Fabrication of electroactive liquid core-**TANI** shell microcapsules by self-assembly on Pickering emulsion surfaces

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ABSTRACT

Electroactive microcapsules with solid oligomeric shell have been successfully prepared during a dialysis process. In this one-pot method, Pickering emulsion template and self-assembly technology are combined. The CV characterization shows the obtained microcapsules exhibit the unique redox electrochemistry for pure tetra(aniline) (**TANI**). The SEM results reveal that an oil-in-water emulsion stabilized by carboxylic acid doped **TANI** (HAc-**TANI**) particles, i.e. Pickering emulsion, forms at the beginning of dialysis. The FT-IR and UV-vis spectra analysis shows that then the assembled particles are locked by the self-assembly of HAc-**TANI** molecules on Pickering emulsion surfaces via electrostatic interactions and π-π stacking interactions. The obtained air-dried electroactive microcapsules with robust oligomeric shell can retain their integrity. Therefore, they become more suitable for encapsulating hydrophobic functional molecules in industry applications.

1. Introduction

The formation of well-defined micro/nanostructures of conducting polymers continues to attract considerable attention in recent years [1–3]. Among the family of conducting polymers, the well-known poly(aniline) (**PANI**) has been extensively applied to many areas such as chemical sensors, energy storage, and anticorrosion due to its unique acid/base, redox electrochemical properties [3–5]. Oligo(aniline)s are a class of conjugated oligomeric materials that act as model compounds of the **PANI** [6–10]. These conjugated oligomeric materials have attracted increasing interest because they not only retain the unique optical and electrical properties of **PANI**, but also possess excellent solubility and well-defined molecular structures [11–14].

Recently, microcapsules have attracted growing attention due to their potential applications in encapsulation and the delivery of active ingredients [15–17]. Owing to their unique electroactive properties, conducting polymers, especially **PANI** and oligoanilines, have been used as shell materials to render microcapsules electrical properties [18,19]. Up to now, electroactive microcapsules have been successfully fabricated by the self-assembly of multiblock polymers or oligomers as well as that of carboxylic acid doped oligomers [20,21]. However, the mechanical strength of conducting microcapsules is low [21,22], making them fragile and unsuitable for many industry applications.

Recently, Pickering emulsion has been proved to be a feasible and effective approach for the fabrication of controllable microcapsules with defined mechanical strength [23]. However, compared with other particles such as silica nanoparticles [24] and carbon nanotubes [25], conducting polymers served as effective Pickering emulsifiers are sparsely reported.

In the previous works, we have successfully fabricated electroactive microcapsules featured with pH-response and nanocapsules with potential-response via self-assembly [20,21]. However, the mechanical strength of microcapsules obtained only by self-assembly of phenyl/amine end-capped tetra(aniline) (**TANI**) molecules was not sufficiently high. In the present work, electroactive and rigid **TANI** microcapsules are fabricated by the self-assembly of HAc-**TANI** molecules on oil-in-water Pickering emulsions surfaces where HAc-**TANI** particles are served as Pickering emulsifiers. The final structures of air-dried microcapsules with electroactive robust oligomeric shell can be preserved.

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2. Experiment work

2.1. Materials

All chemicals were from Tianli Chemical Reagent Co. Ltd except for *N*-Phenyl-1,4-phenylenediamine from Aldrich Chemical Co. Ltd. All chemicals were used as received.

The synthetic route of Ph/NH$_2$ **TANI** in emeraldine base (EB) state (**TANI**-EB) has been reported in previous literature [20,21]. The characterization of **TANI** is shown in the SI, Figs. S1, S2 and Table S1.

