Electrodeposited Lamellar Photoconductor Nanohybrids Driven by Peptide Self-Assembly

Manoj K. Manna,^[a] Sushil K. Pandey,^[b] Indrajit Maity,^[a] Shaibal Mukherjee,^{*[b]} and Apurba K. Das^{*[a]}

Aromatic organic molecules serve as optoelectronic materials owing to their intrinsic optical and electronic properties. Herein, self-assembled lamellar nanostructures as photoconductor hybrids, which are obtained from naphthalene-2-methoxycarbonyl (Nmoc)-capped peptide amphiphiles, are described. Hybrid nanostructures are constructed in a controlled manner by an electrochemical deposition technique in combination with the inorganic $Zn(OH)_2$ phase. Inorganic $Zn(OH)_2$ layers turn into semiconductor ZnO layers upon annealing at 150 °C and lamellar nanostructures are formed in a periodic manner. Synergistic effects of hydrogen bonding and π - π stacking interactions of aromatic peptide amphiphiles are the driving force for the formation of self-assembled lamellar nanostructures. Morphological, structural, and optical studies of such lamellar hybrid nanostructures are reported. Photoconduction of these hybrid nanostructures is also examined in detail.

Introduction

Supramolecular chromophoric π -conjugated aromatic systems^[1] are envisioned to serve as active materials in photoelectronic devices, in particular, for photovoltaics.^[2-5] Intrinsic optical and electronic properties of organic molecules are more important for exploitation in device applications.^[6-8] Controlling the self-assembly of π -conjugated aromatic molecules is important because it provides optical, electronic, and optoelectronic behavior. Aromatic capped self-assembly of small organic molecules has drawn great attention in the field of supramolecular electronics.^[9] In general, crystalline silicon-, cadmium-, palladium-, mercury-, and arsenic-based materials are widely used as conducting materials, but these are hazardous, toxic, and harmful in nature.^[10] Therefore, the design and synthesis of biocompatible and eco-friendly materials with desirable properties are crucial for the development of photovoltaics. On-going research into organic materials enriches the area of organoelectronics in the context of photoconducting devices.

The molecular arrangement at the nanolevel controls the properties of self-assembled materials and directs their application in a specific field. The self-assembly of aromatic organic systems with ordered aromatic π - π stacking interactions can enhance the hole conduction or optical properties.^[11] Further-

| [a] | M. K. Manna, I. Maity, Dr. A. K. Das Department of Chemistry, Indian Institute of Technology Indore Indore (India) E-mail: apurba.das@iiti.ac.in |
|-----|--|
| [b] | S. K. Pandey, Dr. S. Mukherjee Hybrid Nanodevice Research Group (HNRG) Discipline of Electrical Engineering Indian Institute of Technology Indore Indore (India) E-mail: shaibal@iiti.ac.in |
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more, the π - π stacking of the aromatic chromophoric organic system depends on the state of matter and aggregation. Thus, our research is focused on the synthesis of organic–inorganic hybrid materials with improved optoelectronic behavior for the application of photovoltaics.

Recently, various hybrid nanostructures have been synthesized by several chemical methods, including agua chemical,^[12] sol-gel processing,^[13] and hydrothermal techniques.^[14] Some advanced gas-phase technologies, such as vacuum evaporation,^[15] sputtering,^[16] and chemical vapor deposition (CVD) techniques,^[17,18] are also used to fabricate inorganic-organic hybrid materials. These techniques provide structural purity and homogeneity of materials, but require expensive facilities and high-energy providers. Electrochemical deposition is an economically cheap, powerful, bottom-up approach for the production of highly ordered lamellar^[19-22] organic-inorganic hybrid nanostructured films. The nanostructural morphology of electrodeposited films are strongly influenced by electrochemical parameters, including solution concentration,^[23] bath temperature,^[24] electrode potential,^[25] and the chemical structure of the surfactants. Previously, the anionic surfactant sodium dodecyl sulfate (SDS)^[26-28] was widely used as a template for the deposition of ZnO. Currently, various ionic surfactants containing conjugated aromatic segments^[29-30] (dyes) are also used for further development of organoelectronic materials. Recently, Qin et al. described the effect of surfactant on the structures and properties of ZnO films prepared by the electrodeposition technique.^[31] Stupp et al. reported highly ordered nanostructured organic/inorganic lamellar photoconductor hybrids.^[29] They designed various organic surfactants for the development of electronically active materials. Although considerable studies have been performed on hybrid nanostructures comprised of organic π -conjugated systems,^[32,33] electrochemi-



cal deposition of peptide-based hybrid materials has not been explored. Peptides are well known in the construction of various self-assembled nanoarchitectures.^[34, 35] Lim et al. developed self-assembling peptide/inorganic hybrid materials with specific molecular recognition capabilities.^[36, 37] Peptide/metal nanoparticles as efficient catalysts were also reported for the removal of N-terminal protecting groups^[38] and C-C coupling reactions in aerobic conditions.[39] Peptide self-assembly is influenced by various noncovalent interactions, such as hydrogenbonding, hydrophobic, $\pi - \pi$ stacking, and electrostatic interactions.^[40-42]

