Ultrathin 2D Conjugated Polymer Nanosheets for Solar Fuel Generation

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Abstract Two-dimensional (2D) polymers are fascinating as they exhibit unique physical, chemical, mechanical, and electronic properties that are completely different from those of traditional linear or branched polymers. They are very promising for applications in catalysis, separation, optoelectronics, energy storage, and nanomedicine. Recently, ultrathin 2D conjugated polymers have emerged as advanced materials for converting solar energy into chemical energy. The inherent 2D planar structure with in-plane periodicity offers many features that are highly desirable for photon-involved catalytic energy conversion processes, including high absorption coefficients, large surface areas, abundant surface active sites, and efficient charge separation. Moreover, the possibility of finely tuning the optoelectronic and structural properties through precise molecular engineering has opened up new opportunities for design and synthesis of novel 2D polymer nanosheets with unprecedented applications. Herein, we highlight recent advances in developing ultrathin 2D conjugated polymer nanosheets for solar-to-chemical energy conversion. Specifically, we discuss emerging applications of ultrathin 2D conjugated polymer nanosheets for solar-driven water splitting and CO2 reduction. Meanwhile, future challenges and prospects for design and synthesis of ultrathin 2D conjugated polymer nanosheets for solar fuel generation are also included.

Keywords 2D polymers; Conjugated polymers; Nanosheets; Photocatalysis; Energy conversion

INTRODUCTION

The hourly energy delivered to the Earth from the sun is equivalent to the energy consumed by human beings in an entire year. Therefore, efficient conversion and utilization of solar energy is a promising solution to address the increasing environmental issues caused by the consumption of fossil fuels and the worldwide energy crisis.[1−3] However, as a kind of diffusive and uncontrollable radiation energy, solar energy has to be transformed into other forms of energy before it can be stored, transported, and conveniently utilized. Consequently, advanced strategies for efficient solar energy conversion and storage are crucial for a sustainable future. The most common concepts for solar energy conversion are solar-to-chemical, solar-to-electric, and solar-to-thermal energy conversions (Fig. 1). For example, solar energy can be transformed into electricity via photovoltaic effect with semiconducting materials in solar panels; it may yield storable and transportable chemical fuels through artificial photosynthesis by mimicking natural solar energy conversion process in green plants. Moreover, solar energy can be converted into concentrated heat for power generation, water desalination, or even cancer therapy.[4]

The past decades have witnessed a great leap in the progress of solar energy conversion techniques, especially in the discovery and development of new materials and systems.[5−8] Conjugated polymers generally consist of naturally abundant elements such as C, H, and N. They have been regarded as very promising candidates of low-cost and easily processable materials for solar energy conversion.[9−17] The most distinctive feature of conjugated polymers for solar energy conversion is that they can be constructed from different building blocks with various bond-forming reactions. Therefore, the optoelectronic and photophysical properties of conjugated polymers are highly tunable and can be designed systematically through precise molecular engineering.[18−23] This merit could be well exemplified by the study reported by Cooper et al. in 2015, in which they synthesized 15 different conjugated microporous polymers from four phenylene and pyrene monomers through the Suzuki-Miyaura coupling reaction. These as-obtained conjugated polymers exhibited different optical bandgaps from 1.94 eV to 2.95 eV with tunable photocatalytic water splitting performance, indicating that conjugated polymers are very versatile materials for solar energy conversion.[23]

As a subclass of conjugated polymers, two-dimensional (2D) polymers are particularly intriguing for solar energy conversion. They are receiving more and more attention because of their remarkable physical, chemical, mechanical, and optoelectronic properties.[13,14,24−26] Currently, 2D polymers represent a large family of synthetic polymers with diverse structures and applications. Especially, the ultrathin 2D conjugated polymers nanosheets (< 10 nm in thickness,
either exfoliated from bulk 2D polymers or directly synthesized) are highly favorable for solar energy conversion as the ultrathin 2D characteristic feature provides several extraordinary advantages over polymer materials with other dimensions. Firstly, ultrathin 2D polymer nanosheets possess large surface-to-volume ratios which obviously endow them with abundant surface-accessible active sites for catalytic reactions. Secondly, the ultrathin nature is greatly beneficial for enhancing photoresponsiveness and charge separation by reducing the charge carrier migration distance from the bulk to the surface. Thirdly, the planar, sheet-like structure enables facile integration with other materials to form hybrids or heterostructures to further regulate the electronic structures and active sites for improving solar energy conversion efficiencies. Moreover, aside from these dimension-related properties, the high absorption coefficients of conjugated polymers enable effective light-harvesting which is a prerequisite for converting solar energy into other forms of energy. The rise of 2D polymers has created enormous opportunities for converting solar energy into other forms of energy with various emerging applications.

