



## Rapid Communication

## Self-Assembled Peptide Hydrogel With Porphyrin as a Dopant for Enhanced Photocurrent Generation



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## ABSTRACT

Light-harvesting hybrid hydrogel was fabricated based on self-assembly of an aromatic peptide with porphyrin as a dopant for an effective solar-electronic energy conversion. The long-range order assembly of aromatic peptide can act as photoelectron acceptor and conductor to promote the production of photoelectrons by the light antenna porphyrin molecules. In the meanwhile, the doping of porphyrin can effectively reduce the resistance of peptide-based hydrogel, facilitating the transfer of photoelectrons. Photocurrent test result demonstrates the great light response property of the porphyrin/peptide hydrogel with a photoelectron yield as high as  $672 \text{ nA cm}^{-2}$ , which holds great potential for enhanced solar energy conversion.

The green and renewable solar energy has been considered as a secure long-term energy supply to meet the energy shortage challenge in fast-developing human society. In the pursuing of solar energy, great efforts have been devoted to developing highly efficient and stable solar energy conversion systems [1,2]. Numerous light antennas, either artificial dyes [3,4] or natural light-harvesting photosynthetic proteins [5–7], have been applied in solar-to-electrical conversion among which the  $\pi$ -conjugated porphyrins have distinguished themselves as outstanding photoelectron dye for their excellent electrical, optical and catalytic properties [8–10]. The broad absorption features of porphyrins (400–450 nm for Soret band and 500–700 nm for Q bands) guarantee an efficient use of the solar spectrum [11].

However, the solar-to-electrical conversion efficiency of porphyrin-based devices, especially metalloporphyrins based devices are still limited by the fast recombination of photoinduced electron-hole pairs. On the other hand, the poor photostability due to the photobleaching, solvolysis by the solvent and the poor solubility for most of the hydrophobic metalloporphyrin in aqueous environment also cause the gradual loss in their light conversion efficiency [12]. Combining porphyrin and other optoelectronic functional materials to design new nanohybrid architectures seems an ideal solution to the above problems for the well-organized nanoscale architectures often exhibit unique optical and electronic properties. Also, the nanoarchitectures can provide a robust structure for porphyrins and the geometrical constraint imposed by the rigid aggregate framework will make the reactive species more difficult to reach porphyrin molecules and hence improve their photostability [12]. It has been reported that the combination of porphyrin with clay [13], carbon nanotubes [14], titanium based

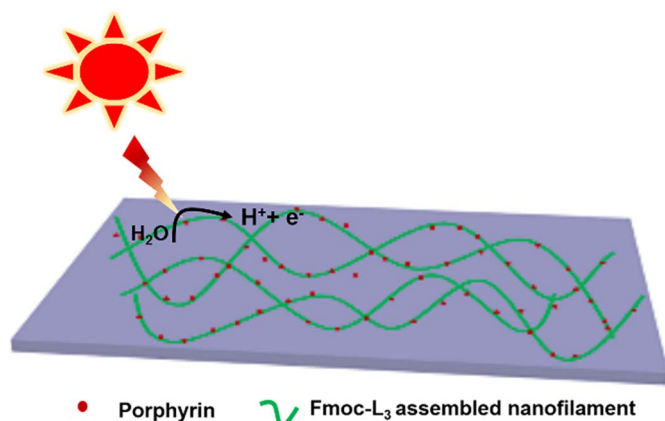
materials [15] and so on to assemble nanoarchitectures can exhibit great solar conversion property.

Short peptides composed of several sequences (di-, tri-) have attracted a lot of interest as building blocks for the construction of various nanoscaled architectures due to their considerable flexibility in molecular design and facile synthetic procedure [16,17]. These nanoarchitectures have been reported to show optical and electric properties comparable to those of conventional semiconductor materials [18]. The easy control over morphologies of assembled nanoarchitectures through the tuning of assembly conditions such as pH, temperature, concentration [19,20] can provide enhanced photoelectron properties due to shape- and size-dependent effects and the collective behavior from the assembled molecules [21–23]. It is predictable that the introduction of aromatic functional group such as Fmoc moiety onto the short peptide molecules can further enhance the photo-electron property of these assembled nanostructures and bring forth the next generation of conducting materials [24,25].

