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Growing Nano-petals on Electrospun Micro/nano Fibers

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Novel architectures: growing petals on micro/nano fibers were fabricated via combining electrospinning with solvent-induced self-assembly. The size and morphology of nanoflowers grown on fibers can be well controlled by solvent, hyperbranched degree and surfactant. Furthermore, these nanoflowers-like micro/nano fibers treated in ethanol indicate stronger fluorescent properties.

Self-assembly and self-organization based on the mutual noncovalent recognition of molecules is a very useful technique to obtain species with well-defined structure and properties.[1–4] In particular, design of supramolecular structures through self-assembly can sufficiently satisfy various demands, such as vesicles,[5] microcapsules,[6] one-dimensional materials,[7] and some highly ordered organic nanomaterials.[8] The constructions of precisely defined molecular materials were designed to perform specific functions such as sensors,[9] field-effect transistors,[10] and photovoltaic.[11]

Phthalocyanines (Pcs),[12] as the typical representative of functional supramolecular materials, are particularly attractive building blocks through self-assembly because the intimate packing of these aromatic macrocycles can result in rich photophysical and photochemical properties. A well-designed nano PC molecular assembly can produce desirable new functions that are not observed in the corresponding monomer due to exciton coupling. Great efforts have been deveploped to construct well-defined nanostructured materials. For example, micro-tubular structure with photovoltaic properties was obtained by simple solvent evaporation method depending on strong π–π interaction,[13] Helical ribbons, hollow nanotubes and nanowire bundles were produced depending on the cooperation of intermolecular hydrogen bonding or metal–ligand coordination bonding with π–π interactions between tetrapyrrole rings.[14] However, self-assembled 3D hierarchical supramolecular nanostructure with controlled morphologies are little reported. It is a big challenge to develop simple and reliable fabrication methods for hierarchically architectures with controlled morphologies, which strongly affect the properties of nano-structured phthalocyanine. Therefore, it is necessary to develop fabrication methods in which the structures can be independently and precisely controlled in different length scales.

Herein, for the first time we propose a simple and effective method to fabricate multi-dimensional nanoflowers-like hyperbranched phthalocyanine iron/polyarylene ether nitriles (HBFePc/PEN) fibers by combining electrospinning with self-assembly of HBFePc. We made electrospinning technique as a platform for fabricating hybrid nanofibers, then postspinning treatment of nanofibers was combined to tune the structure and morphology of nanofibers, enabling the fabrication of complex architectures. Through combining electrospinning with self-assembly of HBFePc, novel multi-dimensional architectures: growing nanoflowers and nanothorns on micro/nano fiber surface can be obtained. Furthermore, these nanoflowers-like microfibers indicate strong fluorescent properties.

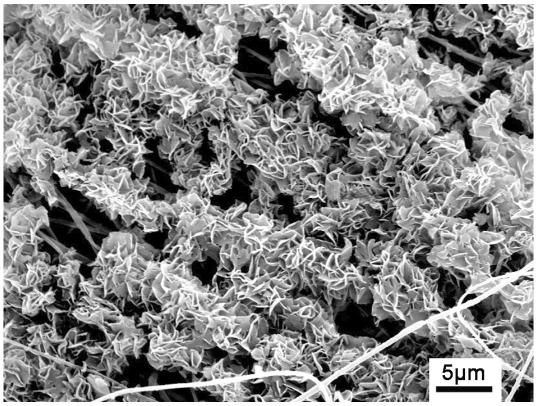

Figure 1. Flowers-like PEN/HBFePc micro/nano fibers.

During the electrospinning of small-molecule HBFePc blending with the high-molecule PEN, the low molecular weight HBFePc with lower viscosity and higher mobility of molecules could migrate to the fiber surface to form core-sheath structure, due to the phase separation.[15] Many distinct HBFePc bead or agglomerates wrapping on the nanofiber surface could be observed from Figure S5 (See Figure S5). After the subsequent solvent treatment in ethanol, the morpholgy of composite fibers can be changed from core-sheath structure to flowers-like like structure. HBFePc nanopetals can grow on PEN fiber surface (as shown in Figure 1).