Herein, we report a strategy for the synthesis of nanoscale lamellar peptide-ZnO hybrid nanostructures for the development of active electronic materials. We have synthesized aromatnaphthalene-2-methoxycaric bonyl (Nmoc)-capped small peptides containing a conjugated naphthalene moiety as the organic component of the hybrid material. The self-assembled organic-inorganic hybrid composite system can modify the conduction mechanism of current carriers, and thereby, influence optoelectronic behavior the through the extent of π - π stacking interactions. The electrons can jump from excited-state aromatic naphthalene moieties of peptides to the ZnO semiconductors.^[43]

Results and Discussion

Prior to electrochemical deposition of organic–inorganic hybrid materials, we synthesized two aromatic Nmoc-capped dipeptides Nmoc-FF-OH (1; F = phenylalanine) and Nmoc-YF-OH (2; Y = tyrosine; Figure 1). All synthetic



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Figure 1. a) Molecular structure of the designed peptide amphiphiles and $Zn(NO_3)_2$ precursor used for electrochemical deposition. b) Digital photograph of the electrodeposited annealed hybrid thin film on an indium tin oxide (ITO)-coated quartz glass substrate. c) Field-emission scanning electron microscopy (FESEM) image of the electrodeposited hybrid film with peptide **2**. d) Schematic illustration of alternate ZnO and peptide layers in the lamellar network structures. e) Schematic presentation of the peptide assembly within the ZnO inorganic phases. The aromatic π - π stacking interactions among the aromatic Nmoc moieties and hydrogen bonding of the peptide amphiphiles are the driving force for the evolution of lamellar nanostructures. Upon excitation with light, excited electrons move through the aromatic Nmoc groups of the peptide amphiphiles into inorganic ZnO lattices and the flow of current produces a photocurrent.



Scheme 1. Solution-phase synthetic procedures for the preparation of peptides Nmoc-FF-OH (1) and Nmoc-YF-OH (2).

aromatic capped peptides used herein are shown in Scheme 1. Peptides with carboxylic acid groups at the end can bind with zinc ions as the inorganic segment and the backbone amide bonds can strongly interact through hydrogen bonds. Herein, we utilize the self-assembly process of peptide molecules to synthesize lamellar hybrids in which nitrogen-capped naphtha-

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Scheme 2. Peptide design for the fabrication of photoconductor nanohybrids.

lene moieties strongly interact through $\pi - \pi$ stacking interactions (Scheme 2). Electrochemical deposition is an effective technique to design organic-inorganic hybrid materials. Lamellar thin films were grown on the surface of electrodes; this enabled their direct integration into functional photoconductor devices. The organic-inorganic hybrid nanostructures were grown as self-assembling architectures on the working electrodes through cathodic deposition from a solution of $Zn(NO_3)_2$ and peptides in a mixture of H₂O/



Figure 2. FTIR spectra of a) annealed hybrid ZnO/1 and peptide 1, and b) annealed hybrid ZnO/2 with peptide 2.

DMSO (1:1). The experimental temperature was set at $80 \,^{\circ}$ C, which was compatible with the organic molecules. The electrochemical deposition follows the electrochemical reaction given by Equation (1).^[44]

$$\frac{NO_{3}^{-} + H_{2}O + 2e^{-} \rightarrow NO_{2}^{-} + 2OH^{-}}{Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_{2}}$$
(1)

Increasing the concentration of OH^- at the working electrode increases the local pH and facilitates the cathodic deposition of $Zn(OH)_{2^{\prime}}$, which is insulating in nature. Upon annealing at 150 °C, the insulator $Zn(OH)_2$ turns into the semiconductor material ZnO [Eq. (2)].

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$$
 (2)

Two semiconducting organic–inorganic lamellar thin films were constructed by using an electrochemical deposition technique by exploiting supramolecular ordering of two different dipeptides containing optoelectronic functionalities. Peptidebased thin films with semiconducting ZnO hybrids were prepared upon annealing electrodeposited peptide– $Zn(OH)_2$ thin films at 150 °C.

FTIR spectroscopy was used to understand the structural information and interactions between the organic and inorganic ganic–inorganic hybrid thin film, which reveals the extensive hydrogen-bonding interactions between the peptide and inorganic layer.^[45] Furthermore, the carbonyl stretching frequency of the carboxylic acid at $\tilde{v} = 1716 \text{ cm}^{-1}$ in native peptide **1** disappears in the ZnO hybrid material owing to strong covalent bonding between the organic and inorganic layers.^[46] For native peptide **2**, the hydroxyl group of the acid appears at $\tilde{v} = 3412 \text{ cm}^{-1}$ with a characteristic carbonyl stretching band at $\tilde{v} = 1694 \text{ cm}^{-1}$. The band for the hydroxyl groups of the acid functionality is broadened and shifted to $\tilde{v} = 3437 \text{ cm}^{-1}$ for the thin film of hybrid ZnO/**2**; this provides evidence of hydrogenbonding interactions between the peptide amphiphiles and the inorganic ZnO layer.^[47,48]