2.2. Preparation of microcapsules

A solvent mixture of glacial acetic acid (HAc) (4.0 ml) and cyclohexane (1.0 ml) was added to **TANI** powder (2.0 mg). The mixture was sonicated for 5 min and a small amount of granular precipitated at the bottom of the vial. Then the whole mixture placed into a dialysis bag (3500 MW cutoff, Viskase) was dialyzed against deionized water under magnetic stirring. The dialysis process did not finish until the pH of the outer deionized water was 7. The obtained robust microcapsule was labeled as **R-Micro**. For comparison, three other control experiments were also carried out via the same dialysis process but without the precipitated granular

(**F-Micro**), without the addition of cyclohexane (**R-Nano**), and without the precipitated granular and cyclohexane (**F-Nano**), respectively.

2.3. Characterization

^{1}H NMR experiment was performed using a 400 MHz Varian VNMR 400 NMR spectrometer. High-resolution mass spectrometry was performed using MicrOTOF II (ESI-TOF) mass spectrometer. Powder X-ray diffraction (XRD) patterns of **TANI**-EB sample was taken on a Rigaku Dmax-RA with a scan rate of 4° min^{-1}. A L2020 Optical microscope (OM) was used to observe the fabricated microcapsules. Scanning electron microscopy (SEM) images were performed on a JEOL JSM-6390A Field Emission Scanning Electron Microscope, and Transmission electron microscopy (TEM) was taken in a JEM model 2100 electron microscope. SEM and TEM samples were prepared by casting a drop of the final solution onto a silicon wafer or a carbon-coated copper grid to dry in air. Dynamic light scattering (DLS) was carried out on a Malvern Zetasize Nano ZS90 apparatus. UV–vis spectra were obtained using an Agilent 8453 spectrophotometer. FT-IR spectra were recorded on a Bruker, TENSOR37 infrared spectrometer. A CHI 660D electrochemical workstation with three electrode cell was used to characterize the electroactive of final solution, i.e. Cyclic
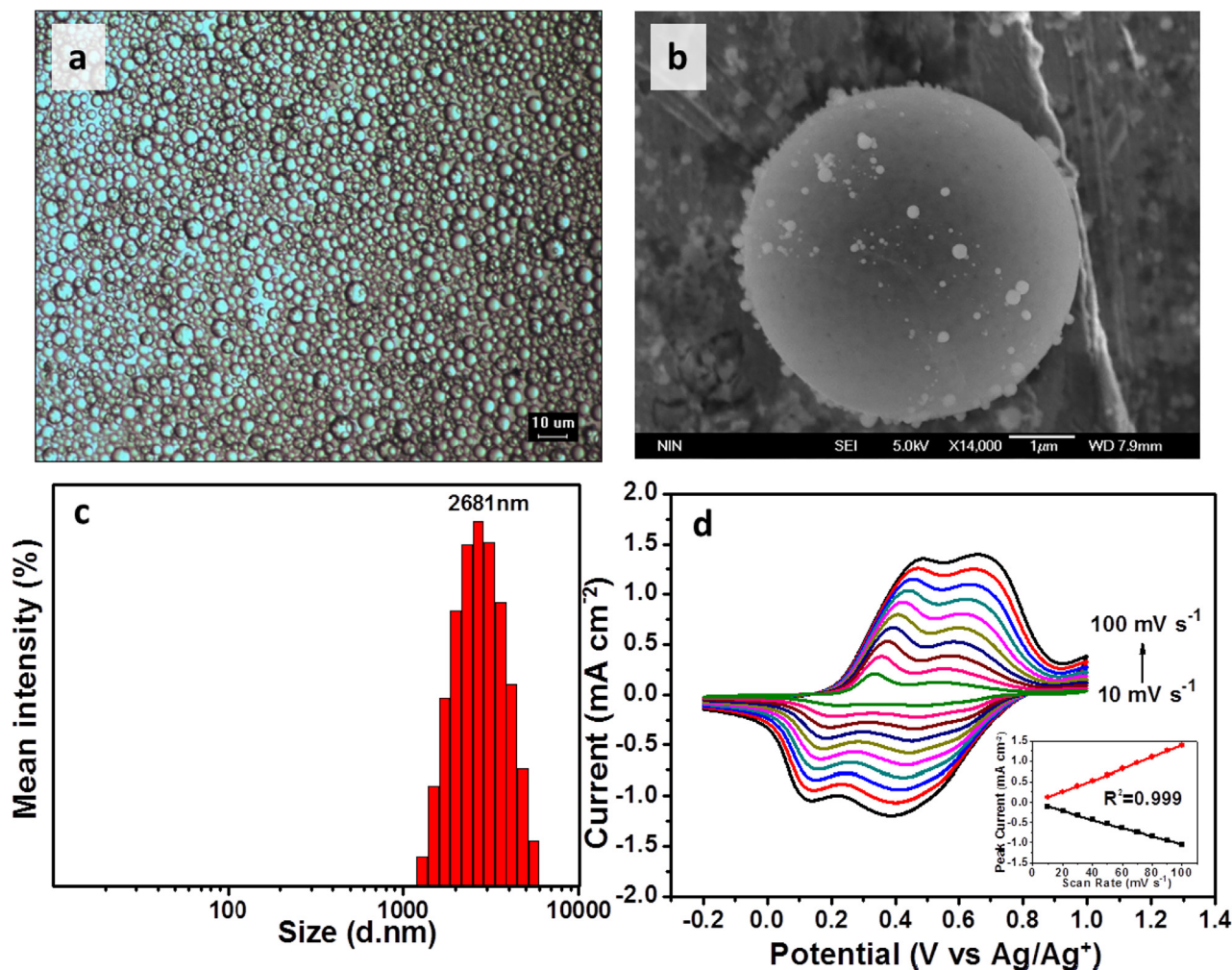

