhibited highly efficient visible-light degradation. Furthermore, to verify the structural advantage independently, compositionally identical flat films were prepared for comparison, confirming the superior performance of the porous architecture. The immobilized porous polymer films maintained over 90% of their initial degradation efficiency even after five consecutive reuse cycles without losing any catalyst particles into the water, offering a practical and scalable design strategy for treating poorly water-soluble environmental hazards.

Introduction

Organic pollutants discharged from industrial processes have become an important environmental concern [1]. In particular, poorly water-soluble organic pollutants are generally more difficult to remove than readily water-soluble contaminants because their limited dispersion in aqueous media reduces opportunities for effective interactions with solid treatment materials [2]. As industrial activities continue to diversify, the demand for efficient treatment technologies capable of handling such poorly water-soluble pollutants is steadily increasing.

Semiconductor photocatalysis has been widely recognized as an environmentally friendly technology for degrading organic pollutants because it can completely mineralize a broad range of contaminants under mild reaction conditions [3]. Nevertheless, the treatment of poorly water-soluble organic pollutants remains considerably more challenging because the insufficient interfacial contact inherently limits the access of pollutant molecules to the photocatalytically active sites [4]. Successful treatment therefore depends critically on improving this interfacial accessibility, which serves as a key prerequisite for the practical application of photocatalytic systems to poorly water-soluble contaminants.

To overcome the accessibility limitation associated with poorly water-soluble organic pollutants, the design of the supporting platform becomes as important as the photocatalyst itself. Among various supporting materials, polymer films have attracted considerable interest because of their mechanical flexibility, ease of handling, low manufacturing cost, and excellent potential for repeated use [5, 6]. In particular, introducing well-defined porous structures into polymer films provides enlarged interfacial areas while creating confined microenvironments that can increase the probability of interactions between pollutant molecules and photocatalytically active sites [7, 8]. Among the various fabrication methods available for porous polymer films, the breath figure (BF) method is one of the simplest and

most versatile approaches, producing highly ordered honeycomb-patterned porous structures through the condensation of water droplets under humid conditions [9, 10]. More importantly, photocatalysts immobilized within such porous polymer platforms can be readily recovered and reused without the secondary contamination commonly associated with dispersed powder photocatalysts, making this strategy particularly attractive for practical environmental applications [11].

Besides improving accessibility through rational platform design, selecting a visible-light-responsive photocatalyst that can also suppress rapid charge recombination is essential for achieving efficient degradation. A ZnSe/ZnTe hybrid is an attractive candidate for this purpose because it forms a heterojunction that effectively promotes spatial charge separation while maintaining active visible-light responses [12, 13, 14]. Although ZnSe/ZnTe heterostructures have been investigated as powder photocatalysts, their practical application to poorly water-soluble pollutants remains limited because catalyst–pollutant contact is governed by random dispersion in water rather than by controlled interfacial localization. For practical applications, such photocatalysts should be immobilized on stable supporting platforms to enable convenient recovery without secondary contamination. An ideal platform must not only facilitate catalyst reuse but also provide a confined microenvironment capable of enriching poorly water-soluble pollutants directly near the catalytic interfaces. Designing a single immobilized platform that satisfies these requirements remains a significant engineering challenge.

To address this engineering challenge, in the present study, hydrophobic porous polymer films immobilized with visible-light-responsive photocatalysts, namely a ZnSe/ZnTe hybrid, were fabricated by a modified breath figure method [15, 16]. To verify the specific architectural and catalytic benefits of this integrated platform, its performance was systematically compared with compositionally identical flat polymer films as well as porous polymer films immobilized with single-component ZnSe or ZnTe. To isolate true chemical degradation kinetics from initial physical trapping, all experiments were performed strictly after dark adsorption–desorption equilibrium had been established. Furthermore, the primary reactive oxygen species involved in the process were systematically identified to clarify the pore-confined degradation mechanism, and the reusability of the immobilized polymer platform was evaluated through repeated cycles alongside morphological characterization.

Experimental

Reagents

Poly(ϵ -caprolactone) (PCL, ($C_6H_{10}O_2$), average $M_n = 70,000\text{--}90,000\text{ g mol}^{-1}$), zinc chloride ($ZnCl_2 \geq 98\%$), sodium selenide ($Na_2Se \geq 98\%$), sodium telluride ($Na_2Te \geq 98\%$), tetrahydrofuran (THF $\geq 99.9\%$), alizarin dye (powder form, $C_{14}H_8O_4 \geq 97\%$), rhodamine B (RhB $\geq 98\%$), isopropanol ($\geq 99\%$), and p-benzoquinone ($\geq 98\%$) were purchased from Sigma-Aldrich and used without further purification. Deionized water was used throughout all experiments. Circular glass Petri dishes having a diameter of 5 cm were used as substrates for porous film fabrication.

Fabrication of ZnSe/ZnTe Hybrid-Immobilized Porous Polymer Films

ZnSe/ZnTe hybrid-immobilized porous polymer films were fabricated via a modified breath figure (BF) method following our previous reports [15, 16, 17]. Briefly, PCL (250 mg) and ZnCl_2 (20 mg) were dissolved in THF (5 mL) and cast onto a glass Petri dish (5 cm diameter). To prepare porous ZnSe/ZnTe hybrid films, humid conditions were generated using an aqueous solution containing 0.5 mM Na_2Se and 0.5 mM Na_2Te in 100 mL deionized water ($\text{RH} \approx 75\text{--}85\%$). During solvent evaporation, self-assembled water droplets produced a honeycomb-patterned porous structure, while interfacial reactions between Zn^{2+} and chalcogenide species resulted in the immobilization of ZnSe/ZnTe within the pores. The films were formed at room temperature for 2–3 h, followed by ambient drying prior to characterization.

As a reference, ZnSe/ZnTe hybrid-immobilized flat polymer films were also fabricated through a two-step process to isolate the effect of the porous architecture from that of the semiconductor composition. PCL (250 mg) and ZnCl_2 (20 mg) were dissolved in THF (5 mL), cast onto a glass Petri dish (5 cm diameter), and dried under ambient conditions (25°C). The resulting flat film was immersed in an aqueous solution containing 0.5 mM Na_2Se and 0.5 mM Na_2Te for 2 h to allow interfacial reactions to occur. After completion of the interfacial reaction, the film was removed, rinsed thoroughly with deionized water to remove residual Na_2Se and Na_2Te , and finally dried under ambient conditions. The fabrication procedures for the ZnSe/ZnTe hybrid-immobilized porous and flat polymer films are schematically illustrated in Scheme 1.