Thus far, there are many reviews covering different aspects of synthetic 2D polymers. However, a systematic report dedicated to developing synthetic ultrathin 2D conjugated polymer nanosheets for converting solar energy into solar fuels has not been presented yet. Herein, starting with the rational design and synthesis of ultrathin 2D conjugated polymer nanosheets, we highlight recent advances in employing ultrathin 2D conjugated polymer nanosheets for solar fuel generation. Elucidating the underlying principles and insights would be beneficial for design and synthesis of new 2D conjugated polymers nanosheets in the future. Thus, we particularly emphasize how the electronic and structural properties of ultrathin 2D conjugated polymer nanosheets can determine their solar energy conversion processes. Moreover, future prospects and challenges in solar fuel generation based on ultrathin 2D conjugated polymer nanosheets are also discussed. In light of the significance of solar energy conversion in emerging energy-related research as well as the great potential of ultrathin 2D polymer nanosheets hold in future solar energy utilization, it is anticipated that the synthetic strategies, characterization techniques, and design principles outlined here could advance our understandings on developing polymer-based materials for emerging energy conversion applications and stimulate more efforts from polymer chemistry, polymer physics, and polymer engineering to involve in this research field.

SYNTHETIC ROUTES TOWARD ULTRATHIN 2D CONJUGATED POLYMER NANOSHEETS

Owing to the fascinating features of ultrathin 2D conjugated polymers and their promising potentials in various applications, numerous synthetic strategies have been developed to fabricate high-quality ultrathin 2D conjugated polymer nanosheets. Precise synthesis of 2D polymer nanosheets is of significant importance, not only for structure-relationship studies but also for technological developments. Existing ultrathin 2D conjugated polymer nanosheets are generally synthesized through either the top-down method or the bottom-up method.

Top-down Method
Compared to the bottom-up approach, the top-down method has been demonstrated to be a formidable method for scalable production of ultrathin 2D conjugated polymer nanosheets. The top-down approach is typically involved in the exfoliation of layer-structured bulk polymers into ultrathin...
Graphitic carbon nitride (g-C₃N₄) is a very promising 2D polymer for solar energy conversion.[13,14,26,34,42-44] Ultrathin g-C₃N₄ nanosheets can be achieved by thermal-etching of pristine g-C₃N₄ in open air at 500 °C.[45] In this method, g-C₃N₄ nanosheets with thicknesses ranging from 1.62 nm to 2.62 nm were obtained after 2 h of heat treatment. Unfortunately, this thermal-etching method could only generate ultrathin nanosheets with a low yield of ~6%. Sonication-assisted liquid exfoliation is a more straightforward approach towards ultrathin polymer nanosheets. For example, the g-C₃N₄ can be exfoliated into ultrathin nanosheets during sonication with a yield of ~15% using water as the solvent (Fig. 2b).[44] This was attributed to the good match between the estimated surface energy of g-C₃N₄ (~115 mJ·m⁻²) and water (102 mJ·m⁻²). Subsequent study found out that the exfoliation efficiency in NMP and isopropanol (IPA) was even better than that in water, although their surface energies (~40 mJ·m⁻²) were much lower than the estimated value of g-C₃N₄.[46] This discrepancy might be caused by the mismatch between the actual surface energy of g-C₃N₄ and the calculated value. Very recently, a non-covalent method to simultaneously modify and exfoliate bulk g-C₃N₄ with 1-pyrenebutyrate (Py-COOH, sodium salt) via facile mechanical grinding was developed.[43] The surface-modified nanosheets could be well dispersed in aqueous solutions and, more importantly, showed a friendly interface for efficient conjugation of biomolecules for biosensing. The exfoliation method can be used essentially to generate ultrathin 2D polymer nanosheets from bulk 2D polymers with weak interlayer interactions.

