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Abstract: Due to their high absorption coefficient and long carrier lifetime, halide perovskites are promising candidates for photocatalysts. For this study, the antisolvent crystallization protocol and the colloidal crystal templating approach were combined to fabricate the highly crystalline cesium lead bromide perovskite with inverse opal morphology (IO-CsPbBr₃). Scanning electron microscopy and transmission electron microscope images demonstrate the three-dimensional well-ordered porous structures of the IO-CsPbBr₃ and their single-crystalline features. The presented approach not only provides hierarchical porous structures but also enhances overall crystallinity. When used as catalysts to promote the polymerization of 2,2',5',2''-ter-3,4-ethylenedioxythiophene, the highly crystalline IO-CsPbBr₃ exhibits a superior photocatalytic performance compared to its polycrystalline IO-CsPbBr₃ are well preserved under photocatalytic conditions. This novel approach enables the preparation of a halide perovskite inverse opal with high crystallinity.

Keywords: single crystalline perovskite; inverse opal; photocatalysis

1. Introduction

In the past decade, halide perovskites have been regarded as a fascinating optoelectronic material, and their excellent properties have reformed the development of the photovoltaic and light-emitting diodes field [1-3]. Through their high absorbance coefficient [4] and long diffusion lifetime [5], halide perovskites also show their potential as photocatalysts. Efforts have been devoted to exploring their application in photocatalytic CO_2 reduction [6–8], α -alkylation of aldehydes [9], the activation of C(sp³)-H [10], the degradation of organic dyes [11], the polymerization of 2,2',5',2''-ter-3,4-ethylenedioxythiophene (TerEDOT) [12] and the oxidation of benzyl alcohol [13,14]. Most of the examples have focused on the photocatalytic performance of halide perovskite quantum dots, and the influence of the surface state and halide composition on their photocatalytic performance has been reported [15,16]. Halide perovskite quantum dots possess a single-crystalline nature and a high surface area, which benefits photocatalytic performance. However, due to its high surface energy, the nanoscale halide perovskite may agglomerate. To preserve the morphology of the quantum dots, a surfactant is necessary, which unfortunately may make the electron transfer across the interface sluggish. To this end, a highly crystalline halide perovskite on a micrometer, or even on a larger scale, may circumvent this problem. However, halide perovskites on a large scale have been rarely reported.

The morphology and crystallinity of photocatalysts are two important factors relating to their performance [17,18]. It is well known that hierarchical structure is desirable for the photocatalyst since it may provide more active sites and shorten the carrier diffusion length between the carrier-generated center and the active sites [19]. The inverse opal has been proven to be an advantageous morphology for photocatalysts [20–23]. Tüysüz et al. developed the colloidal templating method to prepare halide perovskite inverse



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opals [24]. The photocatalytic degradation of organic dye over the CsPbBr₃ inverse opal has been investigated, and the enhanced performance of the hierarchical structure has been demonstrated [25]. Meanwhile, crystallinity plays an important role in the performance of optoelectronic materials [26]. Single crystals of halide perovskite also exhibited low trap density and long diffusion length and, thus, are desirable for preparing high-performance materials and devices [27]. However, the preparation of single crystalline optoelectronic materials with hierarchical structures is highly challenging. Snaith's group has reported single crystalline mesoporous TiO₂ for enhanced mobility and device performance [28]. To date, neither the fabrication of hierarchical single-crystalline all-inorganic halide perovskites nor the effect of the crystallinity of halide perovskites on their photocatalytic performance has been reported.

In this work, four colloidal crystals were prepared by using polystyrene microspheres with different diameters, and their long-ranged, ordered arrangement was evidenced by distinct photonic stop bands. Using the colloidal crystals as templates, a series of highly crystalline and polycrystalline CsPbBr₃ inverse opals were prepared. The obtained perovskite inverse opals were employed as photocatalysts to accelerate the polymerization of TerEDOT, and the highly crystalline CsPbBr₃ inverse opals exhibited enhanced photocatalytic performance compared to their polycrystalline counterparts. The significant improvement could be attributed to a higher degree of crystallinity and the inverse opal morphology.