Photocatalytic degradation of dyes

The degradation process was continuously monitored using a flow UV–Vis spectrophotometer (Thermo Scientific Evolution 201) connected to a peristaltic pump following our previous procedure [18]. The photocatalytic activities of ZnSe/ZnTe hybrid-immobilized porous and flat polymer films were evaluated by the visible-light photocatalytic degradation of dyes under irradiation from a 100 W xenon arc lamp (LSF-100H, Asahi Spectra) equipped with a 420 nm cut-off filter (FGB420, Thorlabs). Prior to visible-light irradiation, the alizarin, employed as a model poorly water-soluble dye, solutions were maintained under dark conditions for 30 min to establish adsorption–desorption equilibrium. For the degradation experiments, a 1 cm $\times$ 1 cm film sample was immersed in 3 mL of dye solution. Owing to the limited water solubility of alizarin, 1 mg of alizarin was first dispersed in 0.5 mL of THF using an ultrasonic homogenizer (Sonictopia, STH-750S) and subsequently diluted with deionized water. Porous films immobilized with single-component ZnSe or ZnTe, prepared separately under Na_2Se and Na_2Te humid conditions, were also evaluated for alizarin degradation. For comparison, rhodamine B (RhB), which is readily soluble in water, was employed as a control dye to assess the effect of dye solubility on photocatalytic degradation. Unlike alizarin, RhB solutions were prepared directly in deionized water without the use of THF, and photocatalytic degradation experiments were performed without a prior dark adsorption step.

Identification of Primary Reactive Oxygen Species (ROS)

To identify the primary reactive oxygen species (ROS) involved in the photocatalytic degradation process, radical scavenger experiments were performed. These experiments were carried out only with the ZnSe/ZnTe hybrid-immobilized porous polymer films because the single-component (ZnSe- and ZnTe-immobilized) porous polymer films and the ZnSe/ZnTe hybrid-immobilized flat polymer films exhibited substantially lower photocatalytic activities. After adsorption-desorption equilibrium had been established under dark conditions, 10 μM of either isopropanol (as a hydroxyl radical, $\cdot\text{OH}$, scavenger) or p-benzoquinone (as a superoxide radical, $\cdot\text{O}_2^-$, scavenger) was introduced into the dye solution using a Hamilton syringe pipette immediately before visible-light irradiation. The subsequent degradation profiles were systematically recorded under the same photocatalytic conditions described above.

Characterization

The morphology and elemental composition of ZnSe-, ZnTe-, and ZnSe/ZnTe hybrid-immobilized porous polymer films, together with ZnSe/ZnTe hybrid-immobilized flat polymer films, were characterized using field-emission scanning electron microscopy (FE-SEM, HITACHI S-4300SE) coupled with energy-dispersive X-ray spectroscopy (EDS). The optical properties were investigated using a Thermo Scientific Evolution 201 UV–Vis spectrophotometer and a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies) for UV–Vis absorption and photoluminescence (PL) measurements, respectively. The crystalline structures of the films were analyzed using an X-ray diffractometer (Rigaku Ultima IV), while the surface chemical compositions and oxidation states were examined by X-ray photoelectron spectroscopy (XPS, AXIS SUPRA+, Kratos Analytical Ltd). Static water contact angles were measured using a contact-angle goniometer (CAM 100, KSV Model Theta Lite) to evaluate the surface wettability of the ZnSe/ZnTe hybrid-immobilized porous and flat polymer films.

Results and discussion

Figure 1a shows SEM images of hydrophobic porous polymer films immobilized with ZnSe, ZnTe, and ZnSe/ZnTe hybrid prepared by a modified breath figure method. Well-defined honeycomb architectures were retained after semiconductor immobilization, indicating that the interfacial reactions proceeded without disrupting the original porous morphology. Higher-magnification images further reveal conformal semiconductor coatings along the pore-wall surfaces, demonstrating that the semiconductor phases were uniformly deposited while preserving the structural integrity of the porous framework. The corresponding EDS spectra further verified the successful formation of ZnSe, ZnTe, and ZnSe/ZnTe hybrid through the expected elemental compositions. In particular, the ZnSe/ZnTe hybrid film simultaneously exhibited characteristic Zn, Se, and Te signals, whereas the single-component films displayed only their respective chalcogen elements. Cross-sectional SEM images further demonstrate that the ZnSe/ZnTe hybrid was uniformly distributed throughout the pore-wall framework rather than being confined to the outer surface. Compared with the smooth pore walls of the bare PCL film, the

immobilized film exhibited a continuous interfacial semiconductor layer surrounding the pore walls while maintaining the original honeycomb architecture, confirming successful immobilization throughout the porous structure. For comparison, Fig. 1b presents flat polymer films immobilized with ZnSe/ZnTe hybrid prepared by a two-step process. The bare PCL film exhibited a smooth and featureless surface, whereas the immobilized film displayed a continuous semiconductor layer with increased surface roughness following the interfacial reaction. The corresponding cross-sectional SEM images together with the EDS spectrum further confirmed the successful formation of ZnSe/ZnTe hybrid layers on the flat polymer substrate.

The optical properties of hydrophobic porous polymer films immobilized with ZnSe, ZnTe, and ZnSe/ZnTe hybrid were characterized by UV-vis absorption and photoluminescence (PL) spectroscopy, as shown in Fig. 2. The ZnSe-immobilized films exhibited relatively strong absorption in the shorter visible-light region, whereas the ZnTe-immobilized films showed absorption extending toward longer wavelengths [19]. In contrast, the ZnSe/ZnTe hybrid-immobilized films exhibited broadened visible-light absorption over an extended spectral range, reflecting the complementary absorption characteristics of the ZnSe and ZnTe components [19, 20]. The PL spectra revealed a pronounced decrease in emission intensity for the ZnSe/ZnTe hybrid-immobilized films compared with the corresponding single-component films under identical excitation conditions. The pronounced PL quenching suggests suppressed recombination of photogenerated charge carriers, which is expected to enhance photocatalytic activity under visible-light irradiation [20, 21]. Because the UV-vis absorption and PL spectra of the corresponding flat polymer films were essentially identical to those of the porous films, except for slight differences in spectral intensity, they are omitted for clarity. These results indicate that the optical properties of the ZnSe/ZnTe hybrid were largely independent of the polymer film morphology. Therefore, the enhanced photocatalytic performance of the porous films discussed below is unlikely to originate from intrinsic differences in the optical properties of the immobilized ZnSe/ZnTe hybrid, but rather from the porous architecture itself.

Figure 3 presents the phase and chemical characterization of the immobilized ZnSe/ZnTe hybrid by XRD and XPS analyses. As shown in Fig. 3a, the XRD patterns of the hybrid-immobilized porous polymer films exhibited diffraction peaks corresponding to both ZnSe and ZnTe, confirming the coexistence of the two semiconductor phases. The diffraction pattern obtained from the corresponding flat polymer film was essentially identical, indicating that the crystalline phase of the immobilized hybrid was independent of the supporting polymer morphology [22]. The XPS survey spectra (Fig. 3b) further verified the elemental compositions of the immobilized films. While the single-component films exhibited the expected Zn/Se or Zn/Te signals, the ZnSe/ZnTe hybrid films simultaneously displayed Zn, Se, and Te signals. Because the survey spectra of the porous and flat hybrid films were nearly identical, only representative high-resolution spectra are presented. The characteristic Zn 2p, Se 3d, and Te 3d binding energies are consistent with the reported values for ZnSe and ZnTe [22, 23, 24], confirming the successful immobilization of the ZnSe/ZnTe hybrid on the polymer films.