Although the top-down approach is facile to prepare ultrathin 2D conjugated polymer nanosheets, the exfoliation yield is generally low (<15%) and the resulting nanosheets usually contain different numbers of layers.[47] Meanwhile, stabilization of the as-exfoliated nanosheets against restacking and aggregation is also challenging for large-scale fabrication. Thus, it is highly desirable to develop alternative approaches to synthesize ultrathin 2D conjugated polymer nanosheets.

**Bottom-up Method**

In contrast with the top-down approach, the bottom-up approach refers to the direct synthesis of ultrathin 2D conjugated polymer nanosheets from molecular components using covalent linkages. In this approach, the key principle is to restrict the polymerization along the vertical direction without affecting the in-plane growth. To achieve this goal, several different methods such as interfacial synthesis and mechanochemical synthesis are explored.

Interfacial synthesis, including solid-liquid,[48] liquid-li-
liquid-air, and solid-vapor interfacial reactions, has been considered as the most extensively used method to fabricate ultrathin 2D conjugated polymer nanosheets. A delicately designed surface can serve as an ideal template for the confined growth of conjugated polymer nanosheets in the two-dimensional direction. For example, ultrathin single-crystalline graphdiyne (GDY) films were formed on graphene nanosheets through a solid-liquid interfacial synthesis method (Fig. 3a). The growth of GDY was confined on the surface of graphene template using hexaethynylbenzene (HEB) as the monomer. Due to the higher binding energy of HEB monomers on graphene than on GDY (1.47 eV versus 0.896 eV), the monomers thermodynamically preferred to adsorb on graphene nanosheets toward the in-plane coupling reaction. Therefore, a much faster in-plane growth rather than out-of-plane growth of GDY nanosheets was expected through the van der Waals epitaxial manner (Fig. 3a). The as-obtained GDY nanosheets were single crystalline and possessed a trilayer structure with an ABC stacking order as observed by HRTEM. Meanwhile, co-condensation between aromatic aldehyde and aromatic amine monomers at a highly oriented pyrolytic graphite (HOPG)/octanoic acid interface through surface-confined growth could lead to large 2D conjugated polymer nanosheets with few defects and single domain extending to more than 1 μm².

Other than the solid-liquid interfacial synthesis, liquid-liquid or liquid-air interfacial synthesis is also widely used to prepare ultrathin 2D conjugated polymer nanosheets. Porphyrin-containing monolayer and few-layer 2D polymer nanosheets were successfully prepared through the Schiff-base polycondensation reaction at liquid-air and liquid-liquid interface (Ref. [54]).

Fig. 3 (a) Synthesis of ultrathin single-crystalline graphdiyne nanosheets on graphene via a solution phase van der Waals epitaxial method. The corresponding high-resolution TEM images are included to show the highly crystalline structure. (Reproduced with permission from Ref. [48]; Copyright (2018) American Association for the Advancement of Science); (b) Formation of ultrathin, highly ordered covalent organic frameworks on graphene via solid-vapor condensation. STM images and corresponding FFT patterns are included to show the highly ordered structure. (Reproduced with permission from Ref. [57]; Copyright (2013) American Chemical Society); (c) Synthesis of ultrathin conjugated polymers via mechanochemical ball milling. High-resolution TEM images and corresponding SAED patterns are included to show the highly ordered structure. (Reproduced with permission from Ref. [58]; Copyright (2017) Royal Society of Chemistry).
quid interfaces, respectively. The monolayer 2D polymer nanosheets with a thickness of 0.7 nm could function as an active semiconducting layer in a thin film transistor, whereas the few-layer 2D conjugated polymer nanosheets showed highly efficient catalytic activity toward hydrogen generation. 2D GDY nanosheets could also be prepared through liquid-liquid and liquid-air interfacial synthesis. Multilayer GDY nanosheets with a thickness of 24 nm and a domain size larger than 25 μm emerged through a successive alkyne-alkyne homocoupling reaction at the dichloromethane/water interface. In contrast, the liquid-air interfacial synthesis proved to be more successful in achieving ultrathin polymer nanosheets. Sprinkling a small amount of HEB onto the surface of aqeuous phase containing catalysts could generate single-crystalline GDY nanosheets with regular hexagonal domains and a uniform thickness of 3.0 nm. Meanwhile, solution synthesis of highly crystalline single-layer/few-layer triazine-based 2D polymer nanosheets was also demonstrated successfully at the interface of dichloromethane and trifluoromethanesulfonic acid.

