

Immobilized Covalent Triazine Frameworks Films as Effective Photocatalysts for Hydrogen Evolution Reaction

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Article

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Abstract

Covalent triazine frameworks (CTFs) have recently been demonstrated as promising materials for photocatalytic water splitting and are usually used in the form of suspended powder. From a practical point of view, immobilized CTFs materials are more suitable for large-scale water splitting applications, owing to their convenient separation and recycling potential. However, existing synthetic approaches mainly result in insoluble and unprocessable powders, which makes their future device application still a huge challenge. Herein, we report an aliphatic amine-assisted interfacial polymerization method to obtain free-standing, crystalline CTFs film with excellent photoelectric performance. The lateral size of the film was up to 250 cm², the average thickness can be regulated from 30-500 nm. The crystalline structure was confirmed by high-resolution transmission electron microscope (HR-TEM), powder X-ray diffraction (PXRD), and small-angle X-ray scattering (SAXS) analysis. Intrigued by the good light absorption, crystalline structure, and big lateral size of the film, it was immobilized on a glass support that exhibited good photocatalytic hydrogen evolution performance (5.4 mmol h⁻¹ m⁻²) and was easy to recycle.

Introduction

Covalent triazine frameworks with aromatic triazine linkages are a subclass of covalent organic frameworks (COFs). CTFs are constructed by covalently linking light elements (C, N, and H), which exhibit intriguing physical/chemical properties such as high porosity, high nitrogen content, and good thermal/chemical stability.¹⁻³ These unique properties endow CTFs with great prospects in various applications including gas separation and storage, energy storage, photo/electro/thermo-catalysis.⁴⁻⁹ In the development process of CTFs, substantial improvement has been made in preparation method and crystallinity, but the problem of processability always exists and still limits their practical application.

In early studies, it is technically difficult to obtain CTFs under mild conditions because of the high reaction energy barrier of the aromatic nitriles trimerization reaction. The high temperature of ionothermal method causes the partial carbonization of the CTFs structure and the materials were obtained in the form of black powders.¹⁰ CTFs prepared by acid catalysis need strong and corrosive acid such as trifluoromethylsulfonic acid, which was not suitable for acid-sensitive building blocks and practical applications.¹¹ In 2017, we reported a pioneering method for the fabrication of CTFs under ambient conditions by a low-temperature polycondensation approach. However, the CTFs prepared by the low-temperature polycondensation approach were mainly amorphous.¹² Recently, we developed strategies like in situ oxidation and controlling monomer feeding rate to prepare crystalline CTFs.^{7,13}

Crystalline CTFs possess the extended conjugation structure in two dimensions and are attractive materials for photocatalytic hydrogen evolution. Up to now, most of the reported water splitting systems are based on suspended CTFs that are often used in small batches and hard to recycle. To address this issue, film-based immobilized photocatalytic systems have been developed such as panel reactor and photoelectrochemical (PEC) reactors.¹⁴⁻¹⁵ Compared with suspended powder, the film-type

photocatalysts possess inherent advantages: 1) better photocatalytic performance ascribing to the less light scattering and enhanced light absorption that generates more carriers; 2) easy to recycle and scalable since they can be easily integrated into immobilized photocatalytic systems.¹⁶⁻¹⁹ The preparation of CTFs films is, therefore, important for their practical photocatalytic applications. However, CTFs prepared by strategies as mentioned above were insoluble powders consisting of nanoscale semi-crystals and were hard to process and load on supports.^{7,10-13} There are only a few reports for the preparation of CTFs based films, and all of them were prepared by the superacid catalytic method.^{4,6,20-23} The thickness, lateral size, and crystalline nature of such films, however, is difficult to control and it is still a challenge to fabricate CTFs films with large lateral size, and controllable thickness under mild conditions.