2. Results and Discussion

Highly crystalline cesium lead bromide (IO-CsPbBr₃) with inverse opal structure was synthesized by combining the anti-solvent method and the colloidal crystal templating approach (as shown in Scheme 1: synthesis details are presented in the Experimental Section). A series of artificial opal templates were fabricated by filtrating the polystyrene microsphere with different diameters (214 nm, 379 nm, 433 nm and 501 nm) [29]. The distinct photonic stop bands demonstrated the ordered arrangement of the artificial templates. Later, the templates were immersed into the DMSO solution, which contained equimolar amounts of CsBr and PbBr₂, and further treated with methanol. After 24 h at 40 °C, the light-orange-colored composites were obtained, which indicated the formation of CsPbBr₃. Finally, the polystyrene was removed with toluene, and the powder was collected by centrifugation. The samples were prepared by anti-solvent and were denoted as AS-IO-CsPbBr₃. Reference samples were prepared by directly removing the DMSO under vacuum (see Experimental Section for details), which were denoted as RS-IO-CsPbBr₃. Moreover, the AS-IO-CsPbBr₃ and RS-IO-CsPbBr₃ were synthesized by using the artificial opal template of PSs with diameters of 214 nm, 379 nm, 433 nm and 501 nm, which were denoted as 2/IO-CsPbBr₃, 3/IO-CsPbBr₃, 4/IO-CsPbBr₃ and 5/IO-CsPbBr₃, respectively.



Scheme 1. Preparation route of IO-CsPbBr₃.

The highly ordered colloidal crystal template is a prerequisite for preparing the halide perovskites with inverse opal morphology. An ordered, close-packed structure can be evidenced by distinct stop bands, whose wavelength is governed by Bragg's law and depends on lattice spacing, mainly on the diameter of the microspheres [30]. The scanning electronic microscopy (SEM) image exhibited the highly ordered (111) faces of

the template (Figure 1A) and the long-ranged arrangement of the close-packed templates (Supplementary Materials, Figure S1). The reflectance spectra of the samples with different diameters are shown in Figure 1B. As the diameters of microspheres increased from 379 nm to 501 nm, the stop band position shifted from 473 nm to 668 nm. This behavior can be expressed by Bragg's law:

n

$$n\lambda = 2ndsin\theta$$
 (1)

where m is the order of diffraction, λ is the wavelength of the diffracted light, n is the refractive index of the crystalline colloidal arrays, d is the layer spacing, and θ is the angle between the incident light and the diffracting lattice plane. The stop band wavelength of the template with the microsphere diameter of 214 nm was 550 nm, which could be ascribed to the different order of diffraction compared with the other three opal structured templates [31]. As shown in Figure S1, low-resolution scanning electronic microscopy (SEM) images revealed that the template displayed a 3D ordered structure. In the infiltration process, DMSO was selected owing to its incompatibility with polystyrene but good compatibility with halide perovskites at low temperatures. Meanwhile, methanol was used as anti-solvent in the crystallization process because the polystyrene microspheres CsBr and PbBr₂ show poor solubility in methanol. After the template was removal by toluene, a perovskite inverse opal replicate with an ordered structure was obtained (Figure 2A,B).



Figure 1. (**A**) SEM image of the top surface of the opal template (PS: 214 nm). (**B**) Normalized reflectance spectra collected along the (111) plane of the opal structured templates with microspheres of different diameters.



Figure 2. SEM images of 2/AS-IO-CsPbBr₃ (A,B) and 2/RS-IO-CsPbBr₃ (C). Scale bars: 1 μm.

The SEM images in Figure 2A clearly show that the 2/AS-IO-CsPbBr₃ samples were entirely perforated with the well-ordered inverse opal structure. The inner voids were topologically interconnected, and the well-defined 3D ordered macropores were approximately 200 nm, which corresponded to the diameter of the original colloidal microspheres (Figure 2B). Compared to 2/RS-IO-CsPbBr₃ (Figure 2C), 2/AS-IO-CsPbBr₃ showed a more regular inverse opal morphology along with a narrower wall thickness and less

non-structured solid material. The smaller quantity of non-structured solid material is beneficial for photocatalytic activities. On the one hand, the non-structured solids reduced the ability of the reactant to approach the surface of the halide perovskites. On the other hand, the photogenerated carriers in the non-structured solid material have to diffuse a long way through the material before they reach the surface, which increases the possibility of their recombination [25]. Similar phenomena were also observed from the SEM images of other 3/IO-CsPbBr₃, 4/IO-CsPbBr₃ and 5/IO-CsPbBr₃ samples (Supplementary Materials, Figure S1). In the process of infiltration, three different concentrations of perovskite precursor (0.30, 0.45 and 0.6 M) in DMSO solution were studied to optimize the crystallization process. When the concentration of precursor was 0.3 M, porous halide perovskites were observed, but the fraction of inverse opal was low, and the macropores of the material did not connect with each other. By contrast, at higher concentrations of 0.6 M, the fraction of non-structured solid material was increased. The inverse opal structure was prepared by the precursor solution containing 0.45 M PbBr₂, and CsBr (Supplementary Materials, Figure S2) showed the best morphology.