To achieve ultrathin conjugated polymers nanosheets, a self-limiting solid-vapor interfacial synthesis was carried out to fabricate highly ordered monolayer 2D conjugated polymers. Fig. 3(b) shows the scheme for this experimental design. In this approach, precursor A was preloaded onto the surface of substrate by drop-casting before the introduction of precursor B. The entire system was then sealed up in a closed reactor using CuSO₄·5H₂O as thermodynamic regulation agent. When the reactor was heated to a desired temperature, precursor B would vaporize and then land on the surface covered with precursor A. Therefore, the covalent bond would form at the solid-vapor interface, resulting in the successful growth of high-quality ultrathin polymer nanosheets with low defect density and large domain sizes (Fig. 3b).

It is worth pointing out that mechanochemical synthesis of 2D aromatic polyamides under solvent-free ball-milling condition at room temperature has been developed using 1,3,5-benzenetricarbonyl chloride and 1,4-phenylenediamine or 4,4′-diaminobiphenyl as monomers (Fig. 3c). Due to the high reactivity between acryl chloride and amine, the reaction could be finished in less than half an hour under ball milling. The obtained 2D nanosheets not only exhibited a lateral size of micrometers and an ultrathin thickness of a few nanometers but also possessed high crystallinity, excellent thermal stability, and superior solvent dispersibility. The solvent-free conditions were found to be essential to the successful syntheses of these ultrathin 2D conjugated polymers nanosheets.

Until now, various synthetic routes toward ultrathin 2D conjugated polymer nanosheets have been developed. The approaches discussed here hold great promise for the controlled synthesis of ultrathin 2D conjugated polymer nanosheets with tailor-made structures and properties. However, realizing controlled synthesis is merely the first step to employing 2D polymers for solar fuel generation. In-depth understandings of the photophysical properties of synthesized ultrathin 2D conjugated polymer nanosheets using advanced characterization techniques and theoretical calculations are also necessary before they can be implemented for specific solar energy conversion process.

### ULTRATHIN 2D CONJUGATED POLYMER NANOSHEETS FOR SOLAR FUEL GENERATION

Solar-to-chemical energy conversion refers to the process that converts energy carried by solar photons into chemical potential energy in the form of storable and transportable chemical products. The reaction centers in green plants or other photosynthetic organisms are certainly the most sophisticated solar-to-chemical energy conversion systems, which have inspired recent advances in developing artificial photosynthetic systems to mimic the natural photosynthesis to generate chemical fuels by harnessing sunlight. The first step in natural photosynthesis is to catalytically split water into H₂ and O₂ without using any sacrificial agents (i.e., overall water splitting). The photocatalytic overall water splitting once was described as the “Holy Grail” in modern chemistry. Inorganic semiconductors are known for photocatalytic overall water splitting for more than 30 years. Unfortunately, polymer photocatalysts capable of catalyzing overall water splitting are still very rare. Moreover, it is interesting to point out that basically all reported polymer photocatalysts for overall water splitting are based on the 2D structure.

Recently, we demonstrated that conjugated polymer nanosheets prepared from terminal alkynes such as 1,3,5-tris(4-ethylphenylphenyl)-benzene (TEPB) and 1,3,5-triethynylbenzene (TEB) via oxidative coupling could exhibit high photocatalytic activity toward overall water splitting under visible light irradiation (Fig. 4a). Transmission electron microscopy (TEM) images as shown in Figs. 4b and 4c reveal that as-obtained PTEPB and PTEB exhibited a thin, sheet-like structure despite that PTEB were prone to form aggregates due to a slightly larger interlayer interaction energy. More importantly, both polymer nanosheets possessed suitable band structures for photocatalytic overall water splitting (Figs. 4d and 4e). The photocatalytically generated H₂ to O₂ ratio was very close to the theoretical 2:1 stoichiometry, and the average H₂ production rate was 218 and 102 μmol·h⁻¹·g⁻¹ for PTEPB and PTEB, respectively (Figs. 4f and 4g). Both photocatalysts exhibited robust photocatalytic activity for 48 h, indicating that they are highly stable toward water splitting reactions under visible light. The measured apparent quantum efficiency (AQE) could reach 10% at 420 nm with a measured solar-to-hydrogen (STH) value of 0.6%.