The surface wettability of bare and ZnSe/ZnTe hybrid-immobilized porous polymer films, together with their corresponding flat polymer films, was evaluated by water contact angle (WCA) measurements and the results are presented in Fig. 4. The bare porous PCL film exhibited a high WCA of $111.2 \pm 0.1^\circ$, which decreased slightly to $104.4 \pm 0.3^\circ$ after immobilization of the ZnSe/ZnTe hybrid. This slight decrease is attributed to the relatively hydrophilic nature of the immobilized ZnSe/ZnTe hybrid. Nevertheless, the porous film retained a highly hydrophobic surface, preserving the confined hydrophobic microenvironment provided by the honeycomb architecture. The corresponding flat polymer films exhibited lower WCAs ($87.3 \pm 0.3^\circ$ for bare PCL and $78.6 \pm 0.3^\circ$ after immobilization), indicating that the honeycomb porous architecture provides a more hydrophobic interfacial environment than the corresponding flat surface [25, 26]. Such a hydrophobic confined environment can promote the local enrichment of poorly water-soluble organic molecules near the photocatalytically active interfaces, thereby facilitating their degradation under visible-light irradiation.

Although the ZnSe/ZnTe hybrid was selectively immobilized along the pore-wall surfaces, the original honeycomb architecture remained essentially unchanged, allowing the films to retain a highly hydrophobic interfacial environment after semiconductor immobilization. This pore-selective configuration is expected to promote the preferential localization and enrichment of poorly water-soluble dye molecules within the porous framework, thereby increasing their accessibility to the photocatalytically active interfaces. The contribution of such preferential dye enrichment must therefore be distinguished from the intrinsic photocatalytic degradation behavior of the immobilized hybrid.

Therefore, to evaluate the intrinsic photocatalytic activity of the ZnSe/ZnTe hybrid-immobilized porous polymer films, photocatalytic degradation experiments were performed only after adsorption–desorption equilibrium had been established under dark conditions. The dye concentration at the end of the dark adsorption period (C_{ads}) was subsequently used as the initial concentration for evaluating the photocatalytic degradation of the poorly water-soluble alizarin, thereby excluding the contribution of preferential dye adsorption prior to visible-light irradiation. Representative adsorption–desorption equilibrium profiles are presented in Fig. 5a, illustrating the influence of the porous architecture on the initial distribution of alizarin molecules before photocatalytic degradation. For comparison, the photocatalytic degradation of the readily water-soluble RhB was evaluated directly under identical visible-light irradiation conditions without a prior dark adsorption process because its adsorption under dark conditions was negligible (Fig. 5b). The ZnSe/ZnTe hybrid-immobilized porous polymer film exhibited higher photocatalytic activity than the corresponding flat film, indicating that the porous architecture itself provides a beneficial reaction environment even in the absence of significant adsorption effects.

The photocatalytic degradation behavior of alizarin after adsorption equilibrium is shown in Fig. 5c. After the concentration at the end of the dark period (C_{ads}) had been normalized to unity, the ZnSe/ZnTe hybrid-immobilized porous polymer film exhibited markedly enhanced visible-light photocatalytic degradation compared with the corresponding flat polymer film as well as the single-component ZnSe- and ZnTe-immobilized porous polymer films. The superior photocatalytic performance of the porous

ZnSe/ZnTe hybrid film is attributed to the combined effects of the hydrophobic porous architecture, which promotes preferential enrichment of poorly water-soluble dye molecules, and the favorable visible-light photocatalytic properties of the immobilized ZnSe/ZnTe hybrid.

To identify the dominant reactive oxygen species responsible for photocatalytic degradation, radical scavenger experiments were performed using the optimized porous ZnSe/ZnTe hybrid film. As shown in the **inset** of Fig. 5c, p-benzoquinone caused a substantially greater suppression of photocatalytic degradation than isopropanol, indicating that superoxide radicals ($\cdot\text{O}_2^-$) play a more dominant role than hydroxyl radicals ($\cdot\text{OH}$) in the present system. This behavior may be related to the more pronounced contribution of superoxide radicals observed during the photocatalytic degradation of alizarin over the ZnSe/ZnTe hybrid-immobilized porous polymer film.

To quantitatively compare the photocatalytic performances, the degradation profiles shown in Fig. 5 were analyzed using a pseudo-first-order kinetic model (Fig. 6). The ZnSe/ZnTe hybrid-immobilized porous polymer film exhibited the highest apparent reaction rate constant for alizarin degradation, followed by the corresponding single-component porous polymer films and the flat polymer film. For RhB, the difference between the porous and flat polymer films became much smaller, although the porous ZnSe/ZnTe hybrid film still exhibited the higher apparent reaction rate.

The reusability of the ZnSe/ZnTe hybrid-immobilized porous polymer films was evaluated over five consecutive photocatalytic degradation cycles of alizarin. In each cycle, adsorption–desorption equilibrium was first established under dark conditions, followed by visible-light photocatalytic degradation under the same protocol used for the initial activity measurements. After each cycle, the films were subjected to ultrasonic cleaning in a THF/water (1:1, v/v) mixture to remove residual dye molecules, followed by rinsing with deionized water, drying under ambient conditions, and reuse in the subsequent photocatalytic cycle. This regeneration procedure was intentionally adopted to minimize the influence of residual adsorbed dye. Before each photocatalytic cycle, the same dark adsorption–desorption equilibrium protocol was re-established so that the photocatalytic activity could be evaluated under identical initial conditions. As shown in Fig. 7, the films retained more than 90% of their initial photocatalytic activity after five consecutive cycles. SEM observations after the cycling tests revealed that the honeycomb porous framework remained largely intact despite slight pore-wall deterioration, indicating that the immobilized ZnSe/ZnTe coating remained firmly anchored to the polymer framework throughout repeated photocatalytic operation and regeneration. These results demonstrate that the immobilized porous polymer films possess excellent reusability and structural robustness, highlighting their practical potential for repeated treatment of poorly water-soluble organic dyes.

Based on the experimental observations described above, the enhanced photocatalytic degradation of poorly water-soluble dyes can be understood as the combined consequence of a hydrophobic confined microenvironment and the visible-light photocatalytic activity of the immobilized ZnSe/ZnTe hybrid, as schematically illustrated in Fig. 8. The modified breath figure process selectively immobilizes the ZnSe/ZnTe hybrid along the pore-wall surfaces while preserving the original honeycomb porous

architecture. Consequently, the porous polymer films retain a highly hydrophobic confined microenvironment, as confirmed by the water contact angle measurements, which preferentially enriches poorly water-soluble dye molecules in the vicinity of the immobilized photocatalyst.

Unlike conventional flat photocatalytic surfaces, where dye molecules remain randomly dispersed in the surrounding solution, the confined porous architecture locally concentrates poorly water-soluble dye molecules around the photocatalytically active interfaces. This confined distribution provides a favorable reaction environment by increasing the accessibility of dye molecules to the immobilized ZnSe/ZnTe hybrid during visible-light irradiation.