In order to investigate the phase of the CsPbBr₃ crystal, the PXRD patterns of the synthesized crystalline powders are shown in Figure 3 [32,33]. The XRD patterns of AS-IO-CsPbBr₃ samples (Figure 3A) matched well with the standard reflection of CsPbBr₃. Moreover, the clear splitting of the (110) and (220) reflections indicated that the grown CsPbBr₃ crystal was in the room-temperature orthorhombic phase [34]. Meanwhile, the XRD patterns of RS-IO-CsPbBr₃ samples (Figure 3B) show similar reflections to those of highly crystalline IO-CsPbBr₃, which indicates that the RS-IO-CsPbBr₃ samples are also in the orthorhombic phase. Although the PXRD patterns confirmed that all the IO-CsPbBr₃ samples are orthorhombic, the difference between the AS-IO-CsPbBr₃ and RS-IO-CsPbBr₃ samples is indistinctive.



Figure 3. Powder X-ray diffraction (PXRD) patterns of the AS-IO-CsPbBr₃ (**A**) and RS-IO-CsPbBr₃ (**B**) powders, prepared using PSs with different diameters and the split diffraction peaks patterns, as shown on the left.

To further investigate the crystallinity of both AS-IO-CsPbBr₃ and RS-IO-CsPbBr₃, TEM measurements were conducted. As shown in Figure 4A, the well-defined structure of 2/AS-IO-CsPbBr₃ could be observed at low magnification, and this result is also consistent with SEM images. the hexagonally aligned macropores inherited the (111) planes of the colloidal crystal template can be clearly identified in the enlarged image (Figure 4B), thus indicating that the top surface of the inverse opal crystal is perpendicular to the electron beam. The HR-TEM images show the interplanar distances of 2/AS-IO-CsPbBr₃ were 4.1 Å, corresponding to the (112) face of CsPbBr₃. Sharp diffraction spots in the corresponding SAED pattern (Figure 4C) can be indexed to the orthorhombic perovskite crystal structure [35]. Indeed, the electron diffraction data obtained from other regions of the sample showed exactly the same patterns, which demonstrates that the complex structure actually has a single crystalline nature. The TEM images and the SEAD patterns of the 3/AS-IO-CsPbBr₃, 4/AS-IO-CsPbBr₃ and 5/AS-IO-CsPbBr₃ samples also exhibited well-defined structures and sharp spots (Supplementary Materials, Figure S3). In contrast, the TEM images of the RS-IO-CsPbBr₃ samples were less ordered. More importantly,

the diffraction spots on the SEAD image of RS-IO-CsPbBr₃ (Figure S4) were also sharp, but the arrangements were less regular, which strongly suggested the polycrystallinity of the CsPbBr₃ in the RS-IO-CsPbBr₃ samples. TEM measurements confirmed the higher crystallinity of AS-IO-CsPbBr₃ as compared to RS-IO-CsPbBr₃ samples.



Figure 4. TEM images of (**A**) 2/AS-IO-CsPbBr₃, (**B**) an enlargement of (A) and high resolution-TEM (HR-TEM) (inset) and (**C**) the selected area electron diffraction (SEAD) images of the circle area in (B).

Since visible light (400 nm $<\lambda <$ 800 nm) takes up almost half of the solar energy incident on the earth's surface, absorption of photons within the visible light region is a desirable feature for photocatalysts. As shown in Figure 5A, 2/AS-IO-CsPbBr₃ strongly absorbed visible light up to wavelengths of 560 nm, and 2/RS-IO-CsPbBr₃ exhibited a similar visible light absorbance at the wavelength of 565 nm, which makes both materials potential candidates for photocatalytic applications under visible light. Using the Kubelka–Munk equation, the band gaps for the 2/AS-IO-CsPbBr₃ and 2/RS-IO-CsPbBr₃ samples were 2.30 eV and 2.32 eV (Figure 5B), respectively, which is consistent with the previous reports [36]. Meanwhile, as the diameter of the PS used to assemble the colloidal template increased (to 379 nm, 433 nm and 501 nm), the corresponding IO-CsPbBr₃ samples displayed similar maximum absorbance wavelengths at approximately 560 nm (Supplementary Materials, Figure S5), which demonstrates that this inverse opal crystallization control method is compatible with polystyrene microspheres with different diameters and, thus, is feasible for controlling the morphology of inverse opal structure.



