RSC Advances

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2015, **5**, 34616

Received 4th February 2015
Accepted 9th April 2015

DOI: 10.1039/c5ra02161h

www.rsc.org/advances

Versatile method for the synthesis of porous nanostructured thin films of conducting polymers and their composites†

LingFeng Dai,[a] Yuan He,[a] Xiang Huang,[a] Xin Cui,[a] Shihui Wang,[a] Dongtao Ge,*[a] Nifang Zhao,[b] Yue Li,[b] Yanan Sun[a] and Wei Shi*[a]

A porous nanostructure of $FeCl_3$ prepared by a simple evaporation process was used simultaneously as a template and oxidant to synthesize porous nanostructured thin films of almost all major classes of conducting polymers (CPs) and their composites.

Among the numerous polymer materials that have been investigated for organic electronics, supercapacitors, biosensors, and electromagnetic shielding, conducting polymers (CPs) may be the most important ones due to their unique and attractive properties such as wide range of electrical conductivity, high mechanical flexibility and thermal stability, and more importantly, low cost.[1–6] For practical applications in the aforementioned fields, CPs often need to be processed into films. However, film-forming ability of CPs is usually hindered by their poor processability. To prepare high quality CP films, various methods, including spin-coating,[7] dip-coating,[8] drop-coating,[9] electrochemical deposition,[10–12] binary system deposition,[13] dilute polymerization,[14,15] Langmuir–Blodgett technique,[16] and vapor phase polymerization,[17–19] have been developed. Although all of these methods can obtain CP films, only a few of them are able to result in nanostructured film directly. In fact, nanostructured, especially porous nanostructured CP films, are highly desirable for various emerging applications in material science and nanodevices because of their high specific surface areas, which often enables a good access of ion and electron to the active surfaces and leads to an enhanced performance. Nevertheless, current existing methods for preparing nanostructured CP films, such as electrochemical deposition,[20–22] dilute polymerization,[14,15] binary system deposition,[13] and soft[23] and hard template-assisted method,[24–26] usually have limitations ranging from limited substrate materials, time-consumption, cost effectiveness, the use of toxic organic solvents, reproducibility to lack of scalability. Therefore, a new method that can circumvent these problems, at least to some extent, is still needed.

On the other hand, from the application perspective, CP-based nanocomposite films are probably even more important than pure nanostructured CP films. To date, various nanostructured CP composite films, including CP/polymer and CP/inorganics nanocomposite films, have been prepared for applications in supercapacitors,[27–29] rechargeable lithium batteries,[30,31] artificial muscles,[32] actuators,[33] biosensors,[34,35] organic photovoltaics[36] and organic light-emitting diodes.[37] However, to the best of our knowledge, there are no reports so far on the preparation of porous nanostructured thin films of CPs, CP/polymer composites and CP/inorganics composites respectively by using only one method.

In this communication, a simple and versatile method was developed to prepare porous nanostructured films of CPs, CP/polymer composites and CP/inorganics composites. As depicted in Fig. 1a, the method used porous nanostructure of $FeCl_3$ as template, which was simply prepared by solvent evaporation from $FeCl_3$ solution that dropped directly on to various substrates (step 1). Then the resulting $FeCl_3$ nanostructure simultaneously acted as a template and oxidant to initiate the polymerization of CP monomers.

During the reaction, $FeCl_3$ was gradually consumed and the porous nanostructure of CP reproduced and replaced the $FeCl_3$ nanostructure (step 2). For obtaining porous CP/polymer nanocomposite film (Fig. 1b), the step 2 should be paused after a certain period of time, the residual $FeCl_3$ could be further used to initiate the polymerization of another monomer, thus resulting in the formation of the CP/polymer nanocomposite film (step 3). For preparing CP/inorganics nanocomposite film, as shown in Fig. 1c, the desired inorganics could be introduced

---

[a] *Department of Biomaterials, College of Materials, Xiamen University, Xiamen, 361005, China. E-mail: gedt@xmu.edu.cn; shiwei@xmu.edu.cn; Fax: +86 592 2188502; Tel: +86 592 2188502*

[b] *Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen, 361005, China*

† Electronic supplementary information (ESI) available: Experimental section and data section, which includes EDS spectrum of $FeCl_3$, SEM images of $FeCl_3$ nanostructures obtained at different conditions, digital photos of PPy thin films on various substrates, contact angle of water on PPy nanostructured film, FTIR spectra of PPy, PANI, PEDOT, PPy/PEDOT and PPy/PDA. See DOI: 10.1039/c5ra02161h