Interfacial polymerization, which usually occurs at liquid/liquid interface or liquid/air interface is an effective method to prepare continuous covalent organic frameworks (**COFs**) membranes or films.²⁴⁻³⁶ As analogs of COFs, CTFs films may also be obtained through interfacial polymerization. An important prerequisite for interfacial polymerization is that the monomer/monomer or monomer/catalyst should be soluble in two different phases. Typically, the two phases are water/dichloromethane for liquid/liquid system; and water/air for liquid/air system. Water is a necessary component in both of these systems. However, the poor solubility of most of the COFs or CTFs monomers in water hampers their interfacial polymerization.

Ogata *et al.* have reported that ultrathin films of linear aromatic polymers can be prepared at air/water interface using an imine as a precursor.³⁷ The polar aldehyde monomer was transferred to amphiphilic imine precursor by Schiff reaction with aliphatic amines. The stable interface was created by suspending the imine precursor in water. It can be speculated that if one monomer is transformed into an amphiphilic precursor through a dynamic reaction, and this precursor can be assembled at the interface of liquid (water or other solvents)/air; then the dynamic reaction would release monomer to participate in polymerization at the interface. This approach offers a promising strategy to avoid the requirement of water phase in the interfacial polymerization systems as mentioned above.

In this work, we report a practical and efficient approach for the preparation of free-standing, crystalline CTFs film with large lateral size and controllable thickness by aliphatic amine-assisted interface polymerization. In this case, the DMSO-soluble aldehyde monomer was transformed into a DMSO-insoluble imine precursor by reacting with aliphatic amine. The imine precursor spread on DMSO guided the initial arrangement of aldehyde monomers, and DMSO/air interface was generated at the same time. Thus, the polymerization reaction was confined in the interface instead of the homogeneous reaction of the previous low-temperature polycondensation approach.^{7,12} The crystalline structure was probed by high-resolution HR-TEM imaging, PXRD and SAXS analysis. The film with the large lateral size can be easily loaded on supports as an immobilized photocatalyst. In this context, film loaded on glass was employed to test the photocatalytic hydrogen evolution reaction (**HER**) performance. The immobilized photocatalysts exhibited $5.4 \text{ mmol h}^{-1} \text{ m}^{-2}$ ($10.2 \text{ mmol h}^{-1} \text{ g}^{-1}$) rate for HER under visible light. This work

highlights the controlled synthesis of free-standing, crystalline, and large-size CTFs films based on organic solvent/air interfacial polymerization and provides a rational approach to prepare immobilized photocatalyst, paving the way for the development of CTFs and COFs films for such applications.

Results

Preparation of CTF film. The typical synthesis of CTFs powders involves a homogeneous condensation reaction between amidine and aldehyde in DMSO.¹² To synthesize the CTF film, firstly, an imine precursor was prepared by a reaction between an aldehyde and n-hexylamine (**Scheme 1a**) in n-Hexane. The amidine and Cs_2CO_3 were dissolved in DMSO and then imine precursor was added dropwise at the top of the DMSO layer. Because of the weak polarity of the long carbon chain, the imine precursor was floating at the DMSO layer instead of dissolving in it. The unstable nature of imine bonds under these conditions resulted in its hydrolysis to the aldehyde that participated in the interfacial polymerization reaction (**Scheme 1b**). The polycondensation reaction was kept at 100 °C in an oven for 72 h, resulting in the formation of a visible transparent film in 12 h.

Characterizations of CTF film. The as-prepared film was soft and flexible. The lateral size was up to several hundred square centimeters, which can be adjusted by the size of the reactor (**Figure S1, Video S1**). The film was obviously free-standing and transparent (**Figure 1a–1c**). When transferred to a 4-inch SiO_2/Si wafer, it covered the substrate without noticeable defects (**Figure 1a**). For HR-TEM analysis, the CTF film was dispersed in ethanol with ultrasonic assistance (**Figure 1d – 1f**, and **Figure S2**). HR-TEM images showed that the film was comprised of crystalline nanosheets with lengths ranging from several hundred nanometers to tens of micrometers. The clear lattice fringe with an interplanar lattice spacing of 0.42 nm probably corresponds to the (300) atomic plane (**Figure 1e**), which had been reported in crystalline CTF powder.¹³ The selected area electron diffraction (**SEAD**) analysis (**Figure 1f**) further confirmed the good crystallinity of the film. The a value of the unit cell was calculated

