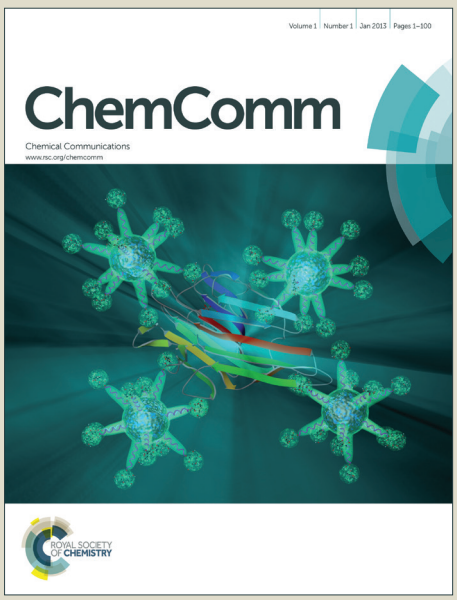
ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Supramolecular Self-Assembly of Three Dimensional Polyaniline and Polypyrrole Crystals

Yulun Tao,[a,b] Juchuan Li,*[c] Anjian Xie,[a] Shikuo Li,[a] Ping Chen,[a] Liping Ni,[a] Yuhua Shen,*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Here, we firstly reported a novel approach for preparing 3D π-π stacked crystals of polyaniline and polypyrrole and show how they self-assemble in suitable solution environment. 3D crystals of polyaniline and polypyrrole show high charge transport properties of 130 S/cm and 150 S/cm, respectively. Remarkably, the 3D crystals of polyaniline obtain excellent anisotropic conductivity.

3D semiconductor crystals are ideal to manipulate devices in integrated circuits [1] because they show the collective effects of the coupling of the electronic and optical properties of neighboring nanostructured building blocks. [2] Therefore, how to prepare 3D semiconductor crystals is fundamental and hot-spot. [3-5] Inspired by 3D supramolecular assembly [6] of biological molecules such as DNA, peptides and nacre in solution system, [7, 8] supramolecular assembly technology extends to preparation of 3D inorganic/organic semiconductor crystals. [9,10] However, 3D assembly of π-conjugated polymer crystals is still a challenge because 3D fantastic self-assembly needs coded nanocrystals [11] with a sufficiently monodisperse distribution of size and shape firstly, then these nanocrystals repeat the "bottom-up" self-assembly into 3D crystal structure along the optimal dynamic path, these configurations may be affected by lots of energy contributions (for example, π-π stacking interaction, van der Waals, electrostatic, dipolar) as well. [12]

In our approach, the desired 3D π-π stacked structures of polyaniline and polypyrrole were firstly obtained by supramolecular assembly. Furthermore, the changes of morphology and crystallization of π-conjugated polymers are freely controlled by polar and non-polar solvents such as ethanol and cyclohexane. The supramolecular self-assembly mechanism is also discussed for 3D nacre-like stacked nanostructures of π-conjugated polymers. The 3D crystals will become magic wand to realize excellent charge transport properties (130-150 S/cm) for organic solar cells and organic field-effect transistors.

The 1D polyaniline helical nanofibers[13] doped with CSA were synthesized as shown in Fig 1a. The nanofibers typically range in diameter of about 60-70 nm. The 0D monodisperse nanospheres of polyaniline could be gained by adding these 1D nanofibers into polar ethanol for 30 d (Fig. 1b). The diameter of these nanospheres is in the range of 500 nm. The detail transformation is shown Fig. S1.