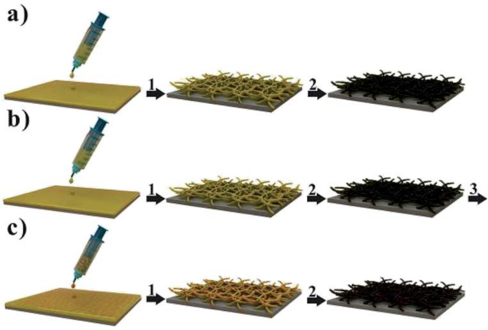

Fig. 1 Schematic representations for the formation of porous nanostructured thin films of (a) CPs (step 1: evaporation of the solvent from $FeCl_3$ solution; step 2: polymerization of CP monomer). (b) CP/polymer composites (step 1 and 2 are the same as above except that the polymerization time of the step 2 is reduced to some extent, step 3: polymerization of another monomer by the residual $FeCl_3$). (c) CP/inorganics composites (step 1: formation of porous $FeCl_3$/inorganics nanocomposite by evaporation of the solvent from a solution containing $FeCl_3$ and inorganics, step 2: formation of porous CP/inorganics nanocomposite by using $FeCl_3$ that contained in $FeCl_3$/inorganics nanocomposite to oxidize CP monomer).

during the step 1 by dissolving them in the $FeCl_3$ solution. After evaporating the solvent, porous nanostructured $FeCl_3$/inorganics composite film was obtained (step 2). Then the composite film was used as template and oxidant to further oxidize the monomers of CPs. With the consuming of the $FeCl_3$, CP/inorganics composite film was formed (step 3). Therefore, three kinds of important CP related porous nanostructured thin films, *i.e.*, CP films, CP/polymer composite film, and CP/inorganics composite film, could be prepared using this method. This versatility, plus other obvious advantages, such as simple and cost-effective formation process of $FeCl_3$ template, no limitation of substrate materials, without the use of toxic organic solvent, and easy to scale up, make this method very attractive in preparing high quality and multifunctional CP related nanostructured thin films for various practical applications.

It is well known that $FeCl_3$ is a commonly used oxidant for preparing a large number of CP nanostructures.[38–45] However, as far as we know, there are no reports to date on using porous $FeCl_3$ nanostructure as a CP nanomaterial template. In fact, template-assisted synthesis is probably the most important method for the synthesis of CP nanostuctures, but often requires harsh reaction conditions to remove hard-templates such as anodic aluminium oxide (AAO).[24–26] In the present work, porous nanostructured $FeCl_3$ was used as both oxidant and template, this effect conveniently results in its simultaneous reduction to $FeCl_2$, which is easily dissolved in water. Therefore, no harsh template-removal conditions were required. Furthermore, $FeCl_3$ is cheap and easy to obtain, which are essential features for a template that can be used only once.

Considering these factors, we suppose the nanostructured $FeCl_3$ we prepared is a desirable template for the synthesis of porous nanostructured thin films of CPs and CP composites.

Porous nanostructured $FeCl_3$ thin film can be formed by evaporation of ethanol from ethanol solution of $FeCl_3$ that dropped on various substrate materials. Fig. 2a shows the SEM image of the $FeCl_3$ film's surface microstructure on metal titanium substrate. The film had a homogeneous, fine-porous network nanostructure comprising branches of ~90 nm thickness. Energy dispersive X-ray spectroscopy (EDS) revealed the structure contained only Fe and Cl elements (Fig. S1, ESI†), confirming the formation of $FeCl_3$ film. To study the formation mechanism of the $FeCl_3$ porous nanostructure, the effects of drying temperature and $FeCl_3$ concentration on the $FeCl_3$ morphology were investigated. We found no homogeneous porous nanostructures formed at drying temperatures below 30 °C (Fig. S2, ESI†). However above 60 °C, $FeCl_3$ film with dendritic morphology was formed that easily fractured (Fig. S3, ESI†), and only between 40 to 50 °C could porous nanostructured morphologies with homogeneous pores be prepared (Fig. S4, ESI†). On the other hand, at a fixed drying temperature of 45 °C, the nanostructure backbone thickness increased from ~90 to 130 nm with increasing of $FeCl_3$ concentration from 0.05 to 0.10 M (Fig. S5, ESI†). Based on the above, we suggest that solvent evaporation plays a key role in the formation of the porous $FeCl_3$ nanostructure. During the evaporation process, the flow of the generated ethanol steam creates the porous $FeCl_3$ nanostructure. The porosity varied with the amount of ethanol steam (determined by drying temperature) and $FeCl_3$ concentration, *i.e.* when both were low, lower porosity of thicker-branched $FeCl_3$ nanostructure was obtained. Since the CP nanostructure was obtained by replication of the porous $FeCl_3$ nanostructure, the ability to adjust $FeCl_3$ nanostructure