to be 14.55 Å based on the HR-TEM image. It must be pointed out that some parts of the film were amorphous, and it was difficult to figure out the exact ratio of the crystalline and amorphous areas. For atomic force microscope (**AFM**) characterization, the CTF film was dispersed in ethanol by ultrasonication and then drop-casted on mica plate. The AFM images indicated that the film was comprised of large nanosheets with sizes beyond 10 μm and the thicknesses of *ca.* 4 nm (**Figure 2g, Figure S4**). However, the lateral size of nanosheets in CTF powders prepared by the homogeneous reaction was only several hundred nanometers to several micrometers.^{7, 12-13, 38} Notably, such large nanosheets contributed to the formation of films rather than powders by the further assembly. In order to confirm the crystallinity of the CTF films, the PXRD characterization was carried out. The diffraction peak around 7.5° was assigned to the (100) reflections and the broad peak at 25° was ascribed to the (001) reflections (**Figure S3**). To provide more information of the ordered structure, SAXS analysis was performed. The SAXS profile displayed scattering signal at $q = 0.50 \text{ \AA}^{-1}$ corresponding to d-spacing 1.256 nm (100) (**Figure 2h, i**). Based on the PXRD and SAXS data, the a value of the unit cell was calculated to

be 14.50 Å, which was very close to the d value derived from the HR-TEM image, further confirming the formation of crystalline CTF film. However, some scattering peaks with higher q value could not be precisely described by SAXS data because of its limited resolution.

The chemical composition of the film was characterized by Fourier transform infrared (FT-IR) spectroscopy (Figure 2a), solid-state NMR spectroscopy (Figure 2b), and X-ray photoelectron spectroscopy (XPS) (Figures 2c – 2d). From FT-IR spectra, the presence of peaks at 1517 cm^{-1} (C=N stretching vibration) and 1353 cm^{-1} (C-N stretching vibration) confirmed the successful formation of the triazine rings (Figure 2a).^{7, 12-13, 38} Peaks near 2900 cm^{-1} could be assigned to the terminal n-hexylamine groups.³⁷ ^{13}C -NMR spectra confirmed the presence of sp^2 carbons of the triazine ring (about 170 ppm), the benzene rings (138 ppm and 128 ppm) (Figure 2b).^{12-13, 38} Some small peaks around 10 - 30 ppm and 116 ppm can be assigned to the terminal aliphatic amine and C=O of the aldehyde groups, respectively.³⁸ Furthermore, the deconvolution of N 1s peaks around 398.9 eV was assigned to nitrogen of triazine ring. The signals at 399.8 – 400.0 eV corresponded to the pyrrolic nitrogen resulting from the partial decomposition of CTFs (Figure 2c – 2d).¹²⁻¹³

The thickness regulation. Controllable film thickness is of great importance for molecular separation performance and photochemical applications.³⁹ In this context, we obtained films with thickness ranging from about 150 to 500 nm by varying the amount of imine precursor (from 0.017 mmol to 0.050 mmol), and the concentration of amidine (from 2.1 mM to 6.3 mM). The morphology and thickness of the films were determined by scanning electron microscope (SEM) and AFM. The SEM in Figure 3a showed that no significant cracks or big particles on the films on copper grid and the surface were smooth at higher magnification (Figure 3b), which confirmed the interface was relatively stable. The carbon and nitrogen distribution by elemental mapping with SEM revealed that both carbon (red) and nitrogen (green) atoms are distributed homogeneously in the film (Figures S2d – f). By decreasing the concentration of amidine from 6.3 mM to 4.2 mM or 2.1 mM, the films could still cover the copper grid without significant cracks (Figure S5a, Figure S5b, and Figure S6a). Some particles can be observed at the edge or surface of the film (Figure S5c, Figure S6b, and Figure S6c). It appears that the CTFs particles were grown on the film, which could not be rinsed off in the workup process. This phenomenon had also been observed previously, which might be caused by the interfacial fluctuations.^{29, 39} The AFM images indicated that the thickness of the films ranged from 540 - 30 nm (Figure S7 – S10), which was in agreement with the results of cross-section SEM images. Defects can be observed from the film with a much lower thickness (Figure S10), which might be caused by the irreversible polymerization reaction and low monomer concentration. These defects might impact their application in the molecule separation field. Therefore, the control experiments suggested that the concentration of monomers played a vital role in the formation of CTFs film and the control over their thickness.