SEM was used to characterize the self-assembled, nanostructured, Nmoc-capped peptide surfactants and ZnO thin films. The morphology of the ZnO thin film without the peptide scaffold was also investigated as a control sample to understand the structural effect of peptides in organic–inorganic hybrid materials. The SEM image shows a hexagonal microrod-like structure (Figure S1 in the Supporting Information). The diameter of the hexagonal ZnO microrods is in the range of 0.7– 1.6 μ m. Interestingly, the interaction of peptides with ZnO completely changes the morphology of the organic–inorganic hybrid thin films. The SEM images show lamellar nanostructures all over the thin films for hybrid samples **1** and **2**

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phases in the hybrid materials. In FTIR spectroscopy, the broad region of $\tilde{v} = 3690-3000 \text{ cm}^{-1}$ is very important for understanding the hydrogen-bonding interactions of amide and hydroxyl groups of acids and alcohols. FTIR spectroscopy shows a relatively narrow band at $\tilde{v} = 3306 \text{ cm}^{-1}$ (Figure 2), which appears for peptide 1, whereas a significant band appears at $\tilde{v} = 3425 \text{ cm}^{-1}$ in the thin film of ZnO hybrid 1. This band is broadened and shifted in the or-





Figure 3. FESEM images of the top view of annealed hybrids 1 (a) and 2 (b), as well as cross-sectional images of hybrids 1 (c) and 2 (d).

(Figure 3).^[20] The SEM image for ZnO hybrid thin film 1 based on 1 shows that the lamellar sheets are deposited across the substrate. The nanostructured sheets are oriented vertically and laterally in a random fashion. The 2D sheets are randomly stacked with each other. The cross-sectional SEM image shows the homogeneous thickness of the deposited peptide-ZnO film with an average thickness of 1.25 µm. The hybrid ZnO thin film based on 2 shows a plate-like morphology that has grown homogeneously by electrochemical deposition across the entire substrate. The cross-sectional SEM image reveals that the plate-like nanostructures are stacked through layer by layer deposition and form a lamellar thin film with an average thickness of 1.82 μ m. Energy-dispersive X-ray spectroscopy (EDS) is used for elemental composition analysis of electrodeposited hybrid materials (Figure S2 in the Supporting Information). The presence of zinc, oxygen, and carbon corresponds to the organic-inorganic hybrid films.

Peptide/ZnO hybrid thin films were characterized by using UV/Vis spectroscopy before and after annealing (Figure 4). The UV/Vis spectra clearly indicate the existence of both organic and inorganic phases in the electrodeposited thin films. The UV/Vis spectroscopy results show an absorbance band at $\lambda =$

370 nm for $Zn(OH)_2/1$ hybrid film before thermal treatment. The $Zn(OH)_2/1$ hybrid film turns into the ZnO/1 film upon thermal annealing at 150 °C. For the annealed film, the UV/Vis spectroscopy results display a well-defined absorbance band at $\lambda =$ 266 nm and a characteristic absorbance maximum at $\lambda =$ 380 nm. The appearance of the absorbance band at $\lambda =$ 266 nm is characteristic of the naphthalene double ring, which clearly signifies the organic phase in the hybrid material.^[49] The other absorbance band at $\lambda = 380$ nm results from the electronic transition between the ZnO band gap for the hybrid material of the ZnO/1 film. The unannealed hybrid thin film of $Zn(OH)_2/2$ shows an absorbance band at $\lambda = 365$ nm, whereas the annealed hybrid thin film of ZnO/2 demonstrates the characteristic band at $\lambda = 265$ nm and a broad band from $\lambda = 310$ to 440 nm with a maximum at $\lambda = 370$ nm. The results clearly indicate the coexistence of ZnO and peptides in the thin film for the hybrid materials. The hybrid films that consist of nanostructures grown from the peptides present some differences in absorption at higher wavelengths; these are related to nanostructures grown with different peptide sequences.

In addition, tuning of the Nmoc-capped peptide sequence influences the lamellar structure of the hybrid materials. The peptide/ZnO hybrid films were characterized by photoluminescence (PL) spectroscopy to understand the functional role of peptides in the lamellar architectures for photodetection (Figure 5). The PL spectrum for the unannealed $Zn(OH)_2/1$ thin film showed a sharp band at $\lambda = 367$ nm and a broad band at $\lambda =$ 420 nm. These bands resulted from the binding of the peptides to Zn²⁺. The PL spectra of the hybrids clearly distinguish ZnO (3.16 eV) nanowire arrays fabricated from a solution of Zn(NO₃)₂ by electrodeposition (Figure S3 in the Supporting Information). After annealing, the insulator Zn(OH)₂ phase turns into the conducting ZnO phase and the PL shows a huge change in the optical properties for the same film. For the annealed ZnO/1 thin film, the PL spectrum shows a PL guenching that is due to the transfer of electrons from the excited state of 1 into the ZnO lattice. Unannealed Zn(OH)₂/2 thin film exhibited a broad band in the range of $\lambda = 370-460$ nm in the PL spectrum, owing to strong binding with the peptides and Zn^{2+} . PL quenching is also observed in the case of the ZnO/2 hybrid represented in Figure 4.^[29]



Figure 4. Absorbance spectra of unannealed and annealed hybrids of a) 1 and b) 2.

technique to achieve structural information about the lamellar architectures of hybrid films and crystal lattices of inorganic materials. The ZnO thin film without peptide support shows several characteristic peaks for the crystal lattices of ZnO hexagonal structures. A series of peaks corresponding to $2\theta = 31.60$, 34.19, and 36.13° are attributed to the (100), (002), and (101) planes of the ZnO nanocrystal (Figure S4 in the Supporting Information). The formation of the lamellar

An XRD study is a fundamental

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Figure 5. PL spectra of hybrids 1 (a) and 2 (b) before and after annealing recorded with $\lambda = 325$ nm laser excitation.