Fortunately, real-time supramolecular self-assembly of polyaniline is firstly observed during 30 d aging experiment (Fig. 1b-e). After uptake of cyclohexane for 1.5 d, the diameter of the swollen nanospheres slightly increases. Flower-like aggregates self assembled by nanocrystals as shown on the right side of Fig. 1c. After aged in cyclohexane for 3 d, uniform nanosheets of polyaniline were formed and self organized to circular ring with diameter of about 3um (Fig. 1d). In fact, the monodisperse nanosheets are coded with stable, specific shape and size due to orderly arrangement of polyaniline and crystallization by driving forces of intermolecular interaction such as hydrophobic forces, van der Waals forces, π-π interactions, etc. Then, the polyaniline nanosheets repeated 3D supramolecular assembly to 50um sized circular ring after 20 d (Fig. 1e). In the inset of Fig. 1f, it is clearly seen that the crystals are assembled by layered nanostructures. The amazing finding is that the nanosheets have single crystalline structures of a hexagonal phase[13] growing along the c-axis, strongly indicated by SAED pattern with sharp diffraction spots in inset of Fig. 1g. 3D crystals have several sharp peaks at 2θ = 11.5°, 16.6° and 25.1° in Fig. S2, fitting very well with *d*-spacings of 7.7, 5.3 and 3.5 Å in the corresponding SAED patterns, respectively. HR-TEM image of crystals indicates polyaniline forms excellent single-crystal structures in Fig. S3. At last, after polyaniline was aged in cyclohenxane for 30 d, the 3D π-π stacked crystals were formed and the thickness of a layer increased to about 180 nm (see STM images in Fig. 1h,i). In a word, nanosheets act as building blocks, repeat the "bottom-up" self-assembly into 3D layered nacre-like nanocrystals. UV-Vis spectra and MALDI-TOF mass spectra of polyaniline crystals were shown in Figs. S4, S5, respectively.

Supramolecular self-assembly is at the heart of crystal engineering,[14] an interesting question is what the driving forces for self-assembly of 3D polyaniline crystals in good order are. Comparing to van der Waals, electrostatic and dipolar, π-π interactions provide an excellent tool for minimize unfavorable electrostatic repulsion by parallel displacement and maximize the attractive dispersion component. Thus, the π-π interactions are of fundamental importance in providing driving forces to generate 3D π-π stacked crystals of polyaniline. During the initial stages, nanospheres swelled to ellipsoids and crystllized to form nanosheets. Then these nanosheets self-assembled into 3D π-π stacked crystal structure.

In order to demonstrate that the method could be applied as the general fabrication procedure of other π-conjugated polymers, polypyrrole is selected for the crystal preparation. The polypyrrole nanofibers doped with $LiClO_4$ were synthesized in

ChemComm Accepted Manuscript

AAO template by electropolymerization. The nanofibers range in diameter of about 60 nm in Fig. 2a. The monodisperse nanoellipsoids of polypyrrole could be obtained by adding these nanofibers into polar ethanol for 30 d (Fig. 2b). After these nanoellipsoids were dispersed into nonpolar cyclohexane undisturbed for 30 d at room temperature, 3D π-π stacked crystals of polypyrrole formed by supramolecular self-assembly as well (Fig. 2c,d). The size of 3D crystals is about 20 μm. Moreover, the crystals show layered structures in the TEM image (Fig. 2e). These layered crystals have a set of twins of monoclinic phase indicated by SAED pattern with sharp diffraction spots (Fig. 2f). Similar 3D π-π stacked arrangement suggests a similar driving force exists between polyaniline or polypyrrole moleculars. The π-π interactions are mainly driving force due to both polyaniline and polypyrrole belong to π-conjugated molecules.

Both polyaniline and polypyrrole 3D crystals can serve as a π-conjugated crystal model. The conductivity along π-π stacking direction is measured by STM method. The height profiles of above 3D crystals are shown in Fig. S6, S7, respectively. The *I-V* curves of both polyaniline and polypyrrole after a series of doping are shown in Figs. 3a, b. (from 0 to 24 hours, respectively) With the extension of time for doping, conductivity of them increases quickly. The most striking feature of these crystals is that the excellent conductivity of polyaniline and polypyrrole reaches δ=130 S/cm and 150 S/cm, respectively.

To further testify anisotropic property of single crystals, we selected a 3D polyaniline crystal form S1 samples. Fig. 4d shows a 3D crystal is measured on SiO_2 substrate. Usually, 4-point-measurement would be carried out in films or larger length nanorods. But for 30 um size crystal, 2 point rather than 4 point is in favour of anisotropic conductivity measurement. Therefore, the direct-current (DC) conductivity measurements were performed with the 2-line probe approach by using the Keithley-Zyvex KZ100 nanoprobing system. Fig. 4f shows *I-V* curve of S1 sample, the calculation suggest that the conductivity is only 0.26 S/cm in surface, compared with the conductivity along π-π stacking direction (130 S/cm). An interesting anisotropic conductivity suggests the 3D polyaniline have typical single-crystal anisotropic properties. Note that the anisotropic conductivity of 3D polyaniline crystals is even higher than the values along π-π stacking direction (50 S/cm) reported before.[15]