Upon visible-light irradiation, the ZnSe/ZnTe hybrid generates photogenerated electrons and holes, which subsequently participate in interfacial redox reactions to produce reactive oxygen species responsible for dye degradation. The radical scavenger experiments identified superoxide radicals ($\cdot\text{O}_2^-$) as the dominant reactive species. This result is consistent with the confined hydrophobic microenvironment of the porous films, where the relatively longer-lived superoxide radicals have a greater opportunity to interact with locally enriched alizarin molecules than the much shorter-lived hydroxyl radicals. This preferential degradation pathway arises from the synergistic integration of the porous polymer architecture and the immobilized ZnSe/ZnTe hybrid. Structurally, the hydrophobic confined microenvironment preferentially enriches poorly water-soluble alizarin molecules within the pore interiors, increasing their local concentration near the photocatalytically active interfaces. Chemically, the immobilized ZnSe/ZnTe hybrid efficiently generates reactive oxygen species under visible-light irradiation, with the scavenger experiments identifying superoxide radicals as the dominant oxidative species. Consequently, the local enrichment of dye molecules within the confined porous architecture maximizes their probability of interacting with the dominant superoxide radicals, thereby promoting efficient interfacial photocatalytic degradation. Consequently, the confined hydrophobic microenvironment increases the effective encounter frequency between locally enriched alizarin molecules and the dominant superoxide radicals, thereby promoting efficient interfacial photocatalytic degradation.

Therefore, the enhanced photocatalytic performance does not arise solely from the visible-light photocatalytic activity of the immobilized ZnSe/ZnTe hybrid, but also from the hydrophobic confined microenvironment created by the porous polymer architecture, which promotes preferential enrichment of poorly water-soluble dye molecules and facilitates their effective interaction with photocatalytically generated reactive oxygen species.

Conclusions

The present study shows that a polymer film platform can be constructed by immobilizing a visible-light-responsive ZnSe/ZnTe hybrid within hydrophobic porous polymer films. This porous polymeric structure provides a confined microenvironment that enriches poorly water-soluble dye molecules near the active interfaces. Scavenger experiments successfully identified superoxide radicals ($\cdot\text{O}_2^-$) as the dominant

reactive species driving the degradation inside the micro-pores. In practical reusability tests, the immobilized porous polymer films maintained over 90% of their initial degradation efficiency even after five consecutive cycles using the same adsorption–desorption evaluation protocol, demonstrating reliable structural stability and reuse. Ultimately, these findings demonstrate that hydrophobic porous polymer films immobilized with photocatalysts function not only as stable supports but also as recyclable platforms that improve pollutant accessibility for the effective degradation of poorly water-soluble dyes.

Declarations

Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contribution

Author Contributions K. P. experimented for the research data, and prepared figures. S. S. experimented for the research data, and prepared figures. B. S. designed experimental equipment. D. H. wrote the main manuscript, and received fund.

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Data availability

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

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Scheme 1

Scheme 1 is available in the Supplementary Files section.

Figures

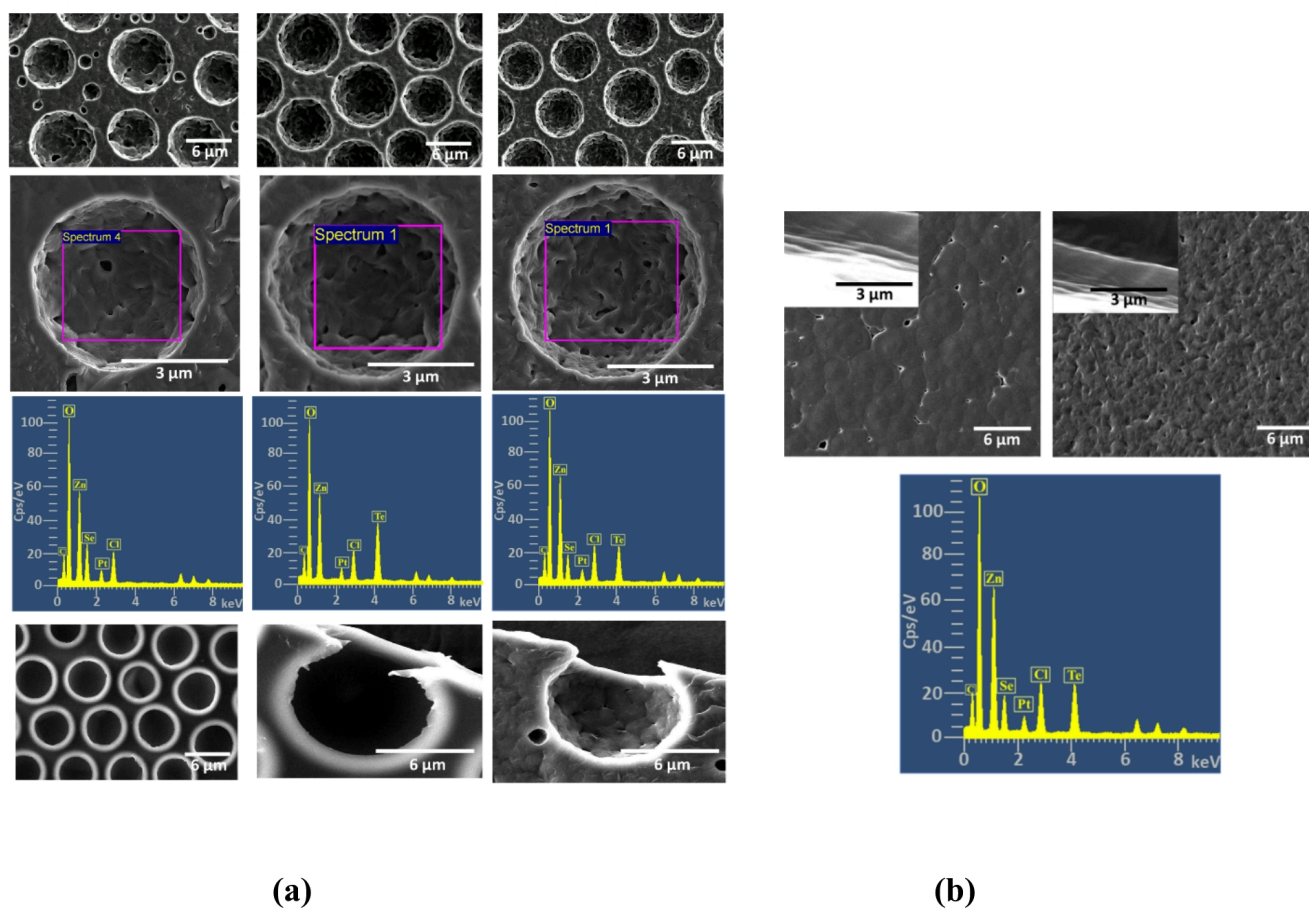


Figure 1

SEM characterization of ZnSe/ZnTe hybrid-immobilized hydrophobic porous polymer films and the corresponding flat polymer films. (a) Top-view SEM images of hydrophobic porous polymer films immobilized with ZnSe, ZnTe, and ZnSe/ZnTe hybrid, along with the corresponding high-magnification pore-wall images and EDS spectra. The bottom row shows SEM images of the bare PCL film, cross-sectional porous PCL film, and cross-sectional ZnSe/ZnTe hybrid-immobilized porous polymer film. (b) Top-view SEM images of the bare flat PCL film and ZnSe/ZnTe hybrid-immobilized flat polymer film. Insets show the corresponding cross-sectional SEM images, and the EDS spectrum of the immobilized film confirms the presence of Zn, Se, and Te.