Figure 6. Powder XRD patterns of hybrid thin films a) ZnO/1 and b) ZnO/2. Powder XRD peak patterns (001) and (001)* refer to lamellar ordering in the hybrid material; (100), (002), (101) indicate lattice planes of the wurtzite ZnO crystal.

structure is also supported by the XRD study. The presence of four characteristic d spacings indicates four distinct stable bilayer arrangements of the thin film of **1**. An X-ray scattering study confirmed the ordered lamellar arrangement with d spacings of 2.3 and 1.65 nm corresponding to (001) and (001)* reflections (Figure 6). Two types of lamellar arrangement are

attributed to the bilayer of peptides in lamellar hybrid 1. Moreover, two distinct peaks corresponding to $2\theta = 31.80$ and 34.49° are attributed to the (100) and (002) planes of the ZnO hexagonal nanoplates. In the case of lamellar hybrid 2, the XRD peak at $2\theta = 3.7^{\circ}$ corresponds to a d spacing of 2.3 nm, which is close to the bilayer of peptide 2. For the peptide-supported hybrid thin film, the crystal planes of ZnO are slightly shifted relative to those of the thin film without a peptide support; this results from interactions of the peptide molecules with the ZnO planes.^[50–52]

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The optoelectronic properties of the organic-inorganic lamellar hybrids were investigated. Current-voltage (I-V) measurements the unannealed Zn(OH)₂/ of 1 film showed no significant current (Figure 7). The electrodeposited hybrid film acts as an insulator before annealing at 150 °C. After annealing, the insulator Zn(OH)₂ is converted into semiconductor ZnO. The conductivity is observed for the ZnO/1 film even under dark conditions (Figure S5 in the Sup-

porting Information). The *I–V* curve shows that the hybrid material can act as a photoconductor upon excitation with a λ = 325 nm laser operating in continuous wave (CW) mode. The widely understood mechanism for the photocarrier generation process in organic–inorganic hybrids is exciton formation in the organic segment under irradiation with photons and sub-



Figure 7. *I–V* characteristics of deposited a) hybrid films of peptide 1: unannealed hybrid (blue), the annealed hybrid under dark conditions (black), and the annealed hybrid under UV light (red) irradiation at $\lambda = 325$ nm; and b) hybrid films of peptide 2: unannealed hybrid (blue), annealed hybrid under dark conditions (black), and the annealed hybrid under UV light (red) irradiation at $\lambda = 325$ nm.

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sequent dissociation for the transfer of the electrons into the ZnO region. The current of the hybrid material increases owing to the presence of aromatic stacked peptide gallery under UV light. The photocurrent of annealed hybrids ZnO/1 and ZnO/2 is measured under UV light exposure of 20 mW cm⁻². The photosensitive nature of such a nanohybrid structure can be quantified by using Equation (3):

$$P = (I_{\text{light}} - I_{\text{dark}})/I_{\text{dark}}$$
(3)

in which l_{iight} is the photocurrent and l_{dark} is the dark current. The photosensitivity of hybrid ZnO/1 is 0.12 at 2 V measured at room temperature. For the ZnO/2-based thin film, the measured photosensitivity is comparatively less than that of hybrid ZnO/1. The photosensitivity of the annealed ZnO/2 film is 0.06 at 2 V. At room temperature, the unannealed Zn(OH)₂/2 thin film behaves as an insulator (Figure 7). The change in voltage does not allow the current to pass throughout the circuit. After annealing at 150 °C, the insulator Zn(OH)₂/2 thin film turns into the semiconductor ZnO/2 thin film, and shows its optoelectronic properties upon changing the optical conditions from dark to UV light (Figure 7). The *I–V* measurement study of such peptide-based hybrid materials shows that such materials can be efficiently used as an optoelectronic photoconducting material.

Conclusion

We developed peptide-ZnO-based semiconductor lamellar nanostructures through electrochemical deposition. All electrochemically deposited Nmoc-capped aromatic dipeptide-ZnObased hybrid lamellar nanostructures show optoelectronic behavior. FTIR data clearly suggested interactions of the peptide motifs with the ZnO inorganic phase. The acid functionalities of aromatic dipeptides were anchored with inorganic ZnO layers. UV/Vis and PL spectroscopy revealed the optoelectronic properties of peptide-based ZnO thin films. Aromatic dipeptides self-assembled through hydrogen bonding and $\pi-\pi$ stacking interactions inside the lamellar nanostructures. The introduction of peptide self-assembly successfully established the hybrid materials as good conducting materials. The PL and UV/ Vis measurement studies showed good optoelectronic properties of these materials. The I-V characteristics of these hybrids both under dark and light illumination indicated that the conductivity of these hybrid nanostructure materials increased owing to the presence of the photon-absorbing active self-assembled peptides. This investigation could play a pioneering role in inspiring the further development of peptide-based hybrid optoelectronic materials.