In natural photosynthetic systems, the highly effective solar energy conversion is achieved by the combination of functional pigments and structured proteins forming high-water content complex. The proteins in the complex can bind the pigments in a specific location to ensure the optimal energy conversion and transfer, avoiding self-quenching induced energy loss [26]. Inspired by the natural photosynthetic systems, herein we demonstrate the combination of 5,10,15,20-Tetraphenyl-21H,23H-porphine zinc (TPP-Zn) and aromatic short peptide Fluoromethoxycarbonyl-Leucine-Leucine-Leucine-OMe (Fmoc-L<sub>3</sub>-OMe) to form hydrogel, which is favorable to maintaining and enhancing the physical/chemical properties of the entrapped component [27], for

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**Scheme 1.** Hydrogel made of peptide/porphyrin nanofilament for enhanced photocurrent.

solar energy conversion (Scheme 1 and Fig. S1A). Porphyrin doped in the hydrogel can act as effective light conversion antenna for enhanced photoelectrons productivity and the assembled peptide matrix can play the role of photoelectron acceptor and transfer to promote the charge separation and facilitate the production of the photoelectrons. Besides, the intrinsic hydrophobicity of Fmoc group in peptides can promote the hydrophobic and  $\pi$ - $\pi$  stacking interactions between the fluorenyl moieties and the aromatic rings in porphyrin molecules, which can assist porphyrin to be trapped into the hydrogel and reduce photobleaching induced low photostability, maintaining the light conversion efficiency of porphyrin. Our design to combine porphyrin with bioendogenous peptide can mimic the natural structure of photosynthetic proteins/pigment complex, which could shield light on the fabrication of more stable artificial solar-electric conversion devices with highly efficient solar energy absorbance, transfer and storage.

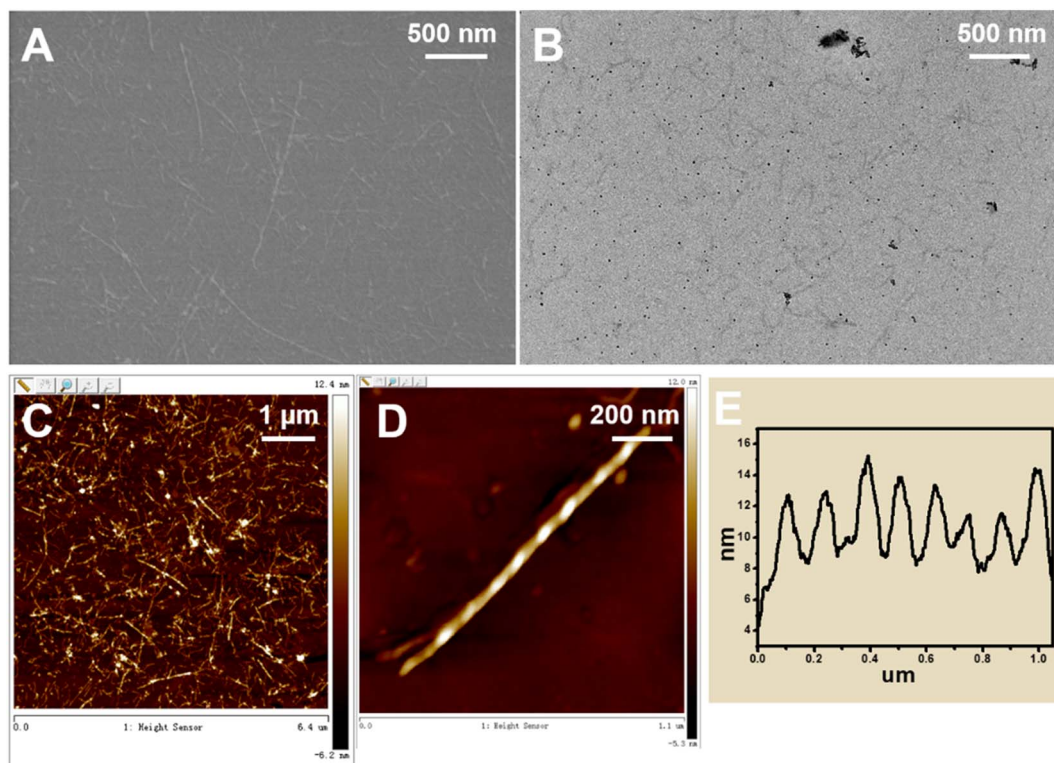
Porphyrin/peptide hybrid hydrogel was prepared under enzyme catalysis (Fig. S1B). The morphology of the hydrogel was characterized