Slight modification of the 2D conjugated structure using 1,3,5-substituted benzene linked by different struts without the 1,3-diyne linkage, however, resulted in the complete loss of photocatalytic activity for overall water splitting. Thus, the 1,3-diyne covalent linkage is essential for controlling the photocatalytic water splitting activity. First-principles calculations further confirmed that photocatalytic overall water splitting was thermodynamically feasible for both 2D polymers.

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Compared to the photocatalytic H₂ evolution reaction, the photocatalytic water oxidation half-reaction is more challenging in the overall water-splitting process as the formation of molecular O₂ is a kinetically sluggish process involving four-electron and four-proton transfer. Therefore, very few polymer-based photocatalysts have shown excellent photocatalytic activity toward water oxidation. Combining both computational and experimental investigations, it was shown that the 2D aza-fused conjugated microporous polymer (aza-CMP) was highly efficient in photocatalytic O₂ generation (Fig. 5a). First-principles calculation on the electronic structure of aza-CMP nanosheets revealed that both valence and conduction band margins (VBM and CBM) were mainly contributed by pₓ orbitals of carbon and nitrogen atoms in the skeletons. Notably, the bandgaps of aza-CMP nanosheets exhibited monotonically decreasing behavior with increasing layer numbers as shown in Fig. 5(b). The aza-CMP nanosheets with an ideal bulk structure could eventually lead to a bandgap of 1.05 eV. The narrow bandgap suggested that aza-CMP nanosheets could efficiently absorb photons over a broad spectral range, including the near infrared (NIR) region. Meanwhile, the VBM of aza-CMP was well positioned below the oxidation potential of H₂O/O₂, suggesting that aza-CMP nanosheets were potentially capable of catalyzing O₂ evolution reaction. TEM and SEM images revealed that the as-synthesized aza-CMP inherently possessed the multilayer, sheet-like structure with sizes up to several micrometers (Fig. 5c). The average O₂
production rate could reach ~1 μmol h⁻¹, which was about eight-fold of that of g-C₃N₄ under the same conditions (Fig. 5d). Moreover, aza-CMP could successfully catalyze the photocatalytic O₂ evolution under NIR light illumination (λ > 800 nm) with an average O₂ production rate of 0.4 μmol·h⁻¹. This is the first kind of metal-free photocatalyst that is able to catalyze O₂ evolution under NIR region.

Taking advantage of the sheet-like structure, as-synthesized aza-CMP nanosheets were further exfoliated into ultrathin nanosheets via the sonication-assisted exfoliation process. The resulting ultrathin nanosheets (~10 nm in thickness) (Figs. 6a and 6b) exhibited a three-fold enhancement in the photocatalytic O₂ production rate and a quantum efficiency of 1.48% at 420 nm due to the improved photoresponsivity and more accessible surface active sites given by the ultrathin sheet-like structure. Furthermore, depositing cocatalysts such as Co(OH)₂ onto the ultrathin aza-CMP nanosheets could further promote the O₂ production rate up to ~14.3 μmol·h⁻¹, which was about ~15 times of that of the bulk aza-CMP (Figs. 6c and 6d). This work systematically demonstrated the advantages of ultrathin 2D structure in solar fuel generation.