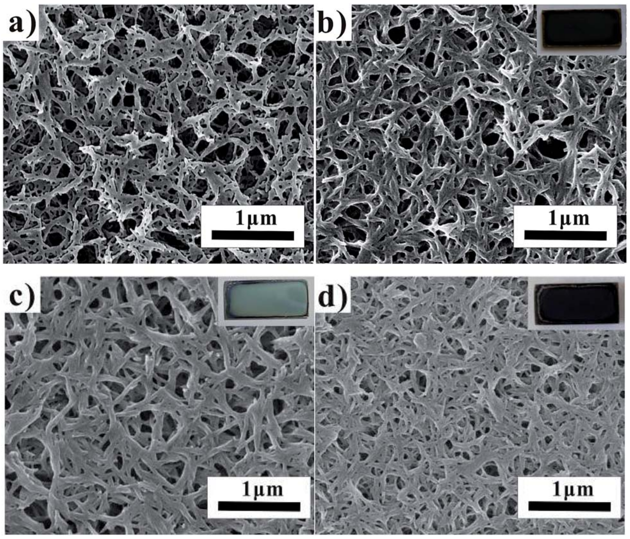

Fig. 2 (a) SEM image of the porous nanostructured $FeCl_3$ thin film obtained by evaporating ethanol from 0.05 M ethanol solution of $FeCl_3$ at 45 °C. (b) SEM image of the porous nanostructured PPy thin film obtained by exposure of the nanostructured $FeCl_3$ (in (a)) to pyrrole vapor at 60 °C for 1 h (inset: digital photo of PPy film on titanium). (c) SEM image of porous nanostructured PANI thin film obtained by exposure of the nanostructured $FeCl_3$ to aniline vapor at 60 °C for 1 h (inset: digital photo of PANI film on titanium). (d) SEM image of porous nanostructured PEDOT thin film obtained by exposure of the nanostructured $FeCl_3$ to EDOT vapor at 60 °C for 1 h (inset: digital photo of PEDOT film on titanium).

by temperature and concentration offers an important means for controlling CP nanostructure morphology.

Because $FeCl_3$ is highly water soluble, the CP synthesis step could not be carried out in aqueous solution. Therefore, we used chemical vapor deposition (CVD) to synthesize CP using polypyrrole (PPy) synthesis as the first example. Polymerization of pyrrole was initiated by exposing the porous $FeCl_3$ nanostructure to pyrrole vapor at 60 °C. Fig. 2b shows the SEM image of the porous PPy nanostructure synthesized using the $FeCl_3$ shown in Fig. 2a for a template. The obtained PPy closely maintained the original morphology of the $FeCl_3$ nanostructure. The FTIR spectrum of the porous PPy nanostructure (Fig. S6, ESI†) shows the characteristic PPy peaks such as the asymmetric and symmetric ring stretching at 1560 and 1471 cm^{-1}, the C–N stretching vibration at 1197 cm^{-1}, and C–C out-of-plane ring deformation vibration at 927 cm^{-1}, which collectively confirm the formation of PPy. The conductivity of the porous PPy nanostructure was measured to be ~0.3 S cm^{-1} using four-probe technique at room temperature. In addition, analysis of the surface wettability of the porous PPy nanostructure revealed superhydrophilic behavior, where the contact angle of a water droplet on PPy surface was almost 0° (Fig. S7, ESI†). It should be pointed out that surface wettability of the PPy film is important for practical applications, particularly in promoting immobilization of hydrophilic probe molecule in sensors and enhancing the penetration and diffusion ability through the film in energy storage/conversion systems. Therefore, it is envisaged that the porous nanostructured PPy thin film may find applications in biosensors and energy storage systems.

As mentioned earlier, $FeCl_3$ is commonly used as an oxidant to polymerize the monomers of various CPs. The present study also established that similar porous nanostructures of polyaniline (PANI) and poly (3,4-ethylenedioxythiophene) (PEDOT) were obtainable on titanium substrates using the $FeCl_3$ template method (Fig. 2c and d), the formation of which was confirmed by FTIR spectra (Fig. S8, ESI†). The conductivity of the porous nanostructured films of PANI and PEDOT were ~0.8 and ~0.2 S cm^{-1}, respectively. These results show the method provides a general route for preparing porous nanostructures of almost all major classes of CPs.