Photocatalytic HER performance study.

The optical and electronic properties of CTFs film were investigated by UV-vis absorption spectroscopy and electrochemical characterization. The solid-state UV-vis diffuse reflectance spectrum showed significant light absorption by CTFs film at wavelength below 500 nm (**Figure 4a**). The film on ITO glass exhibited the current response behavior under visible light irradiation (> 420 nm), indicating the charge-transfer and separation ability (**Figure 4b**). According to Mott-Schottky plots, conduction band minima (CBM) of CTF film was estimated to be -0.80 V (**Figure S11**). The CBM was more negative than the potential of H^+/H_2 (-0.41 V NHE at $pH = 7.0$), which meant the energy level was suitable for the photocatalytic proton reduction reaction.

As an attempt, a simple device for photocatalytic HER performance test was fabricated by transferring the film (~ 500 nm thick) onto a glass slide (size about 19 cm^2) (**Figure 3d**, **Figure 3e**). The photocatalytic hydrogen evolution activity of CTF film was investigated under visible light (> 420 nm) with Pt as cocatalyst, and triethanolamine (TEOA) as sacrificial agent. After irradiating for 1 hour, significant H_2 gas bubbles were clearly observed on the glass slide (**Figure 3g**). The HER rate was calculated to be about $5.4\text{ mmol h}^{-1}\text{ m}^{-2}$ (equal to $10.2\text{ mmol h}^{-1}\text{ g}^{-1}$) (**Figure 3d**). These results confirmed the possibility that the film can be integrated into a photochemical device with the retention of intrinsic properties. The film-based immobilized photocatalysts are endowed with special advantages i.e., easy recycling and good performance, which are critical for practical applications. After photocatalysis, the glass slides can simply be taken out of the reaction cell and the supported films washed with deionized water to avoid the energy and time-consuming separation process in the suspended powder system.¹⁶ Long-term hydrogen evolution experiments of the film showed steady hydrogen production over 4 cycles, indicating that the film was stable under the reaction conditions ($\lambda > 420$ nm, 10% TEOA) (**Figure 3d**) with a little decrease in the H_2 evolution after 2 cycles. It might be caused by some impurity adsorbed on the film surface or a part of the film might be peeled off from the glass during the washing process. Moreover, it was not suitable to directly compare the HER performance due to the different state of photocatalysts, the photochemical performance of CTFs film was still comparable or even better than that of the reported suspended particles of CTFs.^{7, 12, 38} The improvement in photochemical performance may be ascribed to the enhanced light absorption of CTF films. Lights might be absorbed or scattered by a photocatalyst, the scattering of light in suspended particles is however more by all the exposed sides of suspended particles than that by the thin film with a relatively smooth surface. The enhanced light absorption of the thin film-based photocatalyst could produce more charge carriers than the particulate catalyst.¹⁷⁻¹⁹ Overall, the CTFs film was easily integrated into a photochemical device that was found to be very promising for its practical application in photocatalytic HER.