Constructing hybrid structures or heterostructures is another notable strategy to tailor ultrathin 2D conjugated polymer nanosheets for high-performance solar fuel generation.[35,35,66] Therefore, various structures such as 0D/2D, 1D/2D, 2D/2D hybrid structures and heterostructures have been designed for solar energy conversion (Fig. 7). Polymer/ inorganic hybrids have been very successful in fabricating photocatalytic systems for artificial photosynthesis.[67,68] Deposition of 0D cocatalysts onto the surface of 2D polymers could provide trapping sites for photo-generated charge carriers, thus promoting charge separation and resulting in enhanced photocatalytic performance.[34,35,63] For example, Ni₃P nanoparticles were deposited onto g-C₃N₄ through a simple self-assembly method. As-obtained hybrid materials could yield a H₂ generation rate of 474.7 μmol·g⁻¹·h⁻¹ with an apparent quantum yield (AQY) of 3.2% at 435 nm, whereas pristine g-C₃N₄ exhibited much inferior photocatalytic activity (> 420 nm).[69] Meanwhile, single-atom metals were also demonstrated to be effective cocatalysts for 2D polymers due to the abundant coordination sites on the polymer surface.[70] Embedding single Pt atoms into planar 2D g-C₃N₄ surface could result in a tremendously enhanced photocatalytic H₂ generation performance of 318 μmol·h⁻¹, which was nearly 50-fold enhancement compared to that of the pristine g-C₃N₄.[70] Moreover, 1D nanowires and nanorods could also be integrated with ultrathin 2D nanosheets through controlled assembling methods or in situ growth methods.[71,72] Co₅P/g-C₃N₄ 1D/2D hybrid structure photocatalysts were developed and used for photocatalytic water splitting.[72] Photocatalytic measurements revealed that the 1D/2D hybrid structure without any noble metal cocatalysts could generate H₂ at a rate of 53.3 μmol·g⁻¹·h⁻¹. Compared to 0D/2D and 1D/2D hybrid structures, the 2D/2D hybrid structure is more favorable for charge separation.[66] For instance, a direct Z-scheme heterostructure composed of α-Fe₂O₃ and g-C₃N₄ nanosheets via an electrostatic self-assembly approach was reported recently.[73] The optimized hybrid structure exhibited a 13-fold enhancement in photocatalytic H₂ generation with the production rate approaching 398.0 μmol h⁻¹ g⁻¹.

Recently, we proposed and developed a metal-free van der Waals heterostructure based on ultrathin aza-CMP and C₂N nanosheets for photocatalytic overall water splitting (Fig. 8a).[74] The overlapping between ultrathin polymer nanosheets is shown clearly in Fig. 8(b) under TEM observation. The bandgap alignment of aza-CMP and C₂N is present.
in Fig. 8(c), indicating that the photogenerated holes and electrons in aza-CMP and C\textsubscript{2}N, respectively, tended to recombine with each other at the overlapped interfaces whereas the rest photoexcited carriers retained on the individual counterpart to drive redox reactions. The X-ray absorption near-edge structures (XANES) spectroscopy was used to verify the strong interlayer interactions between aza-CMP and C\textsubscript{2}N nanosheets. As shown in Fig. 8(d), the N K-edge peaks at 397.72 and 398.95 eV corresponding to the aromatic C−N=C structure of C\textsubscript{2}N and aza-CMP before mixing, shift to 398.03 and 398.56 eV, respectively, after formation of the van der Waals heterostructure. This marked energy shift validated the formation of heterostructure between aza-CMP and C\textsubscript{2}N as nitrogen atoms in the C−N=C structure of C\textsubscript{2}N received electrons from aza-CMP. Although neither polymer nanosheets were capable of overall water splitting under visible-light irradiation, simultaneous H\textsubscript{2} and O\textsubscript{2} generation with a molar ration of 2:1 was observed when the aza-CMP/C\textsubscript{2}N heterostructures were irradiated with visible light (> 420 nm) (Fig. 8e). This metal-free Z-scheme photocatalytic system exhibited an STH conversion efficiency of 0.23%, which could be improved to 0.40% by exploiting reduced graphene oxide (RGO) nanosheets as solid electron mediators. The formation of heterostructures dramatically improved the photocatalytic activity as the cofacial stacking between ultrathin 2D nanosheets could efficiently boost charge transfer between the interfaces of heterostructures.[74]

Other than the van der Waals heterostructure assembled from ultrathin 2D conjugated polymer nanosheets, in-plane heterostructure emerged as an intriguing structure for con-

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Fig. 6  (a) TEM and (b) AFM images of exfoliated aza-CMP nanosheets; (c) TEM image of the exfoliated aza-CMP photocatalyst deposited with Co(OH)\textsubscript{2} cocatalyst; (d) Photocatalytic O\textsubscript{2} production under visible light irradiation using the exfoliated ultrathin aza-CMP nanosheets with and without the Co(OH)\textsubscript{2} cocatalyst, respectively (Reproduced with permission from Ref. [63]; Copyright (2016) Royal Society of Chemistry)