Currently, CP nanostructures are usually formed electrochemically on the surface of conductive substrates, or chemically in the body of the solution.[46,47] In the present work, the porous nanostructure of $FeCl_3$ can be coated directly on various substrate materials regardless of their conductivity, and thus so can the porous CP nanostructure. We have successfully deposited porous nanostructured PPy thin films on a large variety of substrates, including conducting substrates (for example, titanium, Au-coated Si wafer, and Si wafer) and non-conducting substrates (for example, glass, polyethylene terephthalate (PET), poly (phenylene sulfide) (PPS)) using the $FeCl_3$-templated method (Fig. 3, 4 and S9, ESI†). There is no apparent difference in the coating morphology for either conductive or non-conducting substrates. Therefore, we suppose that the $FeCl_3$-templated method is a simple and versatile method for the deposition of almost any CP film on almost any substrate. Interestingly, the PPy nanostructured film formed on PET substrate could be easily bent (Fig. 3), exhibiting excellent flexibility. This property renders the PPy coating suitable for potential applications in flexible electronics.

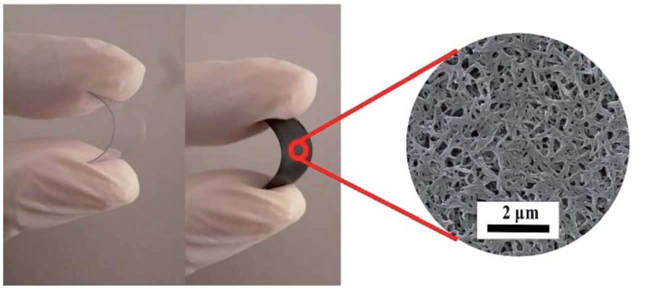

Fig. 3 Photo of the PET substrate and the PPy film formed on it (left) and SEM image of the microstructure of the PPy film (right).

It is obvious that the thickness of the CP film depends on the thickness of the $FeCl_3$ layer. Therefore, transparent CP films should be obtained by forming a thinner layer of $FeCl_3$ nanostructure. Fig. 4a shows the digital photo of the transparent PPy film that coated on coverslip glass. It was measured by UV/Vis spectroscopy that the PPy film has a greater than 90% light transmittance within the visible region (Fig. 4b). The transparency of the PPy film is also demonstrated by the clearly visible Xiamen University logo placed under the glass coverslip. The conductivity of the PPy transparent film was measured to be about 1 S cm^{-1}, which is sufficient for applications in electrostatic dissipation, magnetics shielding, and secondary electrodes. Such conducting, transparent film has great implications for potential applications in flexible organic electronics, optoelectronics, sensors, and energy storage devices.

Besides porous nanostructured CP film, porous CP/polymer nanocomposite film also can be prepared by using $FeCl_3$ nanostructure as oxidant to oxidize two different monomers successively. Fig. 5a exhibits the SEM image of microstructure of PPy/PEDOT nanocomposite film, which was prepared by using $FeCl_3$ to first oxidize pyrrole vapor to PPy and then EDOT vapor to PEDOT. The FTIR spectrum (Fig. S10a, ESI†) confirms the formation of the PPy/PEDOT. To further prove the versatility of the method for the preparation of CP/polymer nanocomposite, another interesting polymer, polydopamine (PDA) was incorporated into PPy to form porous PPy/PDA nanocomposite film. Fig. 5b shows the SEM image of porous

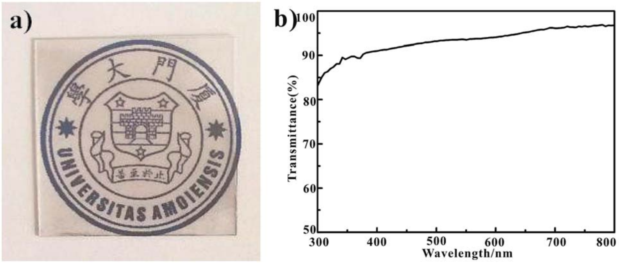

Fig. 4 (a) Digital photo of the transparent nanostructured PPy thin film coated on glass coverslip. (b) UV/Vis-spectroscopy of transparent nanostructured PPy thin film coated on coverslip glass.

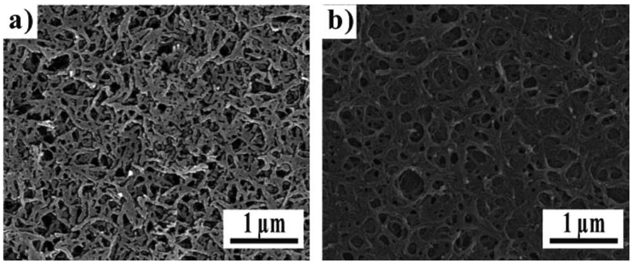

Fig. 5 SEM images of the porous nanostructured thin film of (a) PPy/PEDOT and (b) PPy/PDA.