Experimental Section

Materials and characterization

All reagents and chemicals were obtained commercially. Reagents were distilled from appropriate drying agents prior to use. Naph-thalene-2-methyloxychloroformate (3), Nmoc-Phe-OH (4), and

Nmoc-Tyr-OH (5) were prepared according to procedures reported in the literature.^[49,53,54] Nmoc-Phe-Phe-OMe (6), Nmoc-Tyr-Phe-OMe (7), Nmoc-Phe-Phe-OH (1), and Nmoc-Tyr-Phe-OH (2) were synthesized according to the following procedures.

The general procedures used for peptide coupling are as follows: A solution of 4 (1.29 g, 3.69 mmol) and HOBt (0.56 g, 3.7 mmol) was stirred in DMF (2 mL). A neutralized solution of H₂N-Phe-OMe was extracted from its corresponding hydrochloride salt and concentrated for addition to the reaction mixture followed by DIPC (0.5126 g, 3.7 mmol) at 0°C. The mixture was allowed to stir at room temperature for 12 h. The reaction mixture was diluted with ethyl acetate and the organic layer was washed with $1 \times HCl$ (2× 30 mL), brine, $1 \times Na_2CO_3$ (3×30 mL), and again with brine. The organic layer was dried over Na₂SO₄ and evaporated under vacuum to yield a white solid. Purification of 6 was performed by column chromatography on silica gel (100-200 mesh) with ethyl acetate/ toluene (1:1) as the eluent. A solution of 6 (1.70 g, 3.42 mmol) in dry MeOH (100 mL) was allowed to react with a 2 N solution of NaOH. The progress of the reaction was monitored by TLC. The reaction mixture was stirred up to 6 h. Then, methanol was removed under vacuum. The residue was dissolved in water (100 mL) and washed with diethyl ether (2×20 mL). Then, the pH of the aqueous layer was adjusted to 2 by using $2 \, \text{\tiny N}$ HCl and extracted with ethyl acetate (3×30 mL). The ethyl acetate layer was dried over anhydrous sodium sulfate and evaporated under vacuum to yield 1 as a white solid and used further without purification. Compounds 7 and 2 were also synthesized accordingly.

All NMR spectra were recorded on a Bruker AV 400 MHz spectrometer. Compound concentrations were in the range of 5– 10 mmol L⁻¹ in (CD₃)₂SO and CDCl₃. Mass spectra were recorded on a Bruker micrOTOF-Q II mass spectrometer by positive mode electrospray ionization. All reported FTIR spectra were recorded by using a Bruker (Tensor 27) FTIR spectrophotometer. For the SEM study, electrodeposited films were coated with gold. Then, the micrograps were recorded on a field-gun scanning electron microscope (Jeol Scanning Microscope-JSM-7600F). The XRD measurements were performed by using a Bruker D8 Advance X-ray diffractometer. The X-rays were produced by using a sealed tube and the wavelength of the X-ray was $\lambda = 0.154$ nm (Cu_{Ka}). The X-rays were detected by using a fast counting detector based on silicon strip technology (Bruker LynxEye detector).

Nmoc-Phe¹-Phe²-OMe (6)

Yield = 1.7122 g (3.47 mmol, 90.82%); ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, J = 8.72 Hz, 2H), 7.71 (s, 1H), 7.43 (dd, J = 3.38, 3.48 Hz, 2H), 7.40 (d, J = 8.52 Hz, 2H), 7.19 (m, 5H; Phe¹), 7.12 (m, 5H; Phe²), 6.89 (d, J = 5.52 Hz, 1H; NH of Phe¹), 6.12 (d, J = 7.28 Hz, 1H; NH of Phe²), 5.17 (s, 2H), 4.60 (m, 1H; C^{\alpha}H of Phe¹), 4.34 (m, 1H; C^{\alpha}H of Phe²), 3.59 (s, 3H; -OCH₃), 3.01 (d, 1H; C^{\beta}H of Phe¹), 2.98 (d, 1H, J = 5.76 Hz; C^{\beta}H of Phe¹), 2.94 (d, 1H, J = 6.04 Hz; C^{\beta}H of Phe²), 2.91 ppm (d, 1H, J = 6.04 Hz; C^{\beta}H of Phe²); HRMS (ESI): *m/z* calcd for C₃₁H₃₀N₂O₅Na [*M*+Na]⁺: 533.2052; found: 533.1974.