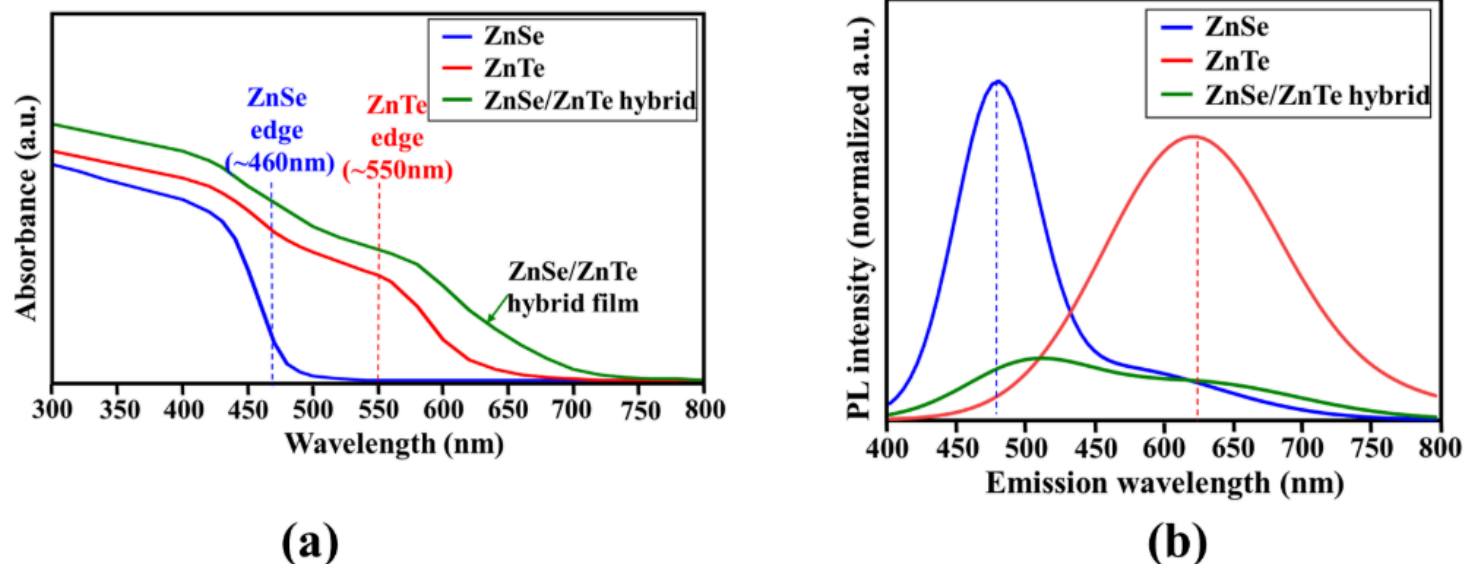
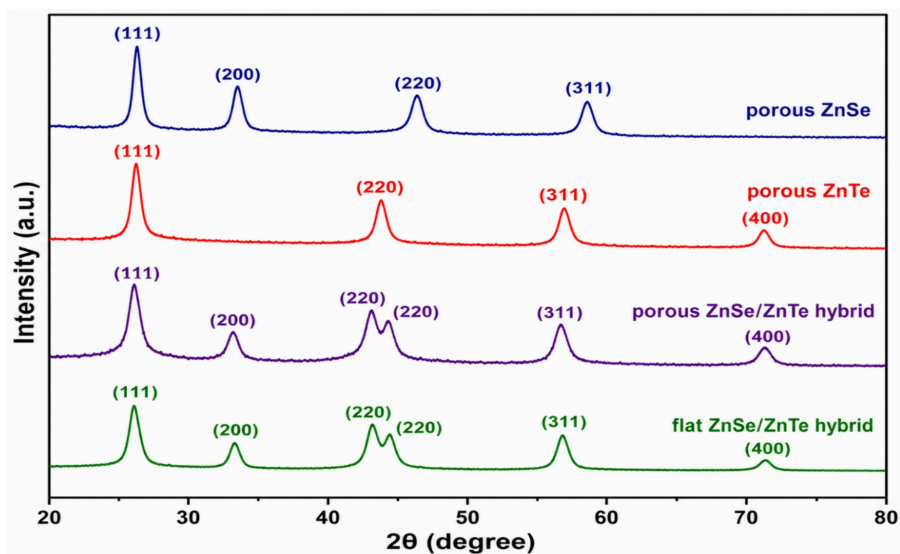
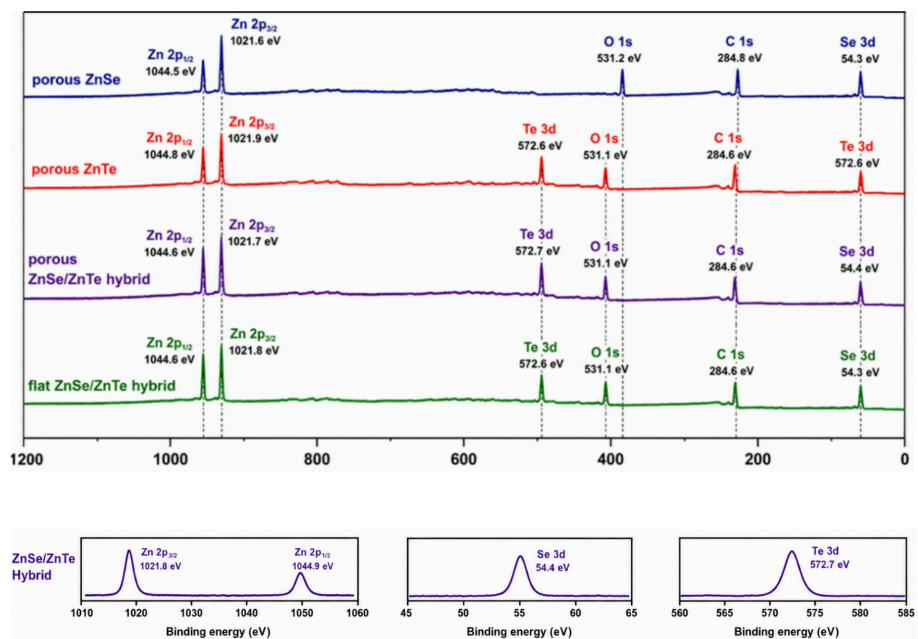


Figure 2

Optical characterization of hydrophobic porous polymer films immobilized with ZnSe, ZnTe, and ZnSe/ZnTe hybrid. (a) UV-vis absorption spectra of ZnSe-, ZnTe-, and ZnSe/ZnTe hybrid-immobilized porous polymer films. The ZnSe/ZnTe hybrid films exhibited broadened visible-light absorption extending over a wider spectral region than the corresponding single-component films. (b) Photoluminescence (PL) spectra of ZnSe-, ZnTe-, and ZnSe/ZnTe hybrid-immobilized porous polymer films measured under identical excitation conditions. The ZnSe/ZnTe hybrid films exhibited markedly suppressed PL intensity relative to the corresponding single-component films, indicating suppressed recombination of photogenerated charge carriers.



