2D Honeycomb-Kagome Polymer Tandem as Effective Metal-Free Photocatalysts for Water Splitting

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1. Introduction

Since Fujishima and Honda first demonstrated the potential of photoexciting TiO$_2$ to split water into hydrogen and oxygen in 1972,[1] solar-driven water splitting has become a promising strategy for producing hydrogen fuel.[2] In order to improve the efficiency of this energy conversion process, great efforts have been devoted to developing effective photocatalysts. Transition metal oxides,[3–5] nitrides,[6] and sulfides[7,8] have shown good activity to photocatalyze water splitting, however, the low quantum efficiency of these bulk materials has significantly limited their practical application.[9,10]

Over the past decade, 2D materials led by graphene have proven their potential as multifunctional platforms in energy storage and conversion systems.[11,12] The large base size and small thickness of 2D materials contribute to many intriguing physicochemical properties,[13] and also make them competitive candidates for photocatalytic water splitting.[14,15] Under light irradiation, the large specific surface area of 2D semiconductors can ensure the absorption of photons in a remarkably short time. Then, the photoexcited electron–hole pairs generated on the surface can effectively participate in the in situ redox reactions of water, thereby greatly suppressing the undesired charge recombination occurring extensively in the bulk counterparts.[16] However, although many 2D inorganic semiconductors have been exhaustively studied as possible photocatalysts for water splitting,[17] few 2D materials can well meet the critical criteria of appropriate band structure and effective light absorption to promote overall water splitting.[18,19]

The emerging materials class of semiconducting 2D polymers offers a opportunity to craft porous and highly ordered skeletons with flexible topologies and desired electronic structures to meet the criteria of photocatalytic water splitting.[20,21] The manufactured lattices of 2D polymers usually show high thermal and chemical stability at ambient conditions,[22,23] which is a crucial precondition for a sustainable photocatalytic application. Many theoretical and experimental investigations have demonstrated the potential of 2D polymers in photocatalytic water splitting, including but not limited to g-C$_3$N$_4$,[24–27] phenyl-triazine oligomers,[28] covalent triazine-based frameworks,[29] azine covalent organic frameworks,[30] and conjugated polymers.[31,32] However, despite that most of these 2D structures can stimulate the hydrogen evolution reaction (HER) process, only few of them can photocatalyze the oxygen evolution reaction (OER). Another problem is that there is no electronic conjugation in most porous frameworks and 2D polymers, suppressing charge transport and consequently charge carrier dissociation, which in turn fosters unwanted recombination. Therefore, the design and screening of 2D polymers that possess appropriate electronic and optical properties for effective overall water splitting is still highly demanding.
Here, based on our previous predictions that a functional lattice made of 2D polymers can be constructed by the control of π-conjugation and electronic structure of the knots,[33] we explored the potential of conjugated 2D honeycomb-kagome polymers made of heteroatom-centered triangulene (HT) derivatives for overall water splitting by employing first-principles calculations. We dig further into the electronic structures of these 2D HT-polymers and observe that the heteroatom imposes a strongly different chemical potential, so that band edges can easily be forced to appropriate positions with respect to the required electrode potentials for HER and OER. We systematically examine the thermodynamic processes of HER and OER on different structures. Our results indicate that the center heteroatom and the bridge functional groups not only determines the electronic structure of these 2D polymers, but also affects the adsorption of water redox intermediates and contributes to exceptionally high photocatalytic activities. N-centered and B-centered 2D HT-polymers can either activate the photocatalytic HER or OER, respectively. The single-band characteristic of these 2D HT-polymers make them excellent candidate materials to build heterogeneous tandem cells of n-type and p-type polymers, which can guarantee effective electron/hole separation for high performance overall water splitting. With tunable morphology, high porosity, good chemical stability, pronounced light absorption, and high photocatalytic activity, 2D honeycomb-kagome HT-polymers and the combined tandem device are predicted to be promising water-splitting photocatalysts.

2. Results and Discussion

2.1. Category of 2D Honeycomb-Kagome HT-Polymers

The experimentally known HT derivative monomers can be divided into two categories, the B-centered (Figure 1a–d), and the N-centered molecules (Figure 1e–h). Each category is further refined by using different bridge functional groups (C=O, O, –CH2 or –CMe2), respectively. Previous experimental studies have demonstrated that the N-centered molecules are powerful building monomers and can be assembled into 2D materials to build heterogeneous tandem cells of n-type and p-type polymers, which can guarantee effective electron/hole separation for high performance overall water splitting. With tunable morphology, high porosity, good chemical stability, pronounced light absorption, and high photocatalytic activity, 2D honeycomb-kagome HT-polymers and the combined tandem device are predicted to be promising water-splitting photocatalysts.