How to control the ordered arrangement of π-conjugated polymer of is an important and interesting problem. Therefore, a novel "Orientation lose-Supramolecular self-assembly" model (Scheme 1) is proposed to explain morphology change and crystallization transition of polyaniline and polypyrrole controlled by the polarity of solvent. In ethanol, the interesting morphology changes of polyaniline from nanofibers to nanospheres are observed by SEM images carefully (Fig. S1). The orientation losing process of nanofibers is owing to stronger hydrogen bond interactions between CSA or ClO^{4-} and ethanol. [16] Moreover, sphere-like nanoparticles will have a lower overall surface energy than an elongated chain in ethanol.

In particular, it is interesting that ordered 3D layered crystals of polyaniline formed (Scheme 1C), after these sphere-like nanoparticles were dispersed into nonpolar cyclohexane. During the initial stages, their irregular polymer chains could easily stretch, aggregate and crystallize into coded nanosheets with highly ordered polymer chains (see molecular simulation in inset of Scheme 1), uniform shape and morphology by intermolecular noncovalent bonding, then these nanosheets self-assembled into 3D π-π stacked crystal structure along the optimal dynamic path. In this experiment, π-π interactions provide an excellent tool for assessing the efficiency of particular synthons of 3D π-π stacked structures with high conductivity. The poly (3-alkylthiophene) nanofiber formation via recrystallization with enhanced electrical conductivities has been also presented. [17-19]

Inserting Graphics

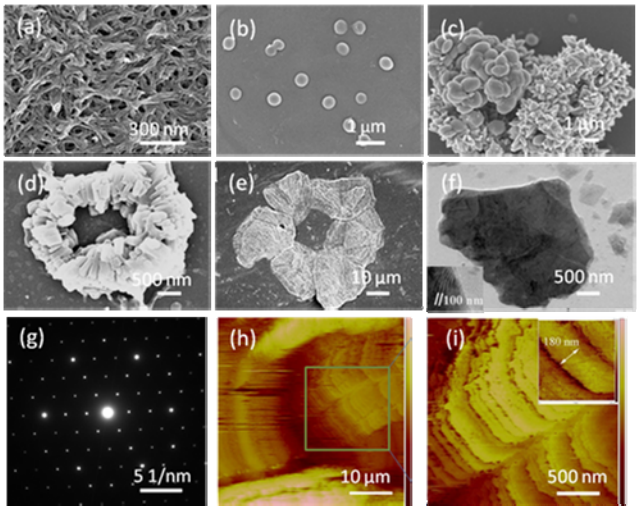


Fig. 1 SEM images of polyaniline (a) nanofibers; (b) nanospheres; (c) nanocrystals and nanospheres after 1.5d; (d) nanosheets after 3d; (e) 3D crystals self-assembly by nanosheets after 20d; (f,g) TEM image and SAED pattern of a piece of nanosheets; (h,i) STM images of 3D crystals after 30d. The nanospheres formed after aging the nanofibers in ethanol for 30 d. The nanocrystals, nanosheets and 3D crystals formed after aging the nanospheres in cyclohexane for 1.5, 3, 20 d and 30 d, respectively.

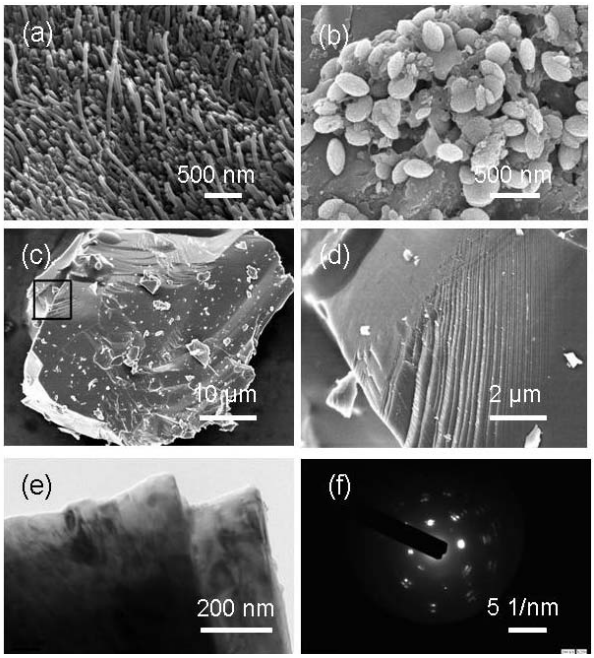


Fig. 2 SEM images of polypyrrole (a) nanofibers; (b) nanoellipsoids; (c,d) 3D π-π stacked crystals; (e,f) TEM image and SAED pattern of 3D π-π