Figure 5. Normalized absorbance UV/Vis spectra (**A**) and Tauc plots (**B**) of 2/AS-IO-CsPbBr₃ and 2/RS-IO-CsPbBr₃.

To investigate the effect of crystallinity on the photocatalytic performance of halide perovskites, the polymerization of TerEDOT was chosen due to its potential application in optoelectronic device [12]. Similar to the photocatalytic processes of CsPbI₃ quantum dots, TerEDOT plays the role of the hole acceptor, while 1, 4-benzoquinone (Qu) was used as

the electron acceptor. Under visible light illumination, the IO-CsPbBr₃ powders generated a hole and an electron on the valence band and conduction band, respectively. As the hole transferred to TerEDOT and the electron could be transferred to Qu, polymerization occurred (Scheme 2) [12]. In contrast to previous studies, the concentration of TerEDOT in the supernate was monitored by UV/Vis spectrum to analyze the reaction process.



Scheme 2. Illustration of the proposed mechanism for photocatalytic polymerization of TerEDOT over IO-CsPbBr₃ samples under visible light illumination.

Figure 6A,B show the time-dependent absorbance spectra of the polymerization of TerEDOT over 2/AS-IO-CsPbBr₃ and 2/RS-IO-CsPbBr₃, respectively. The UV/Vis spectra of the photocatalytic reaction over 3/AS-IO-CsPbBr₃, 4/AS-IO-CsPbBr₃ and 5/AS-IO-CsPbBr₃ and the corresponding reference samples are shown in Figure S6 (see Experimental Section for details). During the photocatalytic reaction, the time-dependent spectra showed that the absorbance between 440 nm and 520 nm decreased, and the absorbance at 452 nm, indicating the concentration of the TerEDOT, could be used to monitor the reaction. The presented profiles reveal that highly crystalline 2/AS-IO-CsPbBr₃ (Figure 6A,B). In the case of 2/AS-IO-CsPbBr₃, the absorbance of the TerEDOT decreased by 34%, 45% and 55% within the first 15 min, 30 min and 45 min, respectively (Figure 6C). In contrast, the polymerization catalyzed over 2/RS-IO-CsPbBr₃ was slower. The absorbance of the TerEDOT decreased to only approximately 63% at 45 min, which is comparable to the polymerization catalyzed by highly crystalline 2/IO-CsPbBr₃ within the first 15 min.



Figure 6. Time-dependent UV/Vis spectra of the photocatalytic reaction over 2/AS-IO-CsPbBr₃ (**A**) and 2/RS-IO-CsPbBr₃ (**B**). Time-dependent relative concentration of TerEDOT in the supernate in the presence of 2/AS-IO-CsPbBr₃ (blue), 2/RS-IO-CsPbBr₃ (red) and in absence of photocatalysts (black) (**C**).

These observations were attributed to the higher crystalline quality of 2/AS-IO-CsPbBr₃, which contained lower defect density and fewer grain boundaries, and thus eliminated the recombination centers of the photogenerated electrons and holes [37]. Moreover, under the condition of adding the same weight of photocatalysts, 2/AS-IO-CsPbBr₃ had fewer non-structured solids for its more regular inverse opal structures (Figure 2), which consequently increased the number of active sites [38]. Additionally, the polymerization of TerEDOT under illumination in absence of IO-CsPbBr₃ powders is shown in Figure 6C, which reveals that TerEDOT undergoes extremely slow photolytic polymerization in the absence of a catalytic, causing a decrease in the TerEDOT concentration of approximately 4% within 45 min.