Figure 1. Ball-and-stick structures of HT derivative molecules. a) CTPB, b) OTPB,[39] c) MTPB, d) DTPB,[40] e) CTPA,[41] f) OTPA,[42] g) MTPA,[43] and h) DTPA.[42,43] i) The monolayer schematic of 2D CTPA in a 3×3×1 supercell, the unit cell is indicated by the dark dashed line.
networks by surface calcination or solution synthesis. For instance, Bieri et al. have successfully synthesized 2D dimethylmethylene-bridged triphenylamine (DTPA) and methylene-bridged triphenylamine (MTPA) by controlling the calcination temperature in the on-surface coupling process. Steiner et al. realized the synthesis of 2D carbonyl-bridged triphenylamine (CTPA) via Ullmann-type coupling reactions between halogen-substituted CTPA monomers. By combining a rigid azatriangulene precursor and a hot dosing approach, Galeotti et al. recently prepared mesoscale ordered 2D oxygen-bridged triphenylamine (OTPA) and CTPA and further validated our previous theoretical predictions on the intriguing electronic band structure using ARPES measurements. These theoretical and experimental findings make it rather appealing to explore the possibilities of using 2D HT-polymers for photocatalytic water splitting. Note that the previous theoretical predictions about the electronic structures of 2D CTPA and OTPA were found to be in good agreement with the experimental results, thus verifying the reliability of the Herd–Scuseria–Ernzerhof hybrid functional (HSE06) calculations performed in this work.

In view of the feasibility of synthesizing N-centered HT-polymers (N-HT-polymers) from the corresponding HT monomers, B-centered HT-polymers (B-HT-polymers) can be expected to be prepared by similar manner. Therefore, and as the valence band edge of the B-centered HT polymers typically is below the electrode potential of the oxygen evolution reaction, we examined both types of 2D polymers as possible photocatalysts in this work, including the B-HT-polymers of carbonyl-bridged triphenylborane (CTPB), oxygen-bridged triphenylborane (OTPB), methylene-bridged triphenylborane (MTPB), and dimethylmethylene-bridged triphenylborane (DTPB), and the N-HT-polymers of CTPA, OTPA, MTPA, and DTPA, respectively. As illustrated in Figure 1i, the D3h symmetry of the HT monomers manifests the honeycomb-kagome geometry of the 2D polymers.

2.2. Electronic Properties of 2D Honeycomb-Kagome HT-Polymers

Our previous study has demonstrated that the 2D HT-polymers are polar, single-band semiconductors with either exclusively electrons (n-type, B center) or holes (p-type, N center) as charge carriers. Because of the effective intermolecular \( \pi \) conjugation, these 2D HT-polymers show moderate bandgaps in the range of 1.8–2.8 eV (Figure 2a–c, e–g) and exhibit high charge carrier mobilities (Table 1). The two additional examples included in this study, DTPB (Figure 2d) and DTPA (Figure 2h), follow the overall characteristics of the 2D HT-polymers (see also Figure S1 and Table S1, Supporting Information).

To facilitate overall water splitting, the potential photocatalyst should possess appropriate band alignments matching the redox potentials of water. In particular, the conduction band minimum (CBM) of the 2D semiconductor should be larger than the \( \text{H}^+/\text{H}_2 \) potential (~4.44 V vs vacuum) and the

![Figure 2.](image-url) Band structures of 2D HT-polymers (obtained at the HSE06 level of theory). The band edges have been corrected by the vacuum potential. The Fermi level is indicated by the black dashed line.
valence band maximum (VBM) should be smaller than the O$_2$/H$_2$O potential (−5.67 V vs vacuum). Meanwhile, photoexcited electrons and holes should provide sufficient driving force to stimulate the HER and OER process, respectively. As illustrated in Figure 2b–e, 2D OTPB, MTPB, DTPB, and CTPA show band alignments suitable for overall water splitting at pH = 0, whereas the band edges of 2D CTPB, OTPA, MTPA, and DTPA (Figure 2a,f–h) are not appropriate to drive both OER and HER in the same material. However, as the edges of the mobile CB in B-HT-polymers are alternatively above the mobile VB in N-HT-polymers, it is possible to combine both materials types in tandem cells to facilitate overall water splitting. Details will be discussed later.

