Fluorescein supramolecular nanosheets: A novel organic photocatalyst for visible-light-driven H₂ evolution from water

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Photocatalytic water splitting for hydrogen evolution is one of the most promising approaches to address energy and environmental issues [1–4]. Metal-free photocatalysts, usually containing low cost and earth-abundant C, N and O elements, are more advantageous than the traditional metal-based photocatalysts and have attracted considerable interest for many years [5–10]. In the reported metal-free photocatalysts, polymer carbon nitride (PCN) is extensively studied, but the relatively large band gap (~2.7 eV) and the low activity limit its photocatalytic applications [11–17]. Therefore, to develop a novel wide light range and high-efficiency metal-free photocatalysts for H₂ production is very essential.

Supramolecule usually refers to the molecular aggregates assembled by intermolecular interactions (hydrogen bonds) or constructed with other hybrid structures and has been used directly for energy harvesting and transformation, such as water splitting, pollutant degradation and sensor [18–20]. The supramolecules with flexible skeletal structure through the different molecular self-assembly patterns have larger conjugated structure, more efficient charge transfer and separation, and broader absorption range than single molecule and polymer [21,22]. Among very few supramolecular photocatalysts, although the widely reported metal-contained porphyrin hybrids have good photocatalytic performance for H₂ production, metal-free porphyrin systems present a relatively poor activity, the metal composition confines their further applications due to high cost, metals toxicity and complicated preparation process [23,24]. Recently, Zhu and co-workers [25] reported a non-covalent self-assembled perylene-3,4,9,10-tetracarboxylic diimide (PDINH) supramolecular composed of metal-free organic

molecules, working as a visible-light photocatalyst for O₂ production and photodegradation. However, the conduction band (CB) of PDINH supra-molecular is (−0.049 V *versus* normal hydrogen electrode (NHE)); thus crippled in the application of H₂ production from water. Therefore, it is very significant to develop the easy obtained and novel metal-free supramolecular photocatalysts for H₂ production from water. The fluorescein, first synthesized in 1871, has been widely used in labelling and sensing biomolecules, as well as ophthalmology because of its high absorption in the visible region and low toxicity [26–29]. Herein, we demonstrate that the fluorescein supramolecular crystal self-assembled by single molecule is highly efficient for H₂ production from water under visible light. The morphology can be easily self-assembled into nanosheets *via* a simple dissolution-recrystallization process. To date, this is the first report on H₂ production under visible light over fluorescein supramolecular crystal, which extends the family of organic supramolecular photocatalytic materials. This study may open up new insights into the search of other metal-free and organic photocatalysts.

We applied Gaussian09 package to calculate the distribution of the frontier orbitals of the fluorescein single molecule. A B3LYP functional was adopted with 6-31++G as the Gaussian basis with diffusion functions. Fig. 1 shows the molecular structural formula and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HOMO is mainly populated along the xanthene structure (Fig. 1c), while the LUMO are largely localized among the benzofuranone (Fig. 1d). In addition, due to the conjugated structure, the generated electrons can rapidly transfer to

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Figure 1 The structure formula (a), optimized structure with Gaussian09 package (C, gray; H, white; and O, red) (b) of fluorescein single molecule. The electronic density distribution of HOMO (c) and LUMO (d).

benzene ring group, while the holes are driven to the opposite direction, simultaneously leading to the efficient charges separation [30]. Fluorescein supramolecular nanosheets (NS) can be obtained by a self-assembled process *via* a simple dissolution-recrystallization process (Fig. 2a). The morphology of the recrystallized fluorescein supramolecular is NS with ~10 nm in thickness (Fig. 2d, e), while fluorescein-P (purchased from Aladdin Reagent Company) is solid blocks tightly packed by NSs (Fig. 2b, c). The X-ray diffraction (XRD) patterns (Fig. 2f) indicate the supramolecular NS with the similar structure pattern of fluorescein-P exhibits a typical orthorhombic phase with the diffraction peaks at 10.72°, 11.91°, 13.39°, 16.78°,

26.45° and 27.78°, corresponding to the (110), (101), (020), (200), (012), (032) and (113) facets (JCPDS No. 51-2219). The X-ray photoelectron spectra (XPS) of supramolecular NS are shown in Fig. S1. The C 1s spectra can be de-convoluted into three peaks, which are attributed to the C=O bonds (287.8 eV), C–O bonds (286.0 eV) and graphitic C=C bonds (283.9 eV) [31]. The O 1s spectra are assigned to O–H (532.0 eV), O–C (530.9 eV) and O=C (530.0 eV) [32]. The FTIR spectra show typical signals at 1,323 and 1,409 cm^{-1} , which can be assigned to the skeleton vibration of the aromatic rings in the supramolecular NSs (Fig. S2) [33]. A C=O stretching mode at 1,688 cm^{-1} is observed, and the signals at 3,426 and 1,193 cm^{-1} can be assigned to the –OH and C–O–C stretching modes, respectively. Diffused reflective UV-vis spectroscopy (DRS, Fig. 2g) reveals that the orange red powders (inset) have a strong absorption in the visible light region, even extending to 700 nm. The bandgap (E_g) can be calculated to be 2.15 eV from the Tauc plot (Fig. S3). Surface photovoltage (SPV, Fig. S4) presents a positive photovoltage response, indicating the generated carriers can efficiently be separated and rapidly migrate to the surface [34–36].