PPy/PDA film, which was synthesized by first oxidizing vapor of pyrrole monomers to PPy and then oxidizing dopamine monomers in aqueous solution to PDA. The FTIR spectrum proves the formation of the PPy/PDA (Fig. S10b, ESI†). Recently, PDA has been intensively investigated as functional coating for numerous applications due to its ability to adhere to wide range of organic and inorganic materials.[48,49] However, few reports focus on the formation of CP/PDA nanocomposites. Here, we show that the CP/PDA nanocomposite film can be prepared easily by the present $FeCl_3$-template method. It is well known that PPy has good conductivity and biocompatibility, but is difficult to be modified due to the lack of specific interaction on the surface. While the additional functional groups from PDA can address this problem easily. Therefore, the combination of PDA with PPy significantly improves the processability and functionality of PPy, making the porous PPy/PDA nanocomposite film very attractive for potential applications in biomedical science and organic electronics.

Finally, we demonstrate the introduction of $CaCl_2$ into PPy as an example to illustrate the formation of the porous CP/inorganics nanocomposite film. Porous $FeCl_3/CaCl_2$ composite nanostructure (Fig. 6a) was obtained by evaporating ethanol from a solution containing specified amounts of dissolved $FeCl_3$ and $CaCl_2$. The presence of $CaCl_2$ in the resultant template nanostructure was confirmed by EDS (Fig. 6b), and fine porous nanostructured morphologies were produced with $CaCl_2$ content as high as 30 wt%. Fig. 6c shows the SEM image of the obtained PPy/$CaCl_2$ nanocomposite, where exposure of the $CaCl_2/FeCl_3$ nanocomposite to the pyrrole vapor for 1 h still produced the desired porous nanostructured morphology.

During the past decade, biomedical applications for PPy have attracted much attention.[50–52] A promising example is the use of PPy as a coating material for dental and orthopedic implants.[53,54] However, PPy exhibits poor osteoconductive properties and thus does not bond directly to living bone; this impedes patient healing and might ultimately result in long-term failure of the implant. Introduction of Ca^{2+} to the implants has proved an effective way to increase its osteoconductivity,[55–57] where Ca^{2+} induces the deposition of apatite on the implant surface and promotes attachment and proliferation of osteoblasts, and superior osseointegration bonding between implant and bone.[58–60] However, since PPy is insoluble and infusible, it is difficult to introduce Ca^{2+} into PPy nanostructure by conventional methods.