Discussion

Researchers were faced three bottleneck problems in the development process of CTFs: (1) the mild and efficient synthesis approach, which impact the chemical structure and band structure of the results materials; (2) crystallinity, which limit the charge transfer and photocatalytic performance; (3) processability, which limit their practical applications. In the past ten years, substantial improvement

has been made in the synthesis approach and crystallinity, but the processability always exists and still limits their practical application. Herein, we have demonstrated the successful synthesis of free-standing, crystalline, large area CTFs film via an aliphatic amine-assisted interfacial polymerization. By tuning the concentration of monomers, the thickness could be easily regulated from 30 to 500 nm. The conjugated network and large lateral size offered an excellent model to investigate their photocatalytic HER performance as immobilized photocatalysts. The HER rate was found to be as high as $5.4 \text{ mmol h}^{-1} \text{ m}^{-2}$ (equal to about $10.2 \text{ mmol h}^{-1} \text{ g}^{-1}$) under visible light. Firstly, the proposed air/organic solvent interfacial polymerization strategy can address the shortcoming of insufficient solubility of monomers in previous interfacial reaction methods in COF and CTF synthesis. Secondly, we also provide a rational approach to prepare immobilized photocatalyst, which is a significant landmark for the development of CTFs and COFs films and their potential integration in future devices for applications in photoelectric, sensing, separation, and energy technologies. Consequently, this study makes meaningful progress to overcome the third bottleneck: processability.

Methods

Synthesis of imine precursor. Imine precursor was synthesized using a reported method.³² Typically, 6.7 mg terephthalaldehyde (0.05 mmol) were dissolved in 1.0 mL n-hexane in a vial, then added 13.2 μL n-hexylamine (0.10 mmol) into the vial. The vial was stirring at 60 °C for 2 h.

The preparation of lower layer solution. Terephthalamidine dihydrochloride (23.5 mg, 0.10 mmol) and cesium carbonate (33.0 mg, 0.10 mmol) were dissolved in 16 mL DMSO and stirring at 100 °C for 30 min. The obtained mixture was used as a lower layer (6.3 mM).

Typical Procedure for the Preparation of the CTFs Film. The lower layer solution was added to a glass culture dish (9.0 cm in diameter) that was placed in an oven. The imine precursor was added on the top of the lower layer solution that was uniformly spread on the DMSO surface. After keeping it for 30 min to let the n-hexane evaporate, the temperature of the oven was increased to 100 °C and kept for 72 h. 200 mL water was added into the dish to let the film float up, and then the film was immersed in DMF, ethanol, and water to remove unreacted monomers and solvent, respectively. After that, the film can be transferred to other substrates or taken out by pipette for characterization or photocatalytic application. The thickness of the film was about 500 nm (by SEM, 6.3 mM).

340 nm film: lower layer: 4.2 mM solution of terephthalamidine dihydrochloride in DMSO (16.0 mL); 33.0 μmol terephthalaldehyde and 66.0 μmol n-hexylamine in 1.0 mL n-hexane.

150 nm film: 2.1 mM solution of terephthalamidine dihydrochloride in DMSO (16.0 mL); 16.0 μmol terephthalaldehyde and 32.0 μmol n-hexylamine in 1.0 mL n-hexane.

30 nm film: 0.21 mM solution of terephthalamidine dihydrochloride in DMSO (16.0 mL); 1.6 μmol terephthalaldehyde and 3.2 μmol n-hexylamine in 1.0 mL n-hexane.

Photocatalytic Experiments. The photocatalytic performance was measured under the irradiation of visible light (> 420 nm) at 15 A current with 300 W Xe lamp (Beijing Perfect Light Co. Ltd., PLS-SXE300). The diameter of the photoreactor was 7.8 cm. The whole photocatalytic process was kept at room temperature (25 °C) with a light intensity of 130 mW cm^{-2} . The hydrogen production was determined by gas chromatography (SHIMADZU, GC-2014C). The film with a thickness of about 500 nm was transferred to a glass slide with 19 cm^2 area that was dried in an oven at 60 °C for 24 h, then the glass was immersed in 20 mL ethanol that contains 10.0 μL $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (10 mg mL^{-1}) and kept for 24 h to load the H_2PtCl_6 . The glass was then immersed in 100.0 mL TEOA aqueous solution (10 vol %, v/v) for photocatalytic HER. After the photocatalytic testing, the film was scraped off and weighed (0.9 mg). Considering the weighing error, the weight was considered as 1.0 mg to calculate the HER rate.