To further verify this phenomenon, photocatalytic polymerization catalyzed over other IO-CsPbBr₃ (3/IO-CsPbBr₃, 4/IO-CsPbBr₃ and 5/IO-CsPbBr₃) samples was studied. As shown in Figure 7A,B, all of the AS-IO-CsPbBr₃ samples exhibit obviously higher photocatalytic performance than that of the corresponding RS-IO-CsPbBr₃, which is consistent with the performance of 2/IO-CsPbBr₃. Moreover, the photocatalytic performances of 3/RS-IO-CsPbBr₃, 4/RS-IO-CsPbBr₃ and 5/RS-IO-CsPbBr₃ did not exhibit significant differences and were lower than that of 2/IO-CsPbBr₃. The effect of morphology on catalytic performance was more significant in the case of AS-IO-CsPbBr₃. In the presence of 3/AS-IO-CsPbBr₃, 4/AS-IO-CsPbBr₃ and 5/AS-IO-CsPbBr₃, the absorbance at 452 nm decreased to 64%, 56% and 50% at 45 min, respectively. This observation applies, in particular, to the area of AS-IO-CsPbBr₃ prepared using microspheres with different diameters (Supplementary Materials, Table S1). These results further confirmed the superior photocatalytic activity of the highly crystalline IO-CsPbBr₃ compared to its polycrystalline counterparts, and the beneficial effect of morphology on the photocatalytic performance was also observed. The photocatalytic activity of 2/IO-CsPbBr₃ may be attributed to two factors. Firstly, when the IO-CsPbBr₃ samples were prepared from polystyrene microspheres with different diameters, 2/IO-CsPbBr₃ had the smallest pore size and probably the most active sites. Secondly, as the void sizes and the wall thickness of 2/IO-CsPbBr₃ also decrease, the photogenerated carriers could be rapidly transferred onto the photocatalyst surface before their recombination in the bulk [19].



Figure 7. Time-dependent relative concentration of TerEDOT in the supernate in the presence of AS-IO-CsPbBr₃ (**A**) and 2/RS-IO-CsPbBr₃ (**B**), prepared from the polystyrene microspheres with different diameters.

In the infrared spectrum of the TerEDOT, the peak at 3104 cm^{-1} was attributed to the C=C–H stretching vibration, while it was not observed in the obtained crystal/polymer composite, which suggested the polymerization of the TerEDOT (Figure S7). Templated structures are usually fragile and may undergo morphological changes or degradation under catalytic conditions. To evaluate the stability of the catalysts, 2/AS-IO-CsPbBr₃ was collected after reacting for 45 min. According to the SEM images, the spent 2/AS-IO-CsPbBr₃ samples appeared to be smaller, which can be explained by abrasion from stirring during the reaction. However, the open porous network and the inverse opal morphology were still well maintained, which confirms the morphological stability of the AS-IO-CsPbBr₃ (Figure S8). Moreover, the XRD pattern of the spent 2/AS-IO-CsPbBr₃ is consistent with that of the freshly prepared 2/AS-IO-CsPbBr₃, which also confirms the stability of the photocatalysts. In addition, the normalized absorbance UV/Vis spectrum and, therefore, also the band gap of the spent 2/AS-IO-CsPbBr₃ remained unchanged (Figure S9). These observations demonstrate the excellent stability of IO-CsPbBr₃ in photocatalytic polymerization.

3. Materials and Methods

Commercially available lead bromide (PbBr₂, 99.999%), cesium bromide (CsBr, 99.999%) and p-benzoquinone (99%) were purchased from Alfa Aesar (Alfa Aesar Company Limited of China, Shanghai, China). The ultra-dry dimethyl sulfoxide (DMSO) was supplied by Aladdin (Aladdin Reagent Company, Shanghai, China). All the other chemicals were purchased from J&K (J&K Scientific Company, Beijing, China). All the chemicals were used without refinement, unless otherwise noted.

3.1. Synthesis of Colloidal Polystyrene Spheres (PSs)

Styrene (30 mL) was washed four times with 100 mL of 0.1 M NaOH in a separatory funnel and then four times with 100 mL deionized water. The standard synthetic procedure was as follows: 280 mL deionized water was poured into a 4-neck round-bottom flask and heated to 80 °C. Then 0.22 g of potassium persulfate was dissolved in 17 mL of deionized water and the obtained solution was injected after the prepared styrene was added. No cross-linking agent was added for the later removal of the latex spheres from the microporous product. The mechanical stirrer had a speed equal to 350 rpm with a variation estimated at 2 rpm, and the temperature was kept at 80 \pm 2 °C for 12 h. After the polymerization was completed, the cooling colloidal solution was filtered through degreasing cotton to remove any large aggregations. Before use, the latex spheres were purified by repeated centrifugation/redispersion cycles and finally diluted to a mass fraction of about 8 wt%. In the above process, the spheres with diameters of 501 nm \pm 20 nm, 433 nm \pm 17 nm, 379 nm \pm 15 nm and 214 nm \pm 10 nm were produced with 45 mL, 30 mL, 20 mL and 8 mL of styrene, respectively. The diameters of the spheres were estimated using scanning electron microscopy (SEM).