### 2.3. Thermodynamics of HER and OER on 2D Honeycomb-Kagome HT-Polymers

Besides appropriate band alignment, an additional necessity for photocatalytic applications is the material’s catalytic performance, which can be assessed by calculating the thermodynamics of the photoelectrode processes based on the computational hydrogen electrode model. Therefore, we studied the thermodynamics of the elementary steps of HER and OER at pH = 0, with and without the effect of light irradiation (Figure 3). Note that although the inappropriate band edge alignment of CTPB, OTPA, MTPA, and DTPA has excluded them as potential single-material photocatalysts, they may be suitable components in tandem electrodes, which justifies the evaluation of the thermodynamics of their surface reactions. We are particularly interested in the impact of the different bridge groups on the catalytic activity without light irradiation. As illustrated in Figure 3a, the active site for the formation of H$_2$ is found to be the edge C site (top schematics) on all examined 2D HT-polymers, except for the cases of 2D CTPA and CTPB. For these two structures, the H atom is more favorably adsorbed on the O site at the bridge (bottom schematics). The summarized free-energy profiles of the two electron (2e) HER process show that the first elementary step is endothermic with positive free energy change ($\Delta G_{HER}$, Table S2, Supporting Information) for all examined structures, indicating an unfavorable HER process of high overpotential ($\eta_{HER}$) on 2D HT-polymers without light irradiation.

The OER process is more involved as it is a 4e reaction, corresponding to the deprotonation of water molecules, and is associated to the formation of different oxygenated intermediates. The first electron transfer step corresponds to the formation of OH$^*$ via the oxidation of a water molecule. The adsorption of OH$^*$ is facilitated by the B center of 2D B-HT-polymers (exhibited in Figure 3b) because that the B atom is electron-deficient and attractive to the OH$^*$ species, whereas the active sites for the adsorption of OH$^*$ are found to be the C site of the 2D N-HT-polymers (Figure 3c). The second electron transfer step represents the formation of O$^*$ by oxidizing OH$^*$. In the third electron-transfer step, two different mechanisms are observed for the B- and N-centered HT-polymers. For B-HT-polymers, the third step corresponds to the oxidation of the second water molecule to form an OOH$^*$ species adsorbed on the B site. However, for N-HT-polymers, the intermediate species of the third step are the O and OH (O=OH$^*$) adsorbed on two neighboring active C sites. The different OER intermediates of the third step on B-HT-polymers and N-HT-polymers contribute to different OER mechanisms, which we refer to as single-site and dual-site process, respectively. In the fourth electron transfer step, the OER is accomplished by forming and releasing an O$_2$ molecule from OOH$^*$ for the single-site process. While for the dual-site OER process, the fourth step can be separated into two sub-steps, one including the formation of O$_4$O$^*$ species and the second one the formation of O$_2$. The Gibbs free energy profiles for the two different OER pathways are summarized in Figure 3b,c. For the single-site process, all the four elementary steps are endothermic on the examined B-HT-polymers except the fourth step on 2D OTPB, MTPB, and DTPB. The rate determining step which shows the highest $\Delta G$ value ($\Delta G_{OER}$) is found to be the first elementary step for OTPB and DTPB, whereas it is the second step for CTPB and OTPB, respectively. The corresponding OP ($\eta_{OER}$) is calculated to be 0.58, 0.73, 0.87, and 0.96 V for CTPB, OTPB, MTPB, and DTPB, respectively. For the dual site process on N-HT-polymers, all the elementary steps are endothermic except for the step of O$_2$ releasing from CTPA. The formation of OH$^*$ of the first step is found to be the rate determining one for all the examined N-HT-polymers with a corresponding $\eta_{OER}$ of 0.96, 0.91, 0.97, and 0.90 V for 2D CTPA, OTPA, MTPA, and DTPA, respectively. The schematics of HER and OER process on B- and N-HT-polymers are illustrated in Figure 3d.