ChemComm Accepted Manuscript

This journal is © The Royal Society of Chemistry [year]

stacked crystals. The nanoellipsoids formed after aging the nanofibers in ethanol for 30 d. 3D π-π stacked crystals formed after aging the nanospheres in cyclohexane for 30 d.

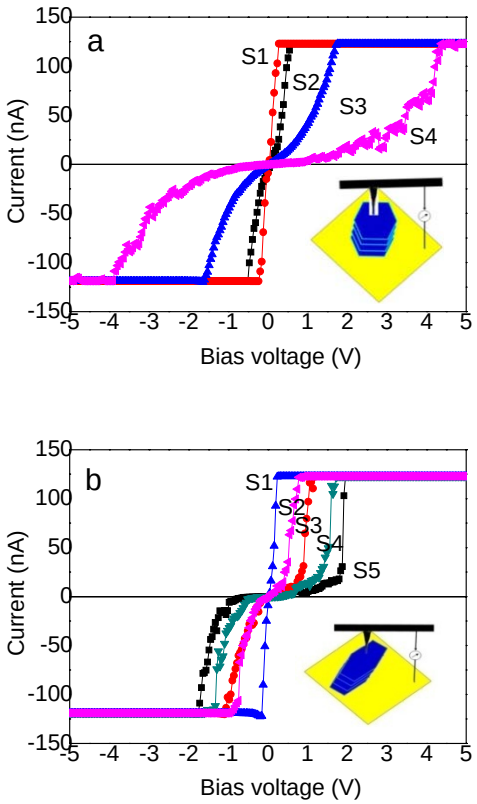


Fig. 3 (a)Tunneling *I-V* curves of 3D crystals of polyaniline along π-π stacking direction. S1-S4 samples doped at mass ratio m_{CSA}/ $m_{polyaniline}$ of 10/1 for 24, 12, 6, 0 hours, respectively. (b) Tunneling *I-V* curves of 3D crystals of polypyrrole along π-π stacking direction. S1-S5 samples doped at mass ratio m_{HCl}/ $m_{polypyrrole}$ of 10/1 for 24, 12, 6, 3, 0 hours, respectively.

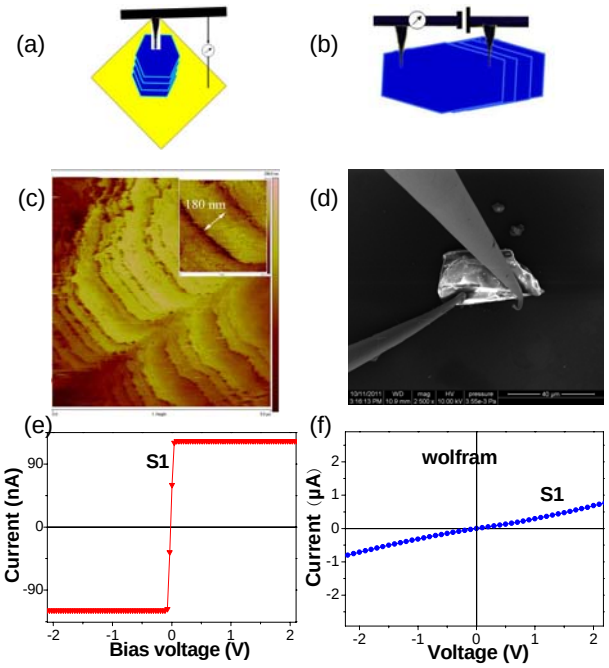
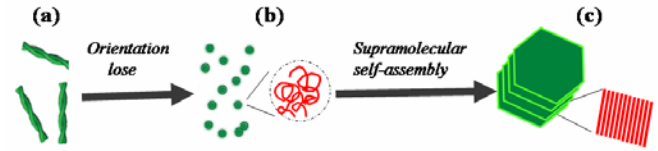


Fig. 4 Anisotropic electrical transport character measurements of 3D polyaniline crystals. (a,b) Electrical measurements of electrode construction; (c,d) STM and SEM images of the 3D crystals, respectively; (e) Tunneling *I-V* curve along π-π stacking direction. (f) *I-V* curve of the S1 sample in surface. S1 sample doped at mass ratio m_{CSA}/ $m_{polyaniline}$ of 10/1.