Photo-Electrochemical Measurements. The EIS and photocurrent measurements were carried out by an electrochemical workstation (CHI760E) equipped with a conventional three-electrode system. A platinum plate electrode and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. Data were measured at least three times.

Data availability

All data supporting the findings of this study are available within the article, as well as the Supplementary Information file, or available from the corresponding authors on reasonable request.

Declarations

Acknowledgments

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Author contributions

B. T. conceived the project and designed the experiments. X. H. performed the experiments and analyzed the data. X. H. and B. T. co-wrote the manuscript. I. H. helped in improving the manuscript

Competing interests

The authors declare no competing interests.

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Figures

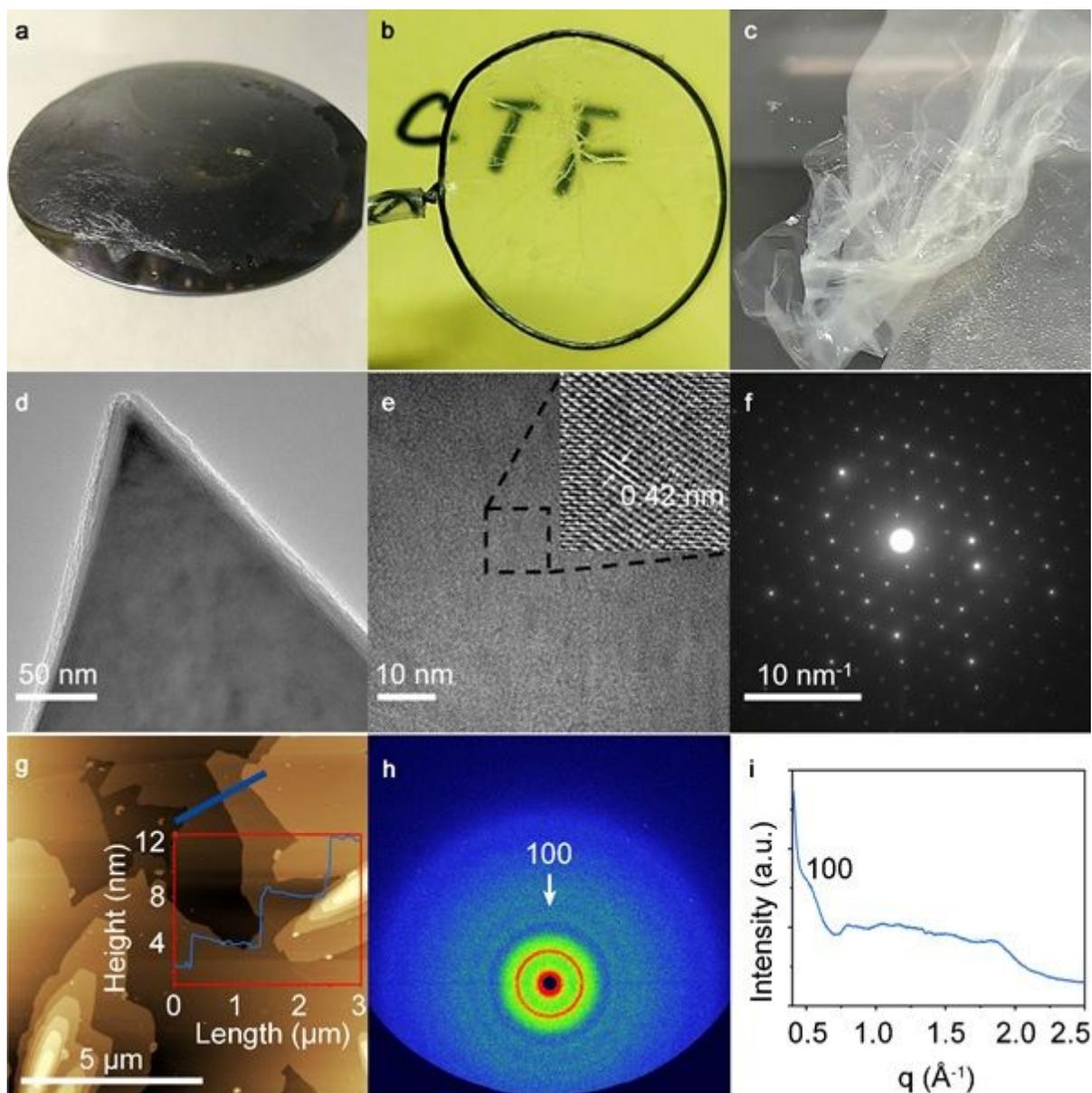


Figure 1

Photographic image of CTF film. a) on 4-inch 300 nm SiO₂/Si wafer. b) the free-standing and transparent CTF film. c) CTF film immersed in the solvent. d) – e) the HR-TEM and f) SEAD. g) the AFM image. h) – i) 2D SAXS profiles and their corresponding 1D SAXS profiles of the CTF film.

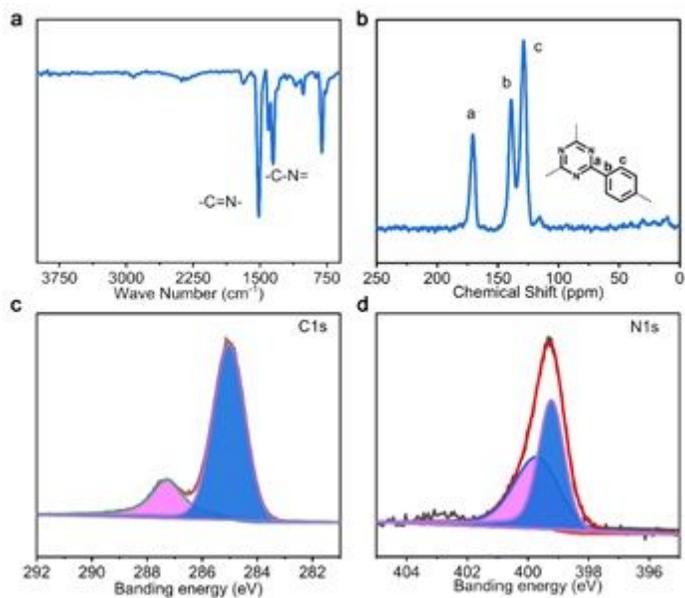


Figure 2

The chemical characterization of CTF film: a) the FT-IR. b) the solid-state NMR spectroscopy. c, d) the X-ray photoelectron spectroscopy.