3.2. Synthesis of 2,2',5',2"-ter-3,4-Ethylenedioxythiophene (TerEDOT)

A solution of 3,4-ethylenedioxythiophene (1.33 g, 9.37 mmol) in 50 mL THF under nitrogen was cooled to -78 °C via a cooling bath. To the stirred pre-cooled solution, 3.7 mL, 9.25 mmol of n-butyllithium (2.5 M in hexane) was added via syringe. After 45 min, the reaction mixture was allowed to warm to 0 °C, and then MgBr2·Et2O (2.50 g, 9.68 mmol) was added in one portion. [1,3-bis(diphenylphosphino) propane]dichloronickel(II) (0.10 g, 0.18 mmol) was added and followed by 2,5-dibromo-3,4-ethylenedioxythiophene (1.07 g, 3.57 mmol). The mixture was allowed to warm slowly to room temperature. The product was purified using a silica column with dichloromethane as eluent. The title compound was isolated as a medium brown solid. The product was characterized by high-resolution mass spectroscopy (HR-MS), ¹H-NMR (the spectrum was shown in Figure S10) and infrared spectroscopy (IR). ¹H NMR (600 MHz, CD₂Cl₂): 4.23 (m, OCH₂CH₂O, 6H), 4.35 (m, OCH₂CH₂O, 6H), 6.28 (m, C=C-H, 2H). EMI-MS (Cl₁₈H₁₄O₆+H⁺): Calcd: m/z = 423; found: m/z = 423. All data are consistent with the known literature.

3.3. Fabrication of 3D Ordered PS Template

The preparation of 3D ordered PS templates from monodisperse spheres with different diameters could be easily achieved by filtration. The colloidal dispersions were carefully poured onto a filter funnel preset with two suitable filter papers under vacuum. After 10–12 h, the face-centered cubic template was formed and dried at 50 °C overnight.

3.4. Preparation of Inverse Opal Structured Highly Crystalline Perovskite

A 0.45M precursor solution of the perovskite was prepared using equimolar amounts of CsBr (0.96 g) and PbBr₂ (1.65 g), dissolved in DMSO (10 mL) at room temperature. Then, a piece of face-centered cubic PS template (500 mg) was infiltrated by this solution (500 μ L) and further treated with vacuum degassing for 10 min to make sure all the spaces between the 3D colloidal spheres were filled with precursor solution. The impregnated monolith was immediately moved into a 50 mL beaker with 10 mL methanol. This mixture was then treated with vacuum degassing for another 10 min before being transferred to

a constant temperature incubator at 45 °C and atmospheric pressure for 24 h. After that, the color of the composition turned orange. The obtained compound was immersed in toluene (50 mL) at room temperature for 12 h, and the perovskite inverse opal was gathered by centrifugation. Tetrahydrofuran was also a good solvent due to its suitable solubility for the PS template. To ensure the PS template was completed removed, this washing–centrifugation process was repeated several times, and the obtained orange powder was dried at 50 °C overnight.

3.5. Preparation of Inverse Opal Structured Polycrystalline Perovskite

A 0.45 M precursor solution of the perovskite was prepared using equimolar amounts of CsBr (0.96 g) and PbBr₂ (1.65 g), dissolved in DMSO (10 mL) at room temperature. Then, a piece of face-centered cubic PS template (500 mg) was infiltrated by this solution (500 μ L) and further treated with vacuum degassing for 10 min to make sure all the spaces between the 3D colloidal spheres were filled with precursor solution. The DMSO was removed under vacuum at 60 °C for 3 h. The obtained compound was immersed in toluene (50 mL) at room temperature for 12 h, and the perovskite inverse opal was gathered by centrifugation. To ensure the PS template was completed removed, this washing–centrifugation process was repeated several times, and the obtained orange powder was dried at 50 °C overnight.