with SEM, TEM and AFM, as shown in Fig. 1. All the images showed that the hydrogel was composed of nanofilaments with a diameter of about 50 nm and length of several hundred nanometers. The enlarged AFM image showed (Fig. 1D) the helical structure of the filament with a helical pitch of about 150 nm.

Fig. 2A showed the FT-IR spectra of the as-prepared hydrogel. The presence of peaks at  $1690\text{ cm}^{-1}$  and  $1638\text{ cm}^{-1}$  demonstrated the formation of  $\beta$ -sheet structure in the filament. The peaks at  $1595\text{ cm}^{-1}$  and  $1540\text{ cm}^{-1}$  can be assigned to the COO symmetrical stretching vibration. This was confirmed by the CD spectra in Fig. 2B in which the signature bond at  $\sim 220\text{ nm}$  could be contributed to the  $\beta$ -sheet type arrangement. The negative Cotton effects at  $304\text{ nm}$  suggested the strong  $\pi$ - $\pi$  stacking interactions between the fluorenyl groups [16,28]. These results suggest that the nanofilament in the hydrogel are probably stabilized by the attractive forces such as  $\beta$ -sheet hydrogen bonds and  $\pi$ - $\pi$  stacking interactions. Interestingly, when increasing the concentration of TPP-Zn in the hydrogel, we could observe an obvious positive peak at  $453\text{ nm}$  and a positive peak at  $493\text{ nm}$ , indicating the chiral assembly of TPP-Zn in the hydrogel. The ordered assembly of peptide and porphyrin is beneficial for the transfer of photoelectrons.

The electronic absorption spectrum of the TPP-Zn doped peptide based hydrogel contains Soret and Q bands peaking at  $432\text{ nm}$  and  $548\text{ nm}$ , respectively (Fig. 2C). The bathochromic shift of the Soret band of TPP-Zn in hydrogel compared to that of porphyrin monomers ( $425\text{ nm}$ ) suggests that TPP-Zn in hydrogel formed J-like aggregates by the aid of Fmoc-L<sub>3</sub>. The absence of splitting of the Q band, in contrast to that of porphyrin monomers, also indicates molecular aggregation of porphyrin in hydrogel.

Fig. 2D showed the WAXS results of the hydrogel. Compared hydrogels with and without TPP-Zn doping, there are no changes in WAXS peaks, demonstrating that the doping of TPP-Zn does not significantly change the assembly structure of peptides. As Fig. 2D showed, there are three peaks with a  $q$  distance ratio of 1:2:3, suggesting the long-range ordered assembly structure within the hydrogel, facilitating the transfer of photoelectrons. The long-range ordered assembly structure could be



**Fig. 1.** Morphology characterization of the hydrogel: A) SEM; B) TEM; C) and D): AFM and E) helical pitch of the filament.

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