Nmoc-Phe¹-Phe²-OH (1)

Yield = 1.50 g (3.02 mmol, 90.91%); ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.30 (d, *J*=7.52, 1H; NH of Phe¹), 7.37 (d, *J*=8.28 Hz, 1H; NH of Phe²), 7.89 (t, 4H), 7.77 (s, 1H), 7.51 (d, 2H), 7.24 (m, 10H), 5.09 (s, 2H), 4.47 (m, 1H; C^{\alpha}H of Phe¹), 4.30 (m, 1H; C^{\alpha}H of Phe²), 3.10 (dd, *J*=4.52 Hz, 2H; C^{\beta}H of Phe¹), 2.94 ppm (d, 2H; C^{\beta}H of Phe²); ¹³C NMR (100 MHz, [D₆]DMSO): δ = 178.0, 176.8, 161.0, 143.3, 142.6,

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139.8, 137.9, 137.7, 134.4, 133.4, 133.2, 133.1, 132.9, 132.8, 131.7, 131.5, 131.4, 131.3, 131.2, 130.8, 70.5, 61.2, 58.7, 42.6, 41.9 ppm; HRMS (ESI): m/z calcd for $C_{30}H_{28}N_2O_5Na$ $[M+Na]^+$: 519.1896; found: 519.3244.

Nmoc-Tyr-Phe-OMe (7)

Yield = 0.50 g (0.95 mmol, 63.29%); ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, 2 H, *J* = 4.2 Hz), 7.79 (s, 1 H), 7.49 (dd, *J* = 3.84, 3.52 Hz), 7.43 (d, *J* = 8.04 Hz, 1 H; NH of Tyr), 7.21 (t, 3 H), 7.01 (d, *J* = 9.28 Hz, 2 H), 6.98 (d, *J* = 6.76 Hz, 2 H; Tyr), 6.68 (d, *J* = 8.28 Hz, 2 H; Tyr), 6.20 (d, *J* = 7.52 Hz, 1 H; NH of Phe), 5.24 (s, 2 H), 4.75 (m, 1 H; C^{\alpha}H of Tyr), 4.33 (m, 1 H; C^{\alpha}H of Phe), 3.66 (s, 3 H), 3.05 (dd, *J* = 5.52, 6 Hz, 2 H; C^{\beta}H of Tyr), 2.96 ppm (d, *J* = 6.76 Hz, 2 H; C^{\beta}H of Phe); HRMS (ESI): *m/z* calcd for C₃₁H₃₀N₂O₆Na [*M*+Na]⁺: 549.2002; found: 549.18564.

Nmoc-Tyr-Phe-OH (2)

Yield = 0.40 g (0.78 mmol, 81.63%); ¹H NMR (400 MHz, [D₆]DMSO): δ = 12.77 (s, 1H; -COO*H*), 9.19 (d, 1H; NH of Phe), 8.24 (d, 1H; NH of Tyr), 7.89 (dd, *J*=2.76, 5.52 Hz, 2H), 7.79 (s, 1H), 7.52 (d, 2H), 7.42 (d, 2H) 7.26 (m, 5H), 7.06 (d, 2H; Tyr), 6.65 (d, 2H; Tyr), 5.12 (s, 2H), 4.47 (m, 1H; C^GH of Tyr), 4.22 (m, 1H; C^GH of Phe), 3.34 (s, 3H), 3.10 (d, *J*=14.04 Hz, 1H; C^βH of Tyr), 2.96 (d, *J*=5.52 Hz, 1H; C^βH of Phe), 2.87(d, *J*=13.8 Hz, 1H; C^βH of Tyr), 2.60 ppm (d, 1H; C^βH of Phe); ¹³C NMR (100 MHz, [D₆]DMSO): δ =172.7, 171.7, 155.7, 137.4, 134.6, 132.7, 132.4, 130.1, 129.1, 128.1, 127.9, 127.7, 127.5, 126.4, 126.3, 126.0, 125.8, 125.4, 114.8, 65.2, 56.2, 53.5, 53.4, 36.7 ppm; HRMS (ESI): *m/z* calcd for C₃₀H₂₈N₂O₆Na [*M*+Na]⁺: 535.1845; found: 535.0381.

PL and I-V measurements

A DongWoo Optron PL setup, affixed with a 20 mW CW He–Cd laser (excitation wavelength = 325 nm, TEM00 mode), 320 mm and 150 mm focal length monochromators, chopper, lock-in amplifier, and a photomultiplier tube (PMT) detector, was deployed to conduct optical studies of annealed and unannealed hybrid films. The UV light He–Cd laser (excitation wavelength = 325 nm, TEM00 mode) was used to measure the photosensitivity of the hybrid materials. The current between the two contacts was measured by using a Keithley source meter (Model 2612A).

Dual ion beam sputtering deposition (DIBSD)

The Elettrorava DIBSD system was deployed to deposit ITO thin films (200 nm) on quartz glass substrates. The angle between the sputtering beam and sputtering target was fixed at 45° off-normal, while the angle between the assist ion beam and substrate was maintained at 60°. Before being inserted into the DIBSD growth chamber, quartz glass substrates were rinsed thoroughly with trichloroethylene, acetone, isopropanol, and deionized (DI) water and subsequently purged with nitrogen gas (purity 99.999%) to remove dust particles and various organic contaminants. Prior to actual film deposition, the assist source was turned on for 10 min to perform substrate precleaning by argon ion bombardment. During material growth, the assist ion beam, consisting of a plasma of argon ions, helped in the reduction of columnar growth, and thereby, enhanced growth uniformity and film adhesion to the substrate. The discharge voltage and current of the assist ion source was kept constant at 70 V and 600 mA, respectively, during ITO thin-film deposition by using a 4N (99.99%) pure 4in-diameter ITO target mounted on a water-cooled target holder inside the DIBSD system chamber. The background pressure inside the process chamber was maintained at approximately 1×10^{-8} mbar, whereas the working pressure during film growth was kept at 3.26×10^{-4} mbar.