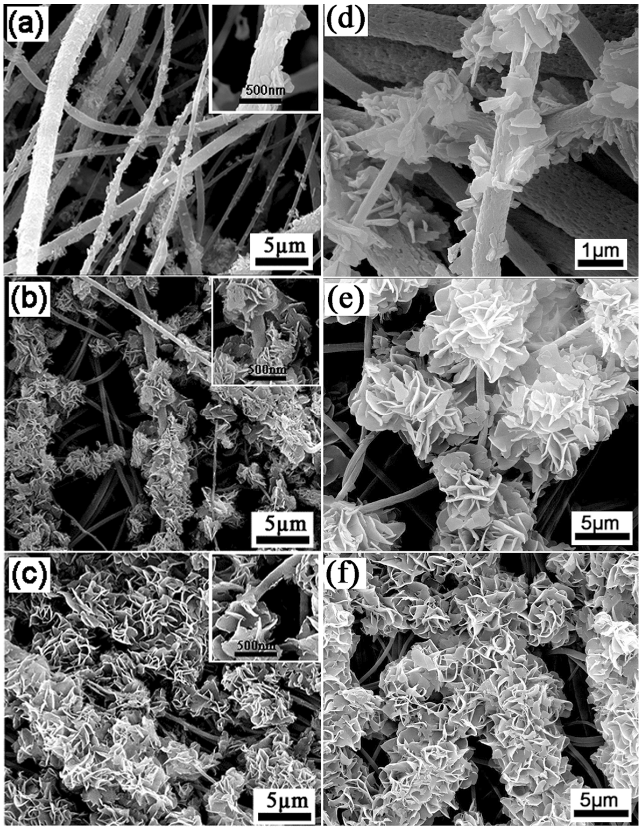

Figure 2. SEM of PEN/HBFePc fibers after different post-treatment time in ethanol for (a) 2, (b) 4 and (c) 10 h, respectively and PEN/HBFePc micro/nano fibers with different hyperbranched degree of HBFePc: (d) treated for 2h, (e) treated for 4h, (f) treated for 6h, respectively.

In order to elucidate the nanopetals growth, a series of time-dependent growth experiments were conducted. Growth process of PEN/HBFePc composite fibers for different treatment duration of 2, 4, and 10 h are displayed in Figure 2a–2c, respectively. It can be seen that the length and thickness of the HBFePc nanopetals can be easily controlled by the treatment time. When the electrospun fiber was kept in ethanol for 2 h, sparse HBFePc nanopetals were formed, wrapping the PEN fiber axis as shown in Figure 2a. When the reaction time reaches 4 h, nanopetals continue growing perpendicular to the fiber. Meanwhile larger scales nanopetals with longer size can be observed (200–400 nm). Prolonging the duration to 10 h, thicker layers of nanopetals appeared surrounding the PEN fibers as shown in Figure 2c, and the size of the more uniform HBFePc nanopetals increased than those treated for 2 h and 4 h, respectively. The lengths of the petals can reach 1 μm (Figure 2c). Thus, the HBFePc nanopetals can serve as seeds for guiding the nanopetals subsequent growth to form flowers-like structure. Figure 2e-2f shows the flowers-like fibers treated in ethanol for 12 h with different hyperbranched degree of HBFePc. With the hyperbranched degree of HBFePc increasesd, the thickness of nanopetals decreases from 19–37 to 10–23 nm, but the density as well as the length further increased. Longer reaction time appeared to be favorable to the formation of thinner, lager and more uniform nanopetals.

So why the composite fibers show flowers-like structure treated in ethanol? Firstly, the structure of HBFePc powder treated in ethanol was discussed. Figure S4b shows the structure of the HBFePc treated in ethanol for 10 h. Only part nano-petals structure can be observed. Futhermore, the thickness of the nanopetals is up tp 150 nm, much thicker than that in the PEN/HBFePc fibers. The powder can't wholly disperse in ethanol and can't contact with ethanol molecule fully. Thus the HBFePc isn't easy to self-assemble into flowers-like structure. However, when HBFePC was electrospun into fibers, it can wrap the 1-D PEN nanofiber and it can show high specific surface areas due to the PEN nanofibers as the support. So It can contact and react with ethanol molecular fully. Then self-assembly into flowers-like structure is easy to be got.

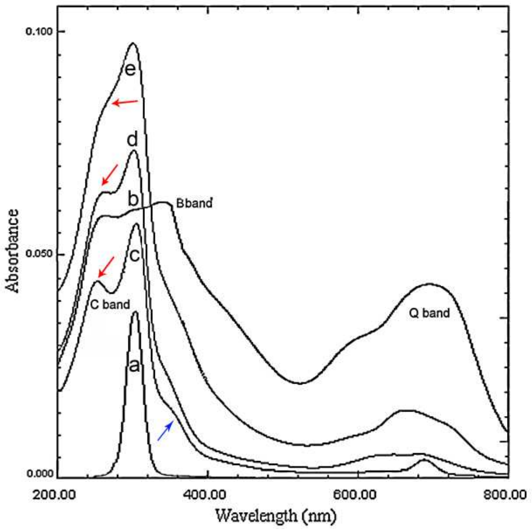

Figure 3. UV–vis absorbance spectra of various samples. (a) pure PEN fibers, (b) pure HBFePc poweders and PEN/ HBFePc composite fibers treated in ethanol for 2 h (c), 4h (d) and 10 h (e), respectively.