(a)



(b)

Figure 3

Phase and chemical characterization of ZnSe/ZnTe hybrid-immobilized polymer films. (a) XRD patterns of ZnSe-, ZnTe-, and ZnSe/ZnTe hybrid-immobilized hydrophobic porous polymer films together with the corresponding ZnSe/ZnTe hybrid-immobilized flat polymer film. (b) XPS survey spectra of ZnSe-, ZnTe-, and ZnSe/ZnTe hybrid-immobilized hydrophobic porous polymer films together with the corresponding

ZnSe/ZnTe hybrid-immobilized flat polymer film. Representative high-resolution Zn 2p, Se 3d, and Te 3d spectra of the ZnSe/ZnTe hybrid are also shown.

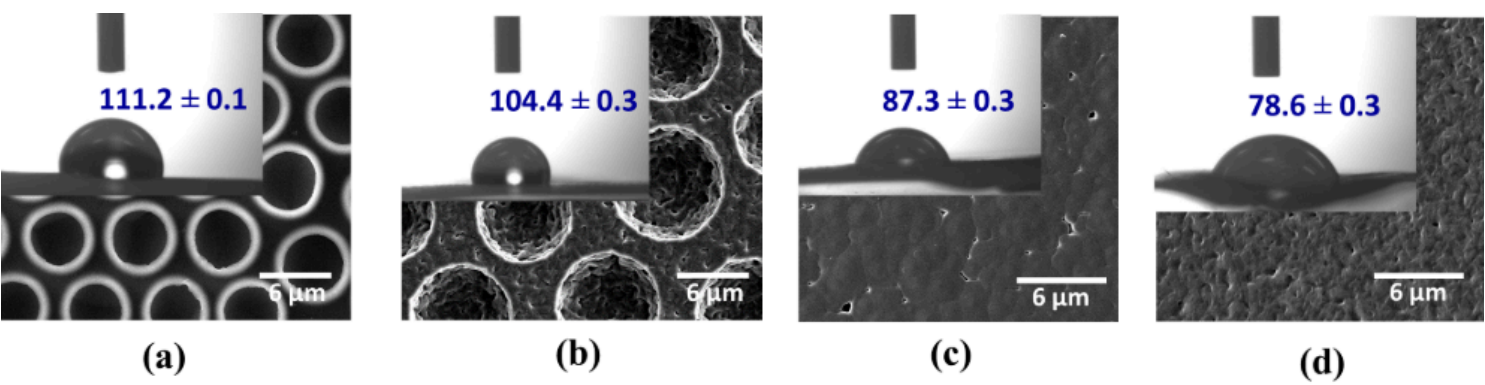


Figure 4

Water contact angle (WCA) measurements and corresponding SEM images of bare and ZnSe/ZnTe hybrid-immobilized porous and flat polymer films. (a) Bare porous PCL film, (b) ZnSe/ZnTe hybrid-immobilized porous PCL film, (c) bare flat PCL film, and (d) ZnSe/ZnTe hybrid-immobilized flat PCL film.

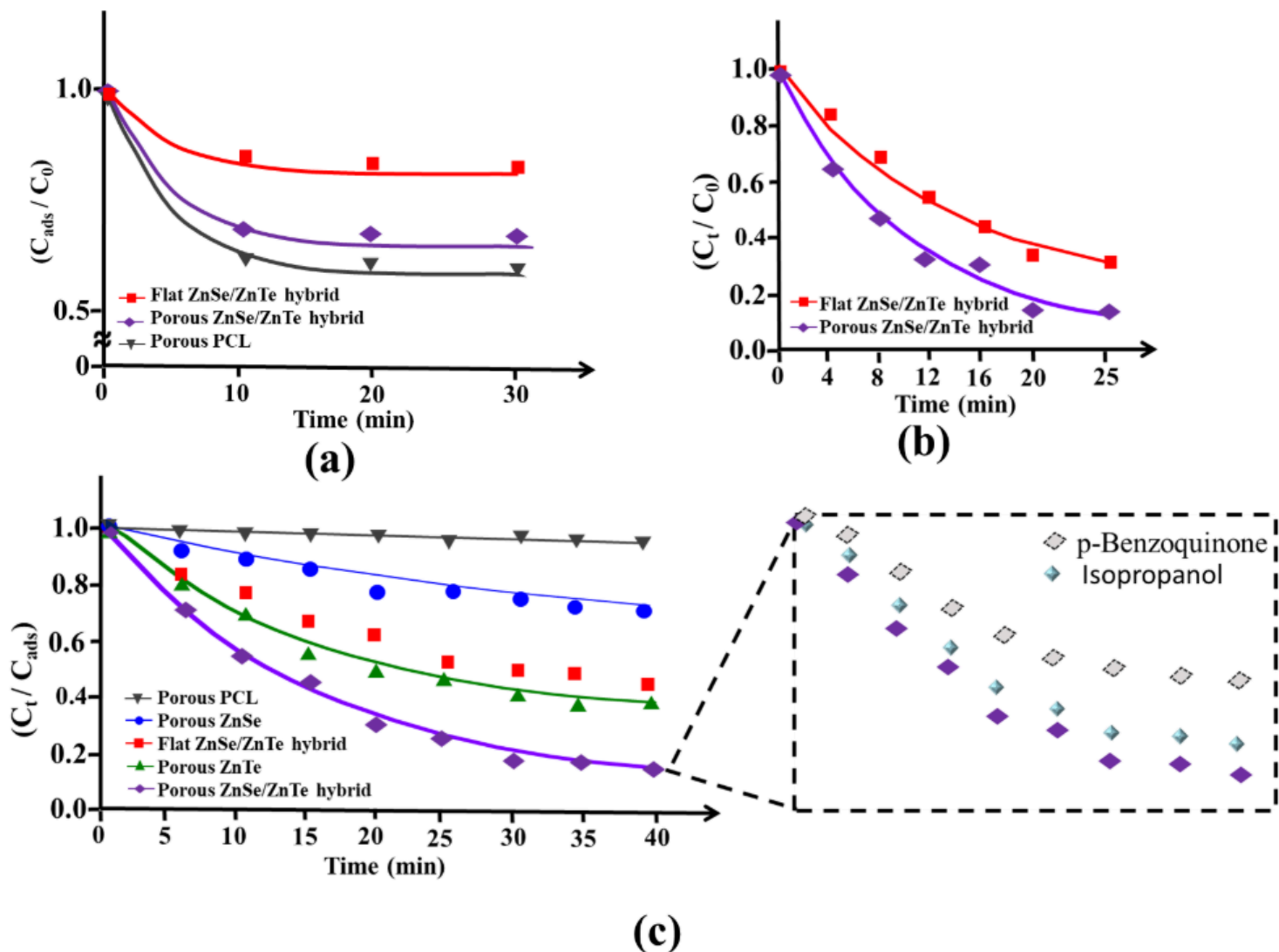


Figure 5

(a) Adsorption-desorption equilibrium profiles of poorly soluble Alizarin dye over various film substrates under dark conditions. (b) Photocatalytic degradation curves of water-soluble dye of rhodamine B (RhB) without a prior dark adsorption process, demonstrating the beneficial effect of the porous architecture for the photocatalytic degradation of a readily water-soluble dye. (c) Visible-light-driven photocatalytic degradation of alizarin after reaching adsorption equilibrium (C_t/C_{ads}); the inset shows the targeted radical scavenger effects (using p-benzoquinone and isopropanol, respectively) specifically evaluated on the optimized porous ZnSe/ZnTe hybrid film to elucidate the primary active species.