While the HT-polymers are a rather narrow class of 2D polymers, they exhibit a significantly different chemistry. Both the centre atoms and bridge functional groups contribute to distinguished HER and OER performances. The lone electron pair of N sites facilitates HER while the electron deficient B center renders the 2D B-HT-polymers more active for OER than the 2D N-HT-polymers. Meanwhile, large bridge groups contribute to reduced HER and OER performances of DTPB and DTPA due to the impact of steric effect. However, in the absence of light irradiation, water splitting cannot spontaneously occur on any 2D HT-polymers.
2.4. Solar-Driven Overall Water Splitting

Upon light irradiation, the photon-generated electrons and holes with a given drive potential for water reduction ($U_{\text{red}}$) and oxidation ($U_{\text{ox}}$) will work independently to overcome $\eta_{\text{HER}}$ and $\eta_{\text{OER}}$ (Table 1), respectively. Namely, the $\Delta G$ value of the electron-transfer steps of HER and OER can be reduced by $eU_{\text{red}}$ or $eU_{\text{ox}}$, respectively. Only if the drive potential is larger than the overpotential, the half reaction can proceed spontaneously under light irradiation. As shown in Figure 3e, the HER process becomes exothermic upon light irradiation for 2D MTPB, OTPA, MTPA, and DTPA, whereas there is still an energy barrier of 0.14, 0.16, 0.92, and 0.11 eV to be overcome for 2D CTPB, OTPB, DTPB, and CTPA, respectively. With the applied $U_{\text{ox}}$, all the elementary steps of OER on CTPB, OTPB, and DTPB become exothermic (Figure 3f), indicating that the OER can take place spontaneously under light irradiation. By contrast, the OER process cannot proceed spontaneously on 2D MTPB, OTPA, MTPA, and DTPA (Figure 3g) due to the remaining energy barrier.

To better understand the photocatalytic performance of different 2D HT-polymers, the contribution of $U_{\text{red}}$ and $U_{\text{ox}}$ in offsetting $\eta_{\text{HER}}$ and $\eta_{\text{OER}}$ for 2D HT-polymers is illustrated in Figure 4a. As the transitions overcome gap and overpotential, 2D OTPA, MTPA, DTPA, and MTPB can facilitate solar-driven HER, while CTPB, OTPB, and DTPB are capable of photocatalyzing the OER half reaction by showing no remaining overpotential. Since the CBM of the B-HT-polymers is above the VBM of the N-HT-polymers, tandem devices can be constructed to realize overall water splitting, e.g., by coupling the half-electrode of a 2D CTPB, OTPB, or DTPB for OER with a 2D OTPA, MTPA, or DTPA half-electrode for HER. Before discussing the possible tandem combinations, we also examine the light-harvesting ability of the 2D HT-polymers to roughly evaluate their efficiency as potential photocatalysts. As shown in Figure S2a of the Supporting Information, 2D HT-polymers exhibit light absorption in the ultraviolet and visible range of the solar spectrum. The absorption coefficient reaches up to $10^5$ cm$^{-1}$, comparable to that of organic perovskite solar cells, indicating the good light harvesting capability. Among all examined...
structures, CTPA shows the highest absorption intensity for light of wavelength in range of 200–400 nm, while CTPB and OTPA exhibit a pronounced visible light absorption at around 500 and 600 nm, respectively (Figure 4b).

Although there are seven tandem cells possible, as illustrated in Figure S2b of the Supporting Information, the composition of CTPB/DTPA (Figure 4c) is by far the most promising candidate by forming a z-scheme heterojunction.[47] Both materials show strong absorption and absorb in complementary parts of the solar spectrum (Figure 4b). As the 2D CTPB and DTPA are single-band semiconductors with strongly different charge transport characteristics, charge carriers of low mobility will remain in the half-electrodes, while the mobile ones will go to the other half-electrode (Figure 4c), resulting in effective electron/hole separation in the tandem system. Meanwhile the high redox ability of the VB of CTPB and CB of DTPA can be maintained in the z-scheme manner to facilitate OER and HER,[48] respectively. Especially, there is a potential difference of 0.45 V between the two half-electrodes, so that 2D CTPB/DTPA can provide a small but sufficient photovoltaic power source to further enhance the photocatalytic efficiency, allowing for a self-sustained installation with hydrogen production and electric power supply. The proposed tandem cell is also effective in a neutral solution because the drive potentials at pH = 7 are still sufficient to overcome the OPs of HER and OER as indicated in Figure 4c.