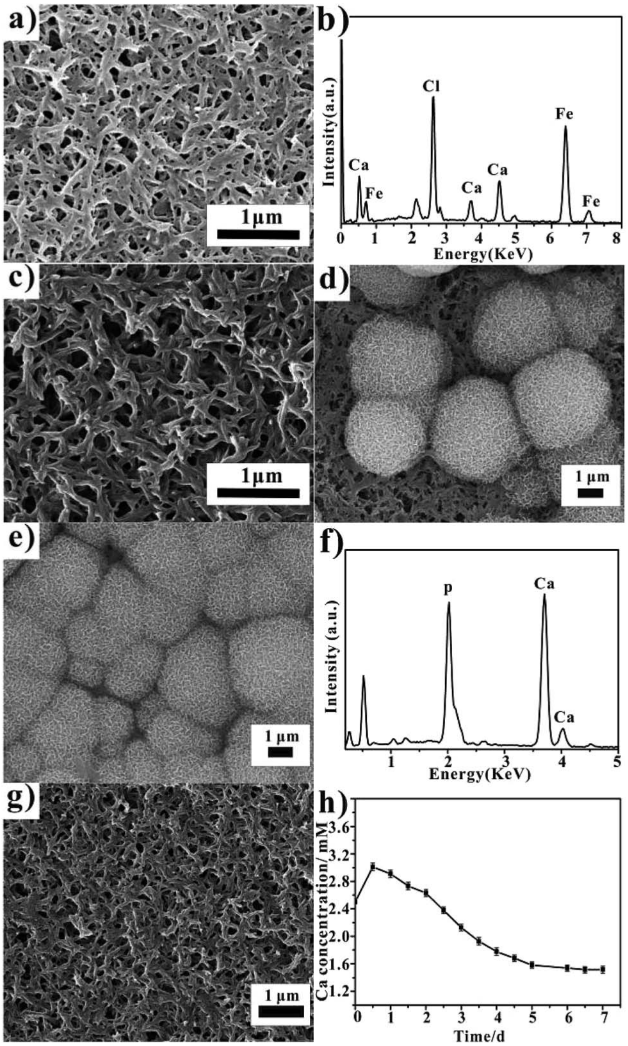

Fig. 6 (a) SEM image of the porous nanostructured thin film of $FeCl_3/CaCl_2$ composite (with wt 10% of $CaCl_2$). (b) EDS spectrum of $FeCl_3/CaCl_2$ nanocomposite thin film in (a). (c) SEM image of the porous nanostructured thin film of PPy/$CaCl_2$ composite. (d) Apatite particles formed on PPy/$CaCl_2$ nanocomposite after soaking in SBF for 48 h. (e) Apatite particles formed on PPy/$CaCl_2$ nanocomposite after soaking in SBF for 96 h. (f) EDS spectrum of the apatite particles in (e). (g) SEM image of the PPy nanostructure without $CaCl_2$ after soaking in SBF for 120 h. (h) Variation in Ca^{2+} concentration of SBF with soaking of porous PPy/$CaCl_2$ nanostructured thin film.

In the present work, introduction of Ca^{2+} into the porous PPy nanostructure to form PPy/$CaCl_2$ nanocomposite was easily accomplished. To evaluate its apatite-forming ability, the PPy/$CaCl_2$ nanocomposite was soaked in simulated body fluid (SBF).[61–63] Fig. 6d and e shows the SEM images of the PPy/$CaCl_2$ nanocomposite surface after soaking in SBF for 48 and 96 h respectively. As shown in Fig. 6d, after 48 h, some of the PPy/$CaCl_2$ nanocomposite surface became covered by spherical particles, and after 96 h, the whole surface was completely covered (Fig. 6e). EDS results indicated that the particles predominantly contained calcium and phosphorus (Fig. 6f) and the ratio of Ca/P was 1.2, thus confirming the particles were bone-like apatite. Notably, no apatite particles formed on porous PPy nanostructure lacking $CaCl_2$ even after soaking in SBF for 120 h (Fig. 6g). Concentration of Ca^{2+} was monitored by inductively coupled plasma mass spectrometry (ICP-MS) after the $PPy/CaCl_2$ nanostructure was placed in SBF. Fig. 6h shows Ca^{2+} concentration first increased and then decreased gradually until a steady state was reached. The increase of the Ca^{2+} was ascribed to the release of Ca^{2+} from the $PPy/CaCl_2$ nanostructure to the SBF, and the following decrease of Ca^{2+} to the deposition of apatite from SBF to the surface of the nanostructure film. Therefore, we reasonably postulate that the introduction of $CaCl_2$ to PPy produced pronounced apatite-forming ability. Noted that besides $CaCl_2$, other inorganics also might be introduced into $FeCl_3$ to establish more kinds of porous CP/inorganics nanocomposite films.

Conclusions

In summary, we have developed an attractive oxidative template method for synthesizing CP-based porous nanostructured thin films. Porous nanostructure of one of the most commonly used oxidants for CP monomers, $FeCl_3$, was used for the first time as template to accomplish the synthesis. Compared to other methods, our method offers following advantages. First, $FeCl_3$ is cheap and easy to obtain, which are essential features for a template that can be used only once. In addition, the formation process of nanostructured $FeCl_3$ template is short and simple, involving only physical evaporation and no additional chemical reactions. Second, it is a general method to prepare porous nanostructured thin films of almost all major classes of CPs on almost any substrate. Third, besides porous nanostructured CP films, porous nanostructured thin films of CP/polymer and CP/inorganics composites also can be formed, making the $FeCl_3$-template method to be the only method so far for simultaneously preparing three kinds of CP-based porous nanostructured films, *i.e.* porous CP, CP/polymer, and CP/inorganics nanostructured thin films. We believe this versatile method could significantly broaden our ability to obtain porous nanostructured thin films of CP and CP-based nanocomposites for use in various fields such as organic electronics, energy storage devices, and biomedical science.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (31271009, 81271689), the Fundamental Research Funds for the Central Universities (no. 2011121001), the Natural Science Foundation of Fujian Province (2011J01331), and the Program for New Century Excellent Talents in University, and the Program for New Century Excellent Talents in Fujian Province University.