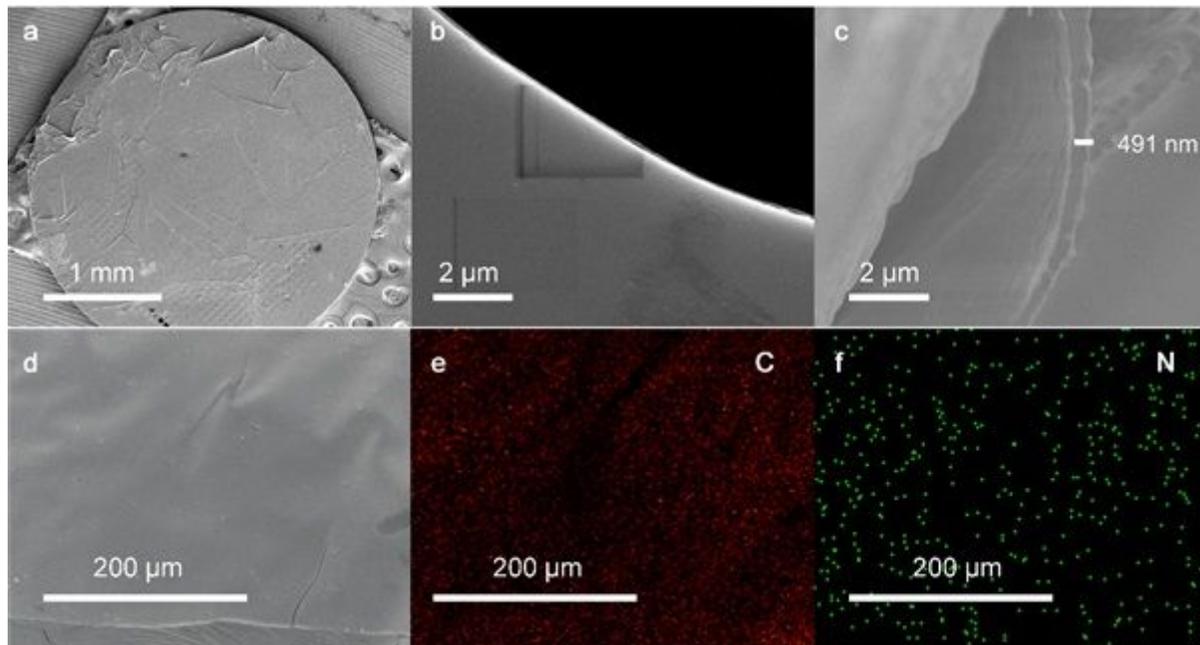


Figure 3

The morphology and thickness of CTF film. a, b) the SEM image of the film supported on TEM copper grid; c) the cross-section SEM image; d) the SEM image; and the element mapping images, e) carbon atom; f) nitrogen atom. The film was prepared with 6.3 mM amidine.

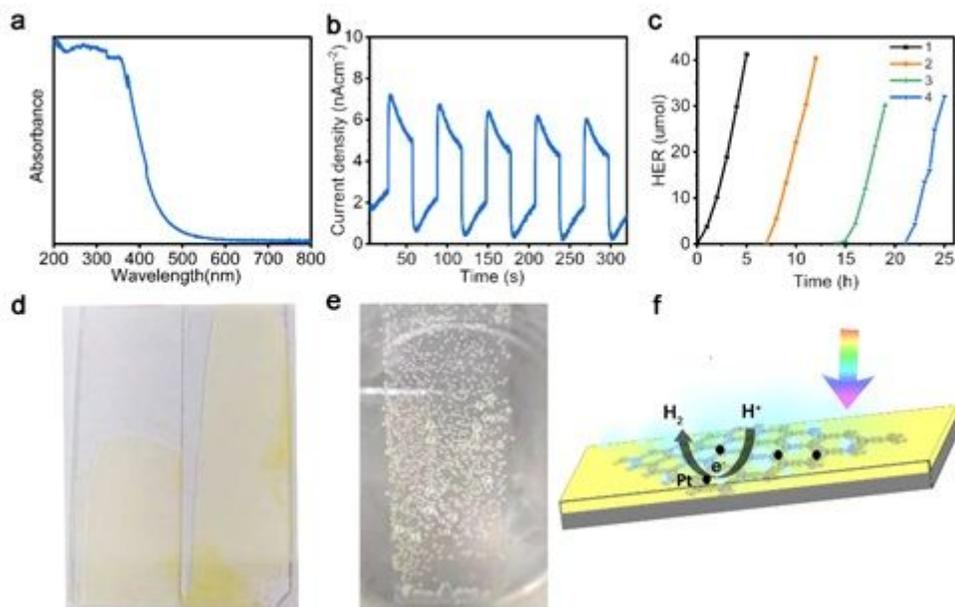


Figure 4

The photoelectric and photocatalytic HER performance of the film. a) The UV-visible light absorption spectrum. b) The photocurrent curve. c) Photocatalytic HER performance of the film on glass in 4 cycles under visible light (> 420 nm). d) The images of the film loading on the glass. e) Image of the glass loaded with the film for photocatalytic HER. f) Schematic diagram of the photocatalytic process.

Supplementary Files

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