Electrochemical synthesis

Electrochemical synthesis was performed in 24 mL of a solution (1:1 (v/v) DMSO/water) of $0.04 \text{ M} \text{ Zn}(\text{NO}_3)_2$ with peptide amphiphile (10–12 mg) in a 100 mL cell vial by using a three-electrode setup (Autolab PG STAT128N) with a Zn counter electrode (Alfa Aesar 99.9997%) and Ag/AgCl reference electrode (KCl Autolab 6.0726.107). Water was required for the reduction of NO₃⁻ to generate OH⁻, and DMSO was added for surfactant solubility. Working electrode ITO substrates were placed upright in the cell and deposition was achieved potentiostatically at -0.9 V for 16 to 24 h, depending on growth time, under constant stirring at 80°C in water bath. Deposited films were rinsed with DI water and ethanol and dried with dry nitrogen. Finally, thin films were annealed at 150°C.

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Keywords: electrochemistry • nanostructures • organic– inorganic hybrid composites • peptides • self-assembly

- [1] S. S. Babu, V. K. Praveen, A. Ajayaghosh, Chem. Rev. 2014, 114, 1973– 2129.
- [2] D. Herrmann, S. Niesar, C. Scharsich, A. Kohler, M. Stutzmann, E. Riedle, J. Am. Chem. Soc. 2011, 133, 18220–18233.
- [3] J. Huang, Z. Yin, Q. Zheng, Applications Energy Environ. Sci. 2011, 4, 3861–3877.
- [4] H. Dong, H. Zhu, Q. Meng, X. Gong, W. Hu, Chem. Soc. Rev. 2012, 41, 1754–1808.
- [5] M. He, F. Qiu, Z. Lin, J. Phys. Chem. Lett. 2013, 4, 1788-1796.
- [6] S. Wu, Q. Tai, F. Yan, J. Phys. Chem. C 2010, 114, 6197-6200.
- [7] C.-H. Kim, S.-H. Cha, S. C. Kim, M. Song, J. Lee, W. S. Shin, S.-J. Moon, J. H. Bahng, N. A. Kotov, S.-H. Jin, ACS Nano 2011, 5, 3319–3325.
- [8] C.-L. Lin, M.-Y. Yeh, C.-H. Chen, S. Sudhakar, S.-J. Luo, Y.-C. Hsu, C.-Y. Huang, K.-C. Ho, T.-Y. Luh, *Chem. Mater.* **2006**, *18*, 4157 – 4162.
- [9] H. Xu, A. K. Das, M. Horie, M. S. Shaik, A. M. Smith, Y. Luo, X. Lu, R. Collins, S. Y. Liem, A. Song, P. L. A. Popelier, M. L. Turner, P. Xiao, I. A. Kinloch, R. V. Ulijn, *Nanoscale* **2010**, *2*, 960–966.
- [10] S. A. Jewett, A. Ivanisevic, Acc. Chem. Res. 2012, 45, 1451-1459.
- [11] A. P. H. J. Schenning, E. W. Meijer, Chem. Commun. 2005, 3245-3258.
- [12] N. Bano, S. Zaman, A. Zainelabdin, S. Hussain, I. Hussain, O. Nur, M. Willander, J. Appl. Phys. 2010, 108, 043103.
- [13] J. Liu, J. C. Berg, J. Mater. Chem. 2007, 17, 4430-4435.
- [14] H. Yan, Z. Yu, K. Lu, Y. Zhang, Z. Wei, Small 2011, 7, 3472-3478.
- [15] L. Wang, M.-H. Yoon, A. Facchetti, T. J. Marks, Adv. Mater. 2007, 19, 3252–3256.
- [16] M. Sessolo, H. J. Bolink, Adv. Mater. 2011, 23, 1829-1845.

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[17] K.-H. Yoon, K.-S. Han, M.-M. Sung, Nanoscale Res. Lett. 2012, 7, 71.