Low resolution transmission electron microscopy (TEM) images further confirm the morphology of nanosheets are kept after loading 1 wt% Pt nanoparticles as cocatalyst (Fig. 3a, c). The Pt nanoparticles are uniformly dispersed on the supramolecular NS (Fig. 3d) and show the 0.227 nm lattice fringe space (inset of Fig. 3d), which is the characteristic (111) facet of cubic phase Pt. The

Figure 2 Experimental schematic diagram (a). FE-SEM images of fluorescein-P (b, c) and supramolecular NS (d, e). XRD pattern (f) and UV-vis DRS spectra (g) of fluorescein-P and supramolecular NSs. Inset of g is the optical image.

Figure 3 TEM images of supramolecular NSs before (a, b) and after (c, d) loading 1 wt% Pt nanoparticles as cocatalyst. Inset of d is the HR-TEM image of Pt nanoparticles.

Brunauer-Emmett-Teller (BET) surface area is $25.2 \text{ m}^2 \text{ g}^{-1}$ and pore size distribution of the fluorescein supramolecular NS (Fig. S5) give a type-IV isotherm with a type-H3

hysteresis loop, and the pore diameter range (5–15 nm) deduced by the pore size distribution curve indicated a mesoporous structure [37,38].

The photocatalytic H_2 production over fluorescein NSs with 1 wt% Pt as cocatalysts was tested under visible light irradiation in L-Ascorbic acid (AA) and oxalic acid (OA) sacrificial agents. The H_2 production rate is $17.06 \mu\text{mol h}^{-1}$ ($\lambda > 420 \text{ nm}$) over 50 mg of photocatalyst when OA serves as sacrificial agent, which is superior than in AA ($10.36 \mu\text{mol h}^{-1}$); while fluorescein-P shows a relatively lower H_2 production rate ($9.47 \mu\text{mol h}^{-1}$) mainly due to smaller surface areas (Fig. S6). The optimal loading of Pt is about 1 wt%, and too much loading (2 or 3 wt%) results in a decrease of H_2 production rate (Fig. S7). The supramolecular NSs exhibit higher activity (Fig. 4a) than PCN synthesized from urea at 550°C according to Chen's report [39], and the corresponding apparent quantum efficiency (QE) of supramolecular NS at $420 \pm 10 \text{ nm}$ reaches 1.2%. However, it is much lower than the state-of-art results from PCN [40–42]. The recycling measurements for H_2 production are shown in Fig. 4b. Clearly, a photocorrosion is observed in H_2 production reaction over supramolecular NS and the rate even re-

Figure 4 The comparison of H_2 production ($\lambda > 420 \text{ nm}$) between fluorescein supramolecular NSs and PCN prepared from urea (a), and the recycling measurements of H_2 production (b). TEM image of supramolecular NSs after photocatalysis for 15 h (c). The XRD pattern of supramolecular NSs before and after photocatalysis for 15 h (d).

Figure 5 The UPS spectrum and possible photocatalytic H_2 production mechanism of fluorescein supramolecular NSs.

duces to $1.96 \mu\text{mol h}^{-1}$ after 15 h. As shown in Fig. 4c, the apparent holes appear on the surface resulted from photocorrosion after the photocatalytic reaction. The XRD pattern presents the samples with no obvious variation after photocatalysis (Fig. 4d). This photocorrosion is very common for many oxides, nitride and sulfides semiconductor photocatalysts, involving ZnO [43,44], CdS [45, 46], $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ [47], TaON [48]; and similar strategies, such as composites with graphene, more suitable sacrificial agent, surface coating protection, will be adopted to enhance photocatalytic stability of supramolecular NSs.

UPS (Ultraviolet photoelectron spectroscopy) is used to determine the HOMO of fluorescein supramolecular NSs (Fig. 5a), which is calculated to be 0.86 eV *versus* normal hydrogen electrode (NHE). The LUMO is thus estimated to be -1.29 eV *versus* NHE from $E_v - E_g$. Fig. 5b shows the possible mechanism of photocatalytic H_2 production. The Pt nanoparticles are reduced by the generated electrons from supramolecular NSs and loaded on the NSs surface. As holes sacrificial agents, oxalic acid can rapidly capture the generated holes. Due to -1.29 eV higher than that of H^+/H_2 (0 V) for LUMO, the generated electrons rapidly transfer to the Pt nanoparticles and have an enough reducing capacity to react with H^+ , producing H_2 on the surface of Pt nanoparticles.

In summary, we developed a metal-free fluorescein supramolecular NSs as a novel organic photocatalyst for H_2 production from water under visible light. The supramolecular NSs were self-assembled *via* recrystallization process, and exhibited superior photocatalytic activity than that of PCN synthesized from urea. Importantly, this is the first report on the H_2 production from water over fluorescein supramolecular NSs under visible light. In addition,

this new material extends the family of metal-free and supramolecular photocatalysts, and may open up new insights into the search of organic photocatalysts.

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tributed to the general discussion and article revision.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting information is available in the online version of the paper.

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荧光素超分子纳米片: 一种可见光分解水产氢的新型有机光催化剂

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摘要 氢能源是未来最理想的清洁能源, 可以利用太阳能和光催化材料分解水获得. 开发廉价、资源丰富、环境友好的光催化材料, 成为近年来能源和环境领域的研究热点. 基于此, 我们报道了一种新型有机光催化材料-不含金属的荧光素超分子纳米片, 其在可见光下显示出高效的光催化分解水产氢活性, 产氢速率接近 $341 \mu\text{mol g}^{-1} \text{h}^{-1}$, 在 $420 \pm 10 \text{ nm}$ 的波段下表观量子效率达到 1.2%. 这是荧光素超分子晶体首次被报道并应用于可见光下分解水产氢, 这一发现丰富了有机和超分子光催化剂的种类.