UV–vis optical spectroscopy has proven to be a powerful tool to study the evolution of the molecule absorption spectra upon aggregation and the formation of ordered states.[16] Figure 3 demonstrates the UV–vis absorption spectrum of PEN/HBFePc fibers. From Figure 3b, the strong Q-band absorption peak of pure HBFePc poweders occurs at 690 nm and a relatively weak peak, seen as a shoulder, appears at 610 nm which should be assigned to metal-to-ligand charge transfer, due to the hyperbranched oligomeric phthalocyanine species.[17] The absorption at 350 nm is assigned to B band (π–π* transitions of the macrocycle). Precedent to B-band peak, a third absorption band at 256 nm is assigned to C band may be assigned to the benzene rings absorption.[13] The absorption peak at about 300 nm is mainly attributed to the absorption peak of PEN backbone. However, compared with the HBFePc spectrum of (b), the B-band of PEN/HBFePc fibers appears at 360 nm which is red shifted slightly as shown in Figure 3c (blue arrow). With increasing the post-treatment time in ethanol, the absorpation peak broadens. In the metal-phthalocyanines, the Soret-band is related to the front orbitals of the central metals in the metal–phthalocyanines,[13] thus this means that the surrounding conditions of the central Fe ions are obviously changed in the fibers. That is, there are a few Fe–O coordination bonds between Fe ions in one molecule and an oxygen atom in another molecule, indicating the intermolecular aggregation were formed. This type of aggregation (J-type aggregate) induced by metal–oxygen coordination was also reported tetra(a-phenoxy) in zinc phthalocyanine molecules.[18] Besides, adding ethanol can inhibited the cofacial π–π stacking of the Pc rings (H-type aggregate). Futhermore, line broadening was also observed for C-band which exhibited line broadening and slight red shifted compared with that of HBFePc as shown in Figure 3 (red arrow). This was attributed to a tight packing between the benzene rings of the substituted 4,4'-bis (3, 4-dicyanophenoxy) biphenyl moieties of HBFePc[13]. This indicates that there exist both the strong J-type aggregate between the phthalocyanine rings and the strong π–π interaction between the benzene rings of the substituted 4,4'-bis (3, 4-dicyanophenoxy) biphenyl moieties of HBFePc, and both these interactions are responsible for the formation of flowers-like structure.

Thus based on the above discussion, a possible formation mechanism was proposed. The 4,4'-bis (3, 4-dicyanophenoxy) biphenyl moieties of HBFePc act as hands for the formation of nanosheet by tight packing between the benzene rings, which dedicated the length of nanosheets, and the nanosheet served as seeds can grow by J type nano aggregates induced by Fe–O coordination interactions, which dedicated the thickness of nanosheet. Then, driven by the minimization of the total energy of the system, the nanopetals aggregate and organize to form flowers-like structure.

On the literatures,[19-21] the surfactants are amphiphilic compounds bearing hydrophilic groop and hydrophobic tail, which can self-assemble into various micelles with increasing surfactant concentration, such as spherical micelle and rodlike micelle. Thus we also investigated the morphology control of the composite fibers under the effect of anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant n-hexadecyltrimethylammonium bromide (CTAB), respectively (more details are shown in Figure S6). With increasing concentration of SDS, the surface morphology of composite fibers treated in ethanol/SDS gradually changed from nanopetals to nanothorns (Figure S6b). However, only rough surface without nanopetals was observed as shown in Figure S6d.

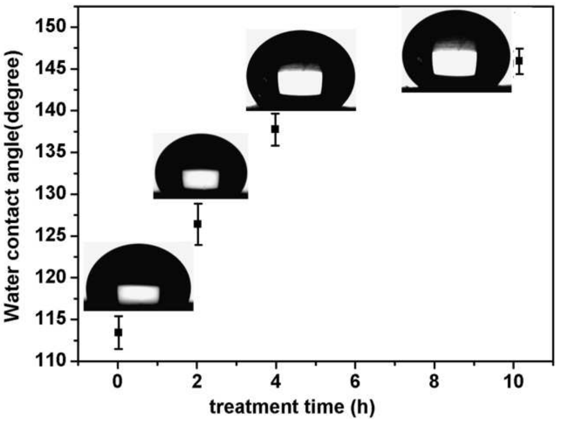

Figure 4 WCA and corresponding shapes of water droplets for the PEN/HBFePc fiber mats with respect to post-treatment time in ethanol.