3.6. Photocatalytic Polymerization of TerEDOT in Solution

The photocatalytic polymerization was carried out in a double jacket photoreactor with a quartz window for on-top illumination with a solar simulator (LCS-100). First, 20.0 mg TerEDOT and 10.0 mg Qu were dissolved in 20 mL dry toluene. Then, 60.0 mg IO-CsPbBr3 was added into the solution, and the mixture was illuminated for 45 min while the temperature was kept constant at 25 °C. A filter (20CGA-495, Newport) was used to cut off the wavelengths below 490 nm. To investigate the polymerization process, the reaction mixture was centrifuged at 3000 rpm for 2 min, and the supernate was diluted by 5-fold in toluene and used for UV/Vis spectrum measurement.

3.7. Characterization

Microstructures of the samples were characterized by field-emission scanning electronic microscopy (SEM, Hitachi FE-S4800, 5 kV), transmission electron microscopy (TEM, JEM-2000, 200 kV), high-resolution TEM images and selected area electron diffraction (SAED). Powder X-ray diffraction (XRD) spectra were recorded on a D8 advance X-ray Diffraction. The UV/Vis spectrum was recorded on a Lambda750 PE spectrometer. The infrared (IR) spectrum was measured on a BRUKER alpha II spectrometer. The high-resolution mass spectroscopy (HRMS) was measured on BRUKER solanX 70 FT-MS, using ESI as an ion source. Proton nuclear magnetic resonance(1H NMR) was measured on a BRUKER AVANCE III 600M, using dichloromethane-d2 (99.5% atom% D) as solvent.

4. Conclusions

In summary, a series of highly crystalline CsPbBr₃ inverse opals were prepared by combining the colloidal crystal templating method and anti-solvent crystallization. The obtained IO-CsPbBr₃ exhibited a well-connected porous structure and high crystallinity. As a result of these advantages, a significant enhancement of photocatalytic performance was observed when the highly crystalline IO-CsPbBr₃ was used as a photocatalyst to promote the polymerization of TerEDOT. Moreover, IO-CsPbBr₃ is stable under photocatalytic conditions in terms of both morphology and crystal structure. The results indicated that the novel highly crystalline IO-CsPbBr₃ could be an attractive material in the field of heterogeneous photocatalysis.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/catal11111331/s1, Figure S1: The SEM images of the face-centered cubic template with polystyrene sphere diameter of (A) 379 nm, (D) 433nm, (G) 501nm, and corresponding (B) 3/AS-IO-CsPbBr3, (C) 3/RS-IO-CsPbBr3, (E) 4/AS-IO-CsPbBr3, (F) 4/RS-IO-CsPbBr3, (H) 5/AS-IO-CsPbBr3, (I) 5/RS-IO-CsPbBr3. Figure S2: The SEM image of 2/AS-IO-CsPbBr3 fabricated by different precursor concentration: 0.3M (A), 0.45M (B). Figure S3: The TEM image of (A) 3/AS-IO-CsPbBr3, (B) 4/AS-IO-CsPbBr3, (C) 5/AS-IO-CsPbBr3, and (A1), (A2), (B1), (B2), (C1), (C2) the SEAD images of the circle area in (A), (B), (C) respectively. Figure S4: The TEM image of (A) 2/RS-IO-CsPbBr3, (B) 3/RS-IO-CsPbBr3, (C) 4/RS-IO-CsPbBr3, (D)5/RS-IO-CsPbBr3, and (A1), (A2), (B1), (B2), (C1), (C2) (D1), (D2) the SEAD images of the circle area in (A), (B), (C), (D) respectively. Figure S5: Normalised absorbance UV/Vis spectra of (A) AS-IO-CsPbBr3 and (B) RS-IO-CsPbBr3. Figure S6: Time-dependent UV-vis spectra of the photocatalytic reaction of (A) 3/AS-IO-CsPbBr3, (B) 4/AS-IO-CsPbBr3, (C) 5/AS-IO-CsPbBr3, and (D) 3/RS-IO-CsPbBr3, (E) 4/RS-IO-CsPbBr3, (F) 5/RS-IO-CsPbBr3. Figure S7: (A) the IR spectrum of TerEDOT and the crystal/polymer composite (the peak at 3104 cm-1 is attributed to the C=C-H stretching vibration of TerEDOT, which could not be found in the crystal/polymer composite). Figure S8: The SEM image of the spent 2/AS-IO-CsPbBr3 in low magnification. Figure S9: XRD patterns (A) and Normalised absorbance UV/Vis spectra (B) of the spent 2/AS-IO-CsPbBr3.

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