Notes and references

1 A. Facchetti, *Chem. Mater.*, 2011, **23**, 733–758.
2 G. A. Snook, P. Kao and A. S. Best, *J. Power Sources*, 2011, **196**, 1–12.
3 M. Gerard, A. Chaubey and B. D. Malhotra, *Biosens. Bioelectron.*, 2002, **17**, 345–359.
4 P. Saini and M. Arora, *New Polymers for Special Applications*, ed. A. D. Gomes, Intech, Croatia, 2012, pp. 71–112.
5 P. Saini, V. Choudhary, N. Vijayan and R. K. Kotnala, *J. Phys. Chem. C*, 2012, **116**, 13403–13412.
6 P. Saini, M. Arora, G. Gupta, B. K. Gupta, V. N. Singh and V. Choudhary, *Nanoscale*, 2013, **5**, 4330–4346.
7 M. L. Machala, L. Muller-Meskamp, S. Gang, S. Olthof and K. Leo, *Org. Electron.*, 2011, **12**, 1518–1526.
8 Z. Y. Hu, J. J. Zhang, S. Z. Xiong and Y. Zhao, *Org. Electron.*, 2012, **13**, 142–146.
9 C. T. Li, C. P. Lee, Y. Y. Li, M. H. Yeh and K. C. Ho, *J. Mater. Chem. A*, 2013, **1**, 14888–14896.
10 X. Y. Cui, J. F. Hetke, J. A. Wiler, D. J. Anderson and D. C. Martin, *Sens. Actuators, A*, 2001, **93**, 8–18.
11 X. Luo and X. T. Cui, *Acta Biomater.*, 2011, **7**, 441–446.
12 A. Baba and W. Knoll, *Adv. Mater.*, 2003, **15**, 1015–1019.
13 J. M. D'Arcy, H. D. Tran, V. C. Tung, A. K. Tucker-Schwartz and R. P. Wong, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 19673–19678.
14 N. R. Chiou, C. Lu, J. Guan, L. J. Lee and A. J. Epstein, *Nat. Nanotechnol.*, 2007, **2**, 354–357.
15 N. R. Chiou and A. J. Epstein, *Adv. Mater.*, 2005, **17**, 1679–1683.
16 S. Yang, L. Fan and S. Yang, *J. Phys. Chem. B*, 2004, **108**, 4394–4404.
17 J. M. D'Arcy, M. F. El-Kady, P. P. Khine, L. H. Zhang, S. H. Lee, N. R. Davis, D. S. Liu, M. T. Yeung, S. Y. Kim and C. L. Turner, *ACS Nano*, 2014, **8**, 1500–1510.
18 J. P. Lock, S. G. Im and K. K. Gleason, *Macromolecules*, 2006, **39**, 5326–5329.
19 J. L. Yagüe, A. M. Coclite, C. Petruczok and K. K. Gleason, *Macromol. Chem. Phys.*, 2013, **214**, 302–312.
20 F. Hui, B. Li, P. G. He, J. Hu and Y. Z. Fang, *Electrochem. Commun.*, 2009, **11**, 639–642.
21 M. Li, Z. X. Wei and L. Jiang, *J. Mater. Chem.*, 2008, **18**, 2276–2280.
22 W. Shi, P. F. Liang, D. T. Ge, J. X. Wang and Q. Q. Zhang, *Chem. Commun.*, 2007, 2414–2416.
23 P. Saini and M. Arora, *J. Mater. Chem. A*, 2013, **1**, 8926–8934.
24 W. Shi, Y. Y. Ma, D. T. Ge and H. R. Jiang, *J. Membr. Sci.*, 2010, **354**, 86–92.
25 K. Wang, H. P. Wu, Y. N. Meng and Z. X. Wei, *Small*, 2014, **10**, 14–31.
26 H. D. Tran, D. Li and R. B. Kaner, *Adv. Mater.*, 2009, **21**, 1487–1499.
27 W. Lei, P. He, S. S. Zhang, F. Q. Dong and Y. J. Ma, *J. Power Sources*, 2014, **266**, 347–352.
28 S. H. Li, D. K. Huang, J. C. Yang, B. Y. Zhang, X. F. Zhang, G. Yang, M. K. Wang and Y. Shen, *Nano Energy*, 2014, **9**, 309–317.
29 X. H. Xia, D. L. Chao, Z. X. Fan, C. Guan, X. H. Cao, H. Zhang and H. J. Fan, *Nano Lett.*, 2014, **14**, 1651–1658.
30 Y. Kiya, A. Iwata, T. Sarukawa, J. C. Henderson and H. D. Abruna, *J. Power Sources*, 2007, **173**, 522–530.

31 M. M. Sun, S. C. Zhang, T. Jiang, L. Zhang and J. H. Yu, *Electrochem. Commun.*, 2008, **10**, 1819–1822.

32 W. Zheng, J. M. Razal, P. G. Whitten, R. Ovalle-Robles, G. G. Wallace, R. H. Baughman and G. M. Spinks, *Adv. Mater.*, 2011, **23**, 2966–2970.