0D/2D hybrid structure  1D/2D hybrid structure  2D/2D hybrid structure

Stacked 2D/2D heterostructure  In-plane 2D/2D heterostructure

Fig. 7  Schematic illustration of various hybrids or heterostructures based on ultrathin 2D conjugated polymers for solar fuel generation
verting solar energy into chemical energy. For example, the in-plane (C\textsubscript{3}N\textsubscript{4}) heterostructure prepared via thermal polymerization could catalyze overall water splitting with a notable AQY of 5% at 420 nm (Fig. 9). It is shown that the diffusion length and lifetime of photogenerated carriers were significantly increased by 10 times compared to that of pristine g-C\textsubscript{3}N\textsubscript{4} without forming the in-plane heterostructure, evidencing that this approach is capable of controlling interlayer charge dynamics and electronic structures. Both spectroscopic investigations and density functional theory calculations indicated that the in-plane heterostructure generated high electron density distribution near the Fermi level, reflecting that the recombination of photogenerated electron-hole pairs was largely suppressed. Therefore, constructing in-plane heterostructures in ultrathin 2D conjugated polymer nanosheets represents another effective approach for harnessing solar energy to produce chemical fuels.

Although particulate photocatalysts are promising for solar-to-chemical energy conversion, the energy conversion efficiency is generally low and far from practical applications. In contrast, the photoelectrochemical (PEC) process is more appealing for solar fuel generation as the carrier re-

Fig. 8 (a) Chemical structures of aza-CMP and C\textsubscript{2}N nanosheets; (b) TEM image of aza-CMP/C\textsubscript{2}N heterostructures; (c) The Z-scheme structure based on aza-CMP and C\textsubscript{2}N nanosheets; (d) The formation of heterostructure is confirmed using the N K-edge XANES; (e) Water splitting performance of as-formed heterostructures with different compositions (Reproduced with permission from Ref. [74]; Copyright (2018), Wiley-VCH)
combination is significantly suppressed by applying external bias. Consequently, the solar energy conversion efficiency can be dramatically improved. Recently, ultrathin 2D conjugated polymer nanosheets exhibited unique potential in PEC cells.[76,77] GDY, which is a newly developed 2D conjugated polymer, was used as the hole transfer layer in the PEC water splitting cell to generate H₂ (Fig. 10a).[76] Owing to the strong π-π interactions between GDY nanosheets and 4-mercaptopyridine modified CdSe quantum dots, the hole transportation and photocurrent performance were markedly improved. The assembled photocathode could generate H₂ with a faradic efficiency as high as (90 ± 5)% and maintained high stability for over 12 h. Meanwhile, the GDY nanosheets could also be used as the hole transport material for PEC O₂ generation.[77] The GDY layer was fabricated onto the BiVO₄ electrode by using a copper envelope catalysis strategy (Fig. 10b). As a result, both the GDY/BiVO₄ electrode exhibited much larger photocurrents under light illumination (Fig. 10c). A photocurrent density of 1.32 mA·cm⁻² was obtained on GDY/BiVO₄ at the potential of 1.23 V versus RHE, which was about twice as high as that of BiVO₄ photoanode under the same applied potential. Moreover, J-t curves with long-term light illumination indicated that the GDY coating could dramatically improve the stability of BiVO₄ electrode due to the rapid extraction of photogenerated holes from BiVO₄ for water oxidation (Fig. 10d).