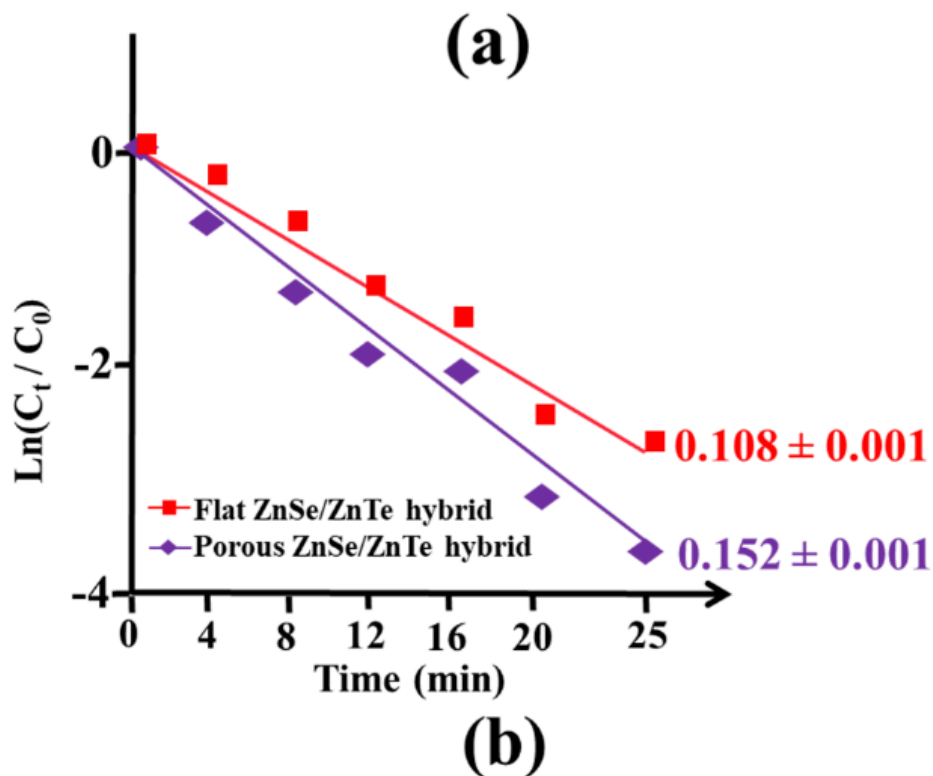
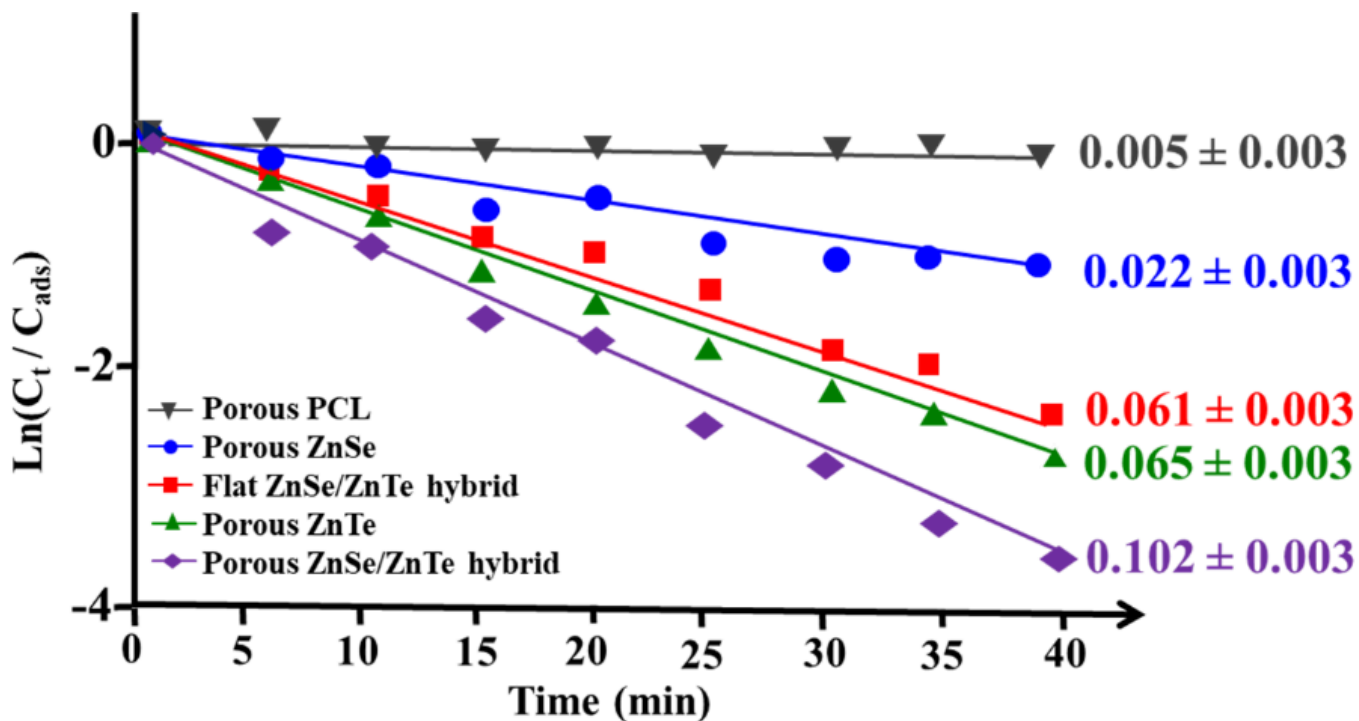


Figure 6

Pseudo-first-order kinetic analysis of the visible-light photocatalytic degradation of (a) alizarin and (b) rhodamine B (RhB). The corresponding flat ZnSe/ZnTe hybrid polymer film is included for comparison. The unit of apparent reaction rate constants (k) is min^{-1} .