33 A. Liu, L. Zhao, H. Bai, H. X. Zhao, X. H. Xing and G. Q. Shi, *ACS Appl. Mater. Interfaces*, 2009, **1**, 951–955.

34 S. Brahim, D. Narinesingh and A. Guiseppi-Elie, *Biosens. Bioelectron.*, 2002, **17**, 53–59.

35 Y. C. Tsai, S. C. Li and S. W. Liao, *Biosens. Bioelectron.*, 2006, **22**, 495–500.

36 J. D. Kwon, P. H. Kim, J. H. Keum and J. S. Kim, *Sol. Energy Mater. Sol. Cells*, 2004, **83**, 311–321.

37 J. P. Singh, U. Saha, R. Jaiswal, R. S. Anand, A. Srivastava and T. H. Goswami, *J. Nanopart. Res.*, 2014, **16**, 2693.

38 C. R. Martin, L. S. Van Dyke, Z. H. Cai and W. B. Liang, *J. Am. Chem. Soc.*, 1990, **112**, 8976–8977.

39 H. J. Ding, M. X. Wan and Y. Wei, *Adv. Mater.*, 2007, **19**, 465–469.

40 Y. Zhu, D. Hu, M. X. Wan, L. Jiang and Y. Wei, *Adv. Mater.*, 2007, **19**, 2092–2096.

41 M. Ikegame, K. Tajima and T. Aida, *Angew. Chem., Int. Ed.*, 2003, **42**, 2154–2157.

42 J. Li, H. Q. Tang, A. Q. Zhang, X. T. Shen and L. H. Zhu, *Macromol. Rapid Commun.*, 2007, **28**, 740–745.

43 M. Chen, X. L. Fang, S. H. Tang and N. F. Zheng, *Chem. Commun.*, 2012, **48**, 8934–8936.

44 M. J. Antony and M. Jayakannan, *J. Phys. Chem. B*, 2007, **111**, 12772–12780.

45 N. Nuraje, K. Su, N. Yang and H. Matsui, *ACS Nano*, 2008, **2**, 502–506.

46 C. Li, H. Bai and G. Q. Shi, *Chem. Soc. Rev.*, 2009, **38**, 2397–2409.

47 M. X. Wan, *Adv. Mater.*, 2008, **20**, 2926–2932.

48 H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426–430.

49 M. E. Lynge, R. van der Westen, A. Postma and B. Städler, *Nanoscale*, 2011, **3**, 4916–4928.

50 N. K. Guimard, N. Gomez and C. E. Schmidt, *Prog. Polym. Sci.*, 2007, **32**, 876–892.

51 R. Ravichandran, S. Sundarrajan, J. R. Venugopal, S. Mukherjee and S. Ramakrishna, *J. R. Soc., Interface*, 2010, **7**, 559–579.

52 S. Nambiar and J. T. W. Yeow, *Biosens. Bioelectron.*, 2011, **26**, 1825–1832.

53 E. D. Giglio, M. R. Guascito, L. Sabbatini and G. Zambonin, *Biomaterials*, 2001, **22**, 2609–2616.

54 S. Sirivisoot, R. Pareta and T. J. Webster, *Nanotechnology*, 2011, **22**, 085101.

55 T. Kawaia, C. Ohtsukia, M. Kamitakaharaa, T. Miyazakib, M. Taniharaa, Y. Sakaguchic and S. Konagaya, *Biomaterials*, 2004, **25**, 4529–4534.

56 T. Miyazaki, M. Imamura, E. Ishida, M. Ashizuka and C. Ohtsuki, *J. Mater. Sci.: Mater. Med.*, 2009, **20**, 157–161.

57 I. A. Kim and S. H. Rhee, *J. Biomater. Sci., Polym. Ed*, 2010, **21**, 1127–1141.

58 K. L. Kilpadi, P. L. Chang and S. L. Bellis, *J. Biomed. Mater. Res.*, 2001, **57**, 258–267.

59 K. M. Woo, J. Seo, R. Zhang and P. X. Ma, *Biomaterials*, 2007, **28**, 2622–2630.

60 H. Yuan, Y. Li, J. D. de Bruijn, K. de Groot and X. Zhang, *Biomaterials*, 2000, **21**, 1283–1290.

61 T. Kokubo, *Biomaterials*, 1991, **12**, 155–163.

62 T. Kokubo and H. Takadama, *Biomaterials*, 2006, **27**, 2907–2915.

63 A. Oyane, H. M. Kim, T. Furuya, T. Kokubo, T. Miyazaki and T. Nakamura, *J. Biomed. Mater. Res., Part A*, 2003, **65**, 188–195.