Note that although OTPB can only facilitate the OER process and CTPA seems inactive for overall water splitting, the small energy barrier of HER (0.16 and 0.11 eV for OTPB and CTPA, respectively) and OER (0.10 eV for CTPA) under light irradiation (Figure 4a) makes it possible to use them as single photocatalysts to facilitate overall water splitting by adding cocatalysts (e.g., Pt).[49,50] Remarkably, the high carrier mobility, high photocatalytic activity for both HER and OER half reactions and high synthetic feasibility of 2D OTPB and CTPA are superior to the previous studied 2D covalent organic frameworks.[28–32] As the band edges of the 2D HT-polymers are closely related to the HOMO–LUMO region of their molecular monomers,[33] building 2D polymers from aromatic organic monomers that have suitable front orbitals and HOMO–LUMO gaps will be a dependable strategy to designing appropriate 2D conjugated polymers as nonmetal photocatalysts for overall water splitting.

3. Conclusion

We have demonstrated a new design concept for photocatalysts made of polar crystalline 2D polymers, which makes use of both molecular and crystal properties for the design concept and of computational screening for identifying the

Figure 4. a) Band edge alignments of 2D HT-polymers in comparison with the redox potentials of water splitting at pH = 0. The remaining overpotentials of HER and OER on different structure surfaces after offsetting the original ones (blue and red shaded vertical bars for HER and OER, respectively) by the drive potential of $U_{\text{drive}}$ and $U_{\text{drive}}$, are indicated by the blue and red values in V, respectively. The half-reaction can proceed thermodynamic favorably if no OP is remained after light irradiation. b) Computed absorption spectra for light incident from the parallel direction of 2D CTPB, CTPA, and OTPA at the HSE06 level of theory. c) Proposed tandem device of 2D CTPB/DTPA for overall water splitting. The blue and red shaded vertical bars indicate the original OP of HER and OER at pH = 0 while the gray ones indicate those at pH = 7. The potential difference is indicated by the black value in V.
most suitable material: first, the well-known steps of materials discovery are applied, i.e., monomers with suitable HOMO–LUMO gap (ranging from 1.8 to 2.8 eV for the heteroatriangulene monomers investigated here) are selected and then stitched together to form crystalline polymers, which are evaluated for suitable bandgap and high absorbance. As such polymers have been experimentally demonstrated, they provide a realistic basis for the forthcoming theoretical investigations. Next, we exploit the underlying polymer lattice topology, resulting in the typical band structure inherent to honeycomb-kagome lattices with Dirac cones and flat bands near the fermi level. As third step, we pin the fermi level by defining the number of π-electrons in the monomers, which results in semiconductors with only one frontier band carrying mobile charge carriers (p- or n-type). Finally, we shift the band edges to suitable positions to allow both for hydrogen and oxygen evolution, and make sure that both reactions run without barriers. Fermi level pinning and potential shifting is achieved by the introduction of heteroatoms into the monomers, namely, boron for lowering and nitrogen for increasing the band edge positions. This way, among the various candidates we could identify CTPB/DTPA as suitable tandem combination, where electrodes of both materials are electrically coupled in a way that the highly mobile charge carriers are transferred between the materials, thus avoiding recombination, while the immobile ones remain and drive the half-electrode barrier-free reactions. The small potential drop occurring during the charge carrier transfer could be exploited photovoltaically, e.g., to power auxiliary equipment leading to a self-sufficient water-splitting system.

Since several 2D HT-polymers have already been experimentally realized, applying them to photocatalyze water splitting will appeal for extensive experimental investigations.

4. Experimental Section

Computational Methods: First-principles calculations were performed on basis of density functional theory as implemented in the Vienna Ab initio Simulation Package. The projector-augmented plane wave approach was employed to describe the ion–electron interactions. The generalized gradient approximation, i.e., the PBE method was employed together with Grimme’s D3 van der Waals corrections to accurately describe the weak interactions between the adsorbenets and the 2D HT-polymers. The lattice vectors and atomic positions were fully relaxed and a convergence threshold of 10−5 eV in energy and 10−2 eV Å−1 for the force within the conjugated gradient method for geometry optimizations and a cutoff energy of 500 eV for the plane-wave basis set were adopted in all computations. The vacuum layer of the 2D structures was set to be 15 Å to avoid spurious interactions between neighboring images along the c direction. The HSE06 method was employed to calculate the band structure and light absorption capabilities. The band edges of 2D HT-polymers were corrected by the vacuum potential, which was taken as the potential energy at the edge of the vacuum layer. The Monkhorst–Pack k-point mesh of the Brillouin Zone was set to 3 × 3 × 1 for all calculations.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in NOMAD at https://dx.doi.org/10.17172/NOMAD/2021.04.11-1.

Keywords

2D polymers, honeycomb-kagome lattices, photocatalysis, semiconductors, water splitting

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