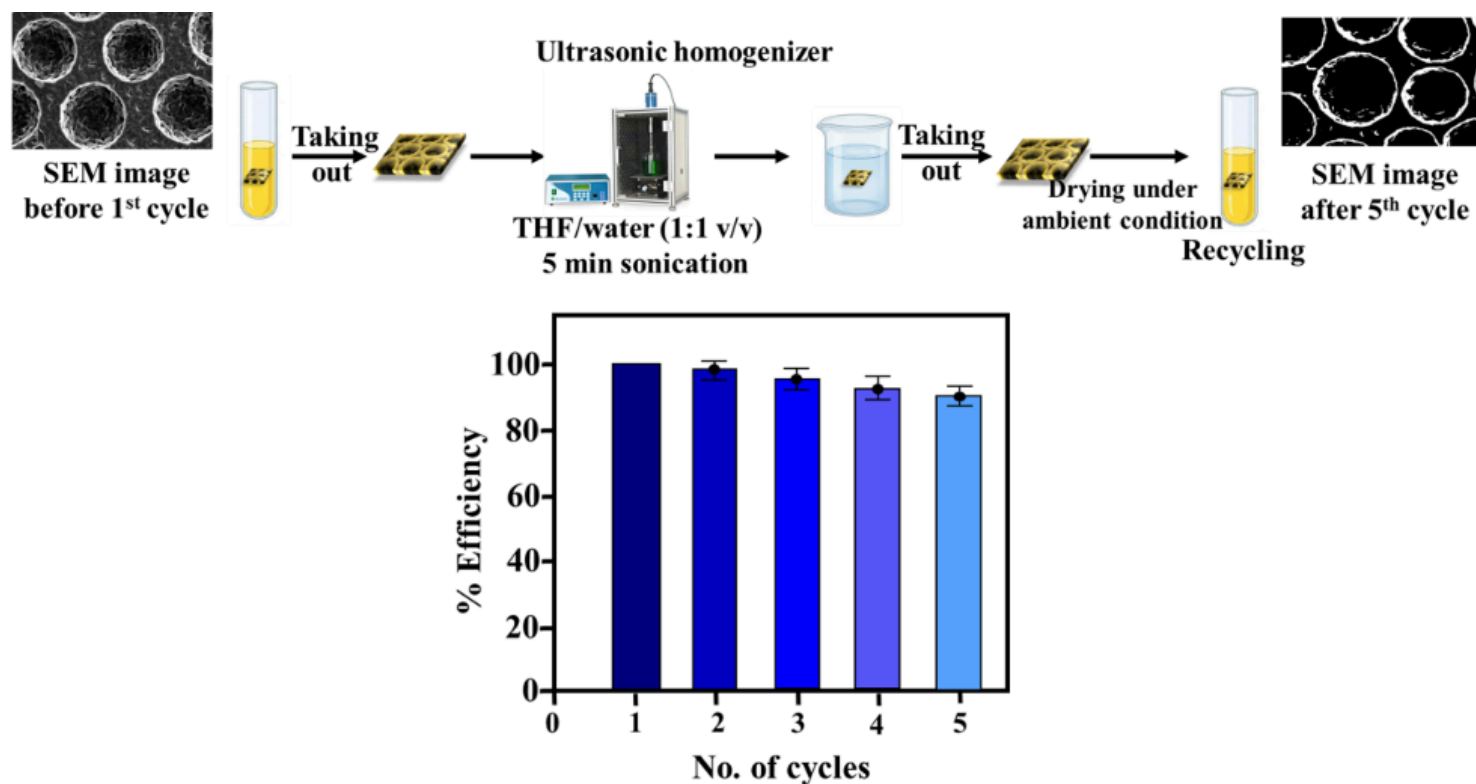


Figure 7

Reusability of ZnSe/ZnTe hybrid-immobilized porous polymer films during five consecutive visible-light photocatalytic degradation cycles of alizarin. In each cycle, adsorption–desorption equilibrium was first established under dark conditions before visible-light irradiation, following the same evaluation protocol used for the initial photocatalytic measurements. Representative SEM images before the first cycle and after the fifth cycle illustrate the structural integrity of the porous framework after repeated photocatalytic operation and regeneration. More than 90% of the initial photocatalytic activity was retained after five consecutive cycles.

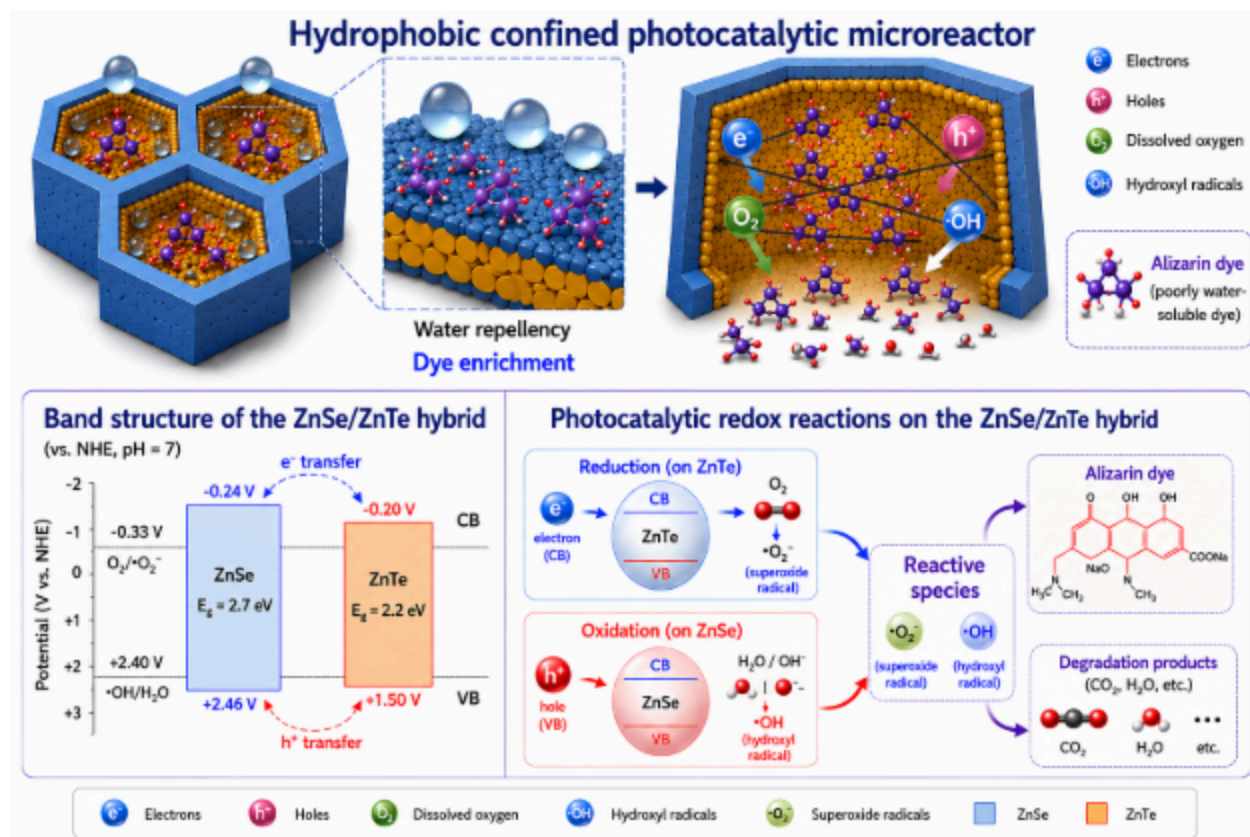


Figure 8

Schematic illustration of the proposed photocatalytic mechanism of ZnSe/ZnTe hybrid-immobilized hydrophobic porous polymer films. **(Top)** The hydrophobic honeycomb porous architecture creates a confined microenvironment that preferentially enriches poorly water-soluble alizarin molecules near the immobilized photocatalytic interfaces through water repellency. **(Bottom left)** Schematic band structure of the ZnSe/ZnTe hybrid, illustrating the relative band-edge positions responsible for visible-light photocatalytic activity. The band-edge potentials were adopted from the literature [27, 28]. **(Bottom right)** Proposed photocatalytic redox reactions occurring on the immobilized ZnSe/ZnTe hybrid, where photogenerated electrons and holes participate in the formation of superoxide ($\cdot O_2^-$) and hydroxyl ($\cdot OH$) radicals, respectively. The radical scavenger experiments indicate that superoxide radicals play the dominant role in the photocatalytic degradation of alizarin.

Supplementary Files

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