With the continuing depletion of fossil fuels and the increasingly rise in greenhouse gases, generating clean and sustainable energy using CO₂ as the source becomes a hot research area. Various photocatalysts have been intensively explored for converting CO₂ into energy-carrying molecules. Unlike conventional approaches such as thermal catalysis, photocatalysis can proceed under ambient conditions. Thus,
photocatalytic \( \text{CO}_2 \) reduction represents one of the most important solar-to-chemical energy conversion processes. Until now, a number of hybrid photocatalysts based on 2D polymers have been developed for photocatalytic \( \text{CO}_2 \) reduction\cite{26,78-81}. The most widely used 2D conjugated polymer is \( g\text-C_3\text{N_4} \) as the conduction band of \( g\text-C_3\text{N_4} \) is suitable for transferring electrons onto \( \text{CO}_2 \) to initiate the reduction process. A notable example is the RuRu'/Ag/\( g\text-C_3\text{N_4} \) hybrid system.\cite{82} This hybrid photocatalyst catalyzed \( \text{CO}_2 \) reduction via the Z-scheme mechanism including step-by-step photoexcitation of \( \text{C}_3\text{N_4} \) and RuRu' (Fig. 11), exhibiting an impressive turnover number (TON) of \( \approx 3.3 \times 10^4 \) for 48 h (with respect to the molar amount of RuRu'). However, the selectivity and stability of this hybrid system became deteriorated after prolonged reaction. By replacing mesoporous \( g\text-C_3\text{N_4} \) with \( g\text-C_3\text{N_4} \) nanosheets in this system, the newly developed photocatalyst exhibited a good TON (> 2000) and high \( \text{CO}_2 \) reduction selectivity (approximately 98%) for photocatalytic reduction of \( \text{CO}_2 \) to HCOOH in aqueous solution.\cite{83} These studies further demonstrated the great promise of ultrathin 2D conjugated polymer nanosheets for photocatalytic \( \text{CO}_2 \) reduction.

![Fig. 11 Photocatalytic \( \text{CO}_2 \) reduction using a hybrid of \( g\text-C_3\text{N_4} \) with a bimetallic Ru(II) complex (Reproduced with permission from Ref. [82]; Copyright (2016) American Chemical Society)](image)

**CONCLUSIONS AND OUTLOOK**

Solar fuel generation is not only crucial in sustainable energy research but also fundamentally important in basic science research. Recent progress in developing ultrathin 2D conjugated polymer nanosheets for solar fuel generation is highlighted here, suggesting that developing 2D conjugated polymer nanosheets are very promising for producing clean, affordable, and sustainable chemical fuels using sunlight as the energy input. The ultrathin 2D conjugated polymer framework with in-plane periodicity provides a simple yet powerful platform for studying structure-property relationships from the molecular level. The design strategies, characterization techniques, and synthetic methods summarized here would be beneficial for promoting further efforts in investigating other solar-to-chemical energy conversion processes such as photocatalytic nitrogen fixation and photocatalytic organic synthesis. It is worth pointing out that ultrathin 2D conjugated polymer nanosheets also hold great promise for other solar energy conversion techniques such as solar-to-thermal and solar-to-electric energy conversions.

Undoubtedly, developing polymer materials for solar fuel generation is still at the early stage and encounters many obvious challenges. First of all, it is still extremely challenging to realize large-scale production of high-quality 2D conjugated polymer nanosheets with controlled sizes and thicknesses. Meanwhile, despite the fact that the bond-forming reactions in polymer synthesis are abundant, polymer photocatalysts with high efficiency and selectivity for specific photochemical reactions are still very limited. This requires more polymer chemists to involve in this research area and explore more 2D conjugated structures. Secondly, tailoring the microstructures of ultrathin 2D conjugated polymer nanosheets would have profound influence on the final energy conversion performance. Thus, more effective strategies are highly desired. Thirdly, the underlying mechanisms responsible for many emerging systems are not thoroughly elucidated yet. Sometimes, even controversial conclusions are reached. In this regard, cutting-edge characterization techniques along with theoretical calculations are imperative for advancing our understandings of reaction pathways and providing deep insights into the photophysical properties of semiconducting 2D polymers, which in turn will lead to design and synthesize more efficient catalytic systems. More importantly, current studies presume that basically all ultrathin 2D conjugated polymer nanosheets may get involved in the energy conversion process as individual counterpart. However, under practical reaction conditions, these nanosheets could assemble into aggregates or other undefined structures. How the macroscopic properties of these nanosheets, especially their assembled structures, can affect the energy conversion process is still unknown. This poses another grand challenge in developing advanced characterization techniques to reveal the ‘actual’ energy conversion process.\cite{84,85} Finally, it should be pointed out that low-cost, stable, and efficient 2D conjugated polymer nanosheets compatible with large-scale synthesis and viable for practical solar-to-chemical energy conversion are still yet to be realized. The race is on.

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