Scheme 1 Proposed formation mechanism of 3D π-π stacked crystals of polyaniline and polypyrrole. (a) nanofibers; (b) nanospheres, nanoellipsoids; (C) 3D π-π stacked crystals.

Conclusions

In conclusion, supramolecular self-assembly is firstly used to prepare 3D π-π stacked crystals of polyaniline and polypyrrole, respectively. The transformation from nanofibers to nanospheres to 3D stacked crystals could be freely controlled by suitable solvent environment. The good conductive properties are originated from high ordered molecular arrangement in the crystals. The 3D π-conjugated crystals as important polymer semiconductor will broadly used to promote 3D electronic devices properties such as 3D transistor properties.

Acknowledgements

This work is supported by the National Nature Science Foundation of China (91022032, 21173001 and 21371003), and Anhui Province Key Laboratory of Environment-Friendly Polymer Materials.

ChemComm Accepted Manuscript

Notes and references

[a] *School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, P. R. China. E-mail: s_yuhua@163.com*
[b] *Department of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, PR China.*
[c] *Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA, E-mail: jlin@g.uky.edu*

† Electronic Supplementary Information (ESI) available: Experimental Section, HRTEM images of 2D nanosheets of polyaniline, MALDI-TOF mass spectra and UV-Vis spectrum of 3D polyaniline. Height profile of 3D crystals of polyaniline and polypyrrole. See DOI: 10.1039/b000000x/

1 A. Rahman, P. Bai, G. Curello, *2013 IEEE International. IEEE*, 2013, 1.
2 H. Liu, D. Lin, Y, Sun, *Chem.-Eur. J*. 2013, **19**, 8689-8689.
3 G. Jia, A. Sitt, G. B. Hitin, *Nat. Mater*. 2014, **13**, 301.
4 A. R. Maity, S.Palmal, S. K. Basiruddin, *Nanoscale*, 2013, **5**, 5506.
5 C. Bouet, B. Mahler, B.Nadal, *Chem. Mater*. 2013, **25**, 639.
6 J. Li, Y. Gao, Y. Kuang, *J. Am. Chem. Soc*. 2013, **135**, 9907.
7 N. Louvain, G. Frison, J. Dittmer, *Eur. J. Inorg. Chem.* 2014, **2014**, 364.
8 T. Young, R. Abel, B. Kim, *PNAS.* 2007, **104**, 808.
9 K. A.Arpin, M. D.Losego, A. N. Cloud, *Nat. Commun*. 2013, **4**.
10 J. A. Rogers, M. G. Lagally, R. G. Nuzzo, *Nature*, 2011, **477**, 45.
11 D. Liu, T. L. Kelly, *Nat. photonics*. 2013, **8**, 133.
12 Z. Yan, H. Xu, S. Guang, *Adv. Funct. Mater.* 2012, **22**, 345.
13 Y. Tao, Y. Shen, L. Yang, *Nanoscale*, 2012, **4**, 3729.
14 K. Ariga, J. P. Hill, M. V. Lee, Sci. Technol. *Adv. Mater.* 2008, **9**, 014109.
15 Y. Yan, R. Wang, X. Qiu, *J. Am. Chem. Soc*. 2010, **132**, 12006.
16 C. Laslau, Z. Zujovic, J. Travas-Sejdic, *Prog. Polym. Sci.* 2010, **35**, 1403.
17 S. Samitsu, T. Shimomura, S. Heike, T. Hashizume, K. Ito, *Macromolecules*. 2008, **41**, 8000-8010.
18 G. Lu, L. Bu, S. Li, X. Yang, *Adv. Mater.* 2014, **26**, 2359-2364.
19 K. M. Coakley, B. S. Srinivasan, J. M. Ziebarth, C. Goh, Y. Liu, M. D. McGehee, *Adv. Funct. Mater.* 2005, **15**(12), 1927-1932.

ChemComm Accepted Manuscript

 This journal is © The Royal Society of Chemistry [year]