- [18] M. Karaman, S. E. Kooi, K. K. Gleason, Chem. Mater. 2008, 20, 2262– 2267.
- [19] C. J. Bruns, D. J. Herman, J. B. Minuzzo, J. A. Lehrman, S. I. Stupp, Chem. Mater. 2013, 25, 4330-4339.
- [20] D. J. Herman, J. E. Goldberger, S. Chao, D. T. Martin, S. I. Stupp, ACS Nano 2011, 5, 565-573.
- [21] B. P. Pichon, A. Mezy, J.-C. Tedenac, D. Tichit, C. A. Gerardin, New J. Chem. 2009, 33, 2350-2354.
- [22] Y. Tan, S. Srinivasan, K.-S. Choi, J. Am. Chem. Soc. 2005, 127, 3596-3604.
- [23] L. Xu, Y. Guo, Q. Liao, J. Zhang, D. Xu, J. Phys. Chem. B 2005, 109, 13519–13522.
- [24] S. Otani, J. Katayama, H. Umemoto, M. Matsuoka, J. Electrochem. Soc. 2006, 153, C551-C566.
- [25] M. Izaki, T. Omi, Appl. Phys. Lett. 1996, 68, 2439-2440.
- [26] K.-S. Choi, H. C. Lichtenegger, G. D. Stucky, J. Am. Chem. Soc. 2002, 124, 12402 – 12403.
- [27] H.-Y. Jing, X.-L. Li, Y. Lu, Z.-H. Mai, M. Li, J. Phys. Chem. B 2005, 109, 2881–2884.
- [28] E. M. P. Steinmiller, K.-S. Choi, Langmuir 2007, 23, 12710-12715.
- [29] M. Sofos, J. Goldberger, D. A. Stone, J. E. Allen, Q. Ma, D. J. Herman, W.-W. Tsai, L. J. Lauhon, S. I. Stupp, *Nat. Mater.* **2009**, *8*, 68–75.
- [30] T. Yoshida, J. Zhang, D. Komatsu, S. Sawatani, H. Minoura, T. Pauporte, D. Linkot, T. Oekermann, D. Schlettwein, H. Tada, D. Wohrle, K. Funabiki, M. Matsui, H. Miura, H. Yanagi, *Adv. Funct. Mater.* **2009**, *19*, 17–43.
- [31] X. Qin, G. Shao, L. Zhao, Mater. Sci. Eng. B 2012, 177, 1678-1681.
- [32] S. I. Stupp, L. C. Palmer, Chem. Mater. 2014, 26, 507-518.
- [33] P. M. Beaujuge, J. M. J. Frechet, J. Am. Chem. Soc. 2011, 133, 20009– 20029.
- [34] B. D. Briggs, M. R. Knecht, J. Phys. Chem. Lett. 2012, 3, 405-418.
- [35] R. Huang, W. Qi, R. Su, J. Zhao, Z. He, Soft Matter 2011, 7, 6418-6421.
- [36] W. J. Jeong, S. J. Choi, J. S. Choi, Y. B. Lim, ACS Nano 2013, 7, 6850– 6857.

[37] B. Kim, S. J. Choi, S. H. Han, K. Y. Choi, Y. B. Lim, Chem. Commun. 2013, 49, 7617-7619.

Full Papers

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- [38] I. Maity, M. K. Manna, D. B. Rasale, A. K. Das, ChemPlusChem 2014, 79, 413–420.
- [39] I. Maity, D. B. Rasale, A. K. Das, RSC Adv. 2014, 4, 2984–2988.
- [40] X. Yan, Y. Cui, Q. He, K. Wang, J. Li, *Chem. Mater.* **2008**, *20*, 1522–1526.
- [41] L. Chen, S. Revel, K. Morris, L. C. Serpell, D. J. Adams, *Langmuir* 2010, 26, 13466–13471.
- [42] I. Maity, D. B. Rasale, A. K. Das, Soft Matter 2012, 8, 5301-5308.
- [43] B. R. Saunders, M. L. Turner, Adv. Colloid Interface Sci. 2008, 138, 1-23.
- [44] J. Lee, Y. Tak, *Electrochem. Solid-State Lett.* **2001**, *4*, C63–C65.
- [45] J. Rouhi, S. Mahmud, N. Naderi, C. R. Ooi, M. R. Mahmood, Nanoscale Res. Lett. 2013, 8, 364.
- [46] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, M. Gratzel, *Nat. Chem.* 2014, 6, 242–247.
- [47] S. Ogata, H. Tagaya, M. Karasu, J. I. Kadokawa, J. Mater. Chem. 2000, 10, 321-327.
- [48] S. Inoue, S. Fujihara, Inorg. Chem. 2011, 50, 3605-3612.
- [49] D. B. Rasale, I. Maity, A. K. Das, Chem. Commun. 2014, 50, 8685-8688.
- [50] B. P. Pichon, C. Leuvrey, D. Ihiawakrim, D. Tichit, C. Geradin, J. Phys. Chem. C 2011, 115, 23695–23703.
- [51] A. C. Cruickshank, S. E. R. Tay, B. N. Illy, R. D. Campo, S. Schumann, T. S. Jones, S. Heutz, M. A. McLachlan, D. W. McComb, D. J. Riley, M. P. Ryan, *Chem. Mater.* 2011, *23*, 3863 3870.
- [52] Y. Tan, E. M. P. Steinmiller, K.-S. Choi, Langmuir 2005, 21, 9618-9624.
- [53] D. B. Rasale, I. Maity, M. Konda, A. K. Das, Chem. Commun. 2013, 49, 4815–4817.
- [54] D. B. Rasale, I. Maity, A. K. Das, Chem. Commun. 2014, 50, 11397-11400.

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FULL PAPERS

Peeling back the layers: Self-assembled lamellar nanostructures as photoconductor hybrids are constructed by an electrochemical deposition technique (see figure). Morphological, structural, photoconduction, and optical studies of such peptide-based hybrid nanostructures are examined in detail.



M. K. Manna, S. K. Pandey, I. Maity, S. Mukherjee,* A. K. Das*



Electrodeposited Lamellar Photoconductor Nanohybrids Driven by Peptide Self-Assembly