Figure 4 show the relationship between the water CA and the post-treatment time of PEN/HBFePc fibers. It can be seen that flowers-like fibers display higher contact angles with more post-treatment time. The WCA can be tuned by the morphology change. The fibrous mats treated for 10 h can exhibit a hydrophobic state with a contact angle of 145^{o}. With the post-treatment time in ethanol increasing, the scales of nanopetals increased, and more interspace can be got as shown in Figure 2. The contribution of the presence of cooperative ternary structures between the petal sheets and nanofibers can made it possible to trap a large amount of air and minimize the real contact area between surfaces and water droplets.[22,23] Thus high WCA can be got.

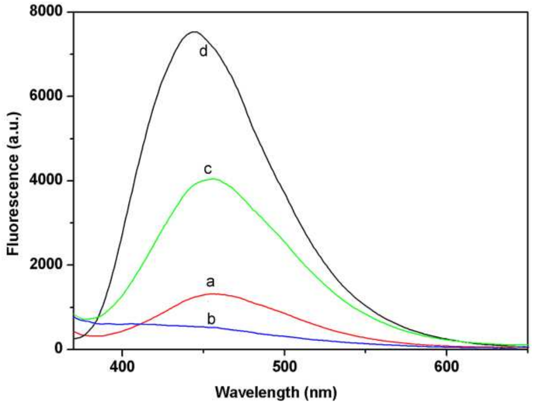

Figure 6. Fluorescence spectra of PEN/HBFePc-4h fibers (a) without treatment, (b) treated in deionized water and (c)HBFePc treated in ethanol and (d) PEN/HBFePc-4h fibers treated in ethanol. Emission spectra (λex =344 nm).

The spectroscopic, photophysical and photochemical behavior of PC aggregates strongly depends upon the relative geometry of the macrocycles, and has been discussed theoretically by Kasha.[24] The optical properties of the aggregates are usually illustrated by Davydov's exciton coupling theory.[25] The changes in these properties resulting from aggregation can have a major impact on the applications of PCs as light-harvesting antenna, molecular wires, non-linear optics and potential photodynamic therapeutic (PDT) agents. H-type PC dimers or higher aggregates are known to be non-photoactive, because such stacking provides an efficient nonradiative energy relaxation pathway, reducing the triple-state population and therefore inhibiting the generation of singlet oxygen, which is directly related to the death of tumor cells.[18,26] H-type aggregate can be formed in the composite fibers treated in deionized water, which is non-photoactive.[18] Thus FL of the deionized water treated PEN/HBFePc is non-fluorescent as shown in Figure 6b. However, The FL intensity of nanopetals-like fibers was significantly enhanced, exhibiting the emission maximum occurring at 455 nm, when exited at 344 nm. This is due to the J-type aggregate of HBFePc.[18] Futhermore, its instensity was stronger than that of HBFePc treated in ethanol. This may be attributed to the 3-D unique architectures. It indicated adding ethanol can not only inhibit the cofacial π–π stacking (H-type aggregate) of the Pc rings, but also enhance the fluorescence property. Additionally, the visible photocatalytic properties of the flowers-like PEN/HBFePc fibers are undergoing

Conclusions

we have prepared novel flowers-like PEN/HBFePc fibers that are generated from the combination of electrospinning with self assembly. The HBFePc nanopetals can grow on PEN fibers by the post-solvent treatment. The morphology and size of nanopetals and nanothorns can be easy controlled. Furthermore, these nanoflowers-like microfibers indicate intense fluorescent properties.

The advantages of this strategy lie in its ability to fabricate a product with tunable morphologies and designed phase structure. This simple and powerful strategy has established an avenue for designing and constructing functional devices with less expensive, finely controlled. Therefore this facile and effective strategy can be extended to provide a new way to research and development of nanosized phthalocyanines application. Further efforts are currently under way in our group to prepare related devices for photovoltaic and photocatalytic applications, combining the merits of electrospinning with the electrical and outstanding optical properties of iron phthalocyanines

Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental Section; SEM images of (a) HBFePc powder and HBFePc powder treated in ethanol, (b) electrospun PEN/HBFePc micro/nano fibers, (c) PEN/HBFePc fibers fibers under the effect of SDS and CTAB, espectively, (d) PEN/HBFePc fibers treated in deionized water;]. See DOI: 10.1039/c000000x/

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