Fig. 1. Optical (a), SEM (b) images, particle size distribution (c), and cyclic voltammetry (in 1.0 M H$_2$SO$_4$ at different potential scan rates: 10–100 mV s^{-1}) of **R-Micro**, with inset showing the relationships between the oxidation and reduction peak current vs. potential scan rate (d).

voltammetry (CV). The reference electrode was Ag/AgCl, counter electrode was Pt foil and working electrode was FTO glass from Pilkington, where the surface was casted by final solution.

3. Results and discussion

According to our previous report, the as-synthesized **TANI**-EB powder exhibited an amorphous morphology (See X-ray data in Fig. S3) [20,21]. However, microcapsules (**R-Micro**) with average diameter of about 2.7 μm are successfully formed by dialyzing the whole mixture against deionized water in this work (Fig. 1). Moreover, the microcapsules are stable after drying in air and even after being exposed to high vacuum and energy during SEM characterization (Fig. 1b). In Fig. 1d, there are two pairs of redox peaks in the CV curve of **R-Micro** sample. Among them (at a scan rate of 100 mV s^{-1}), peak located at 0.391 V vs Ag/AgCl corresponds to the reduction from pernigraniline (PA) state to EB state, with another one at 0.136 V attributing to the reduction from EB state to leucoemeraldine base (LEB) state for simple **TANI** materials [26]. This indicates that the gained microcapsules retain the unique electroactive property of **TANI**. In addition, from inset of Fig. 1d, we can note a liner dependence of the peak currents, as a function of scan rates in the region of 10–100 mV s^{-1}, suggesting that the electrochemical activity of **R-Micro**/FTO electrode is a surface controlled process and the formed film is well-adhered. More CV characterizations of **R-Micro** sample can be seen in Figs. S4 and S5 .

Several ruptured microcapsules were selected to investigate the morphology of the shell. As the red arrows shown in Fig. 2B and C, the surface of the microcapsule is completely absorbed with particles which are most likely cross-linked together by the HAc-**TANI** molecules. In Fig. 2C, the broken microcapsule shows that the interior is hollow and it provides strong evidence that particles adsorbed at the oil-water interface. In terms of the smaller microcapsule existed in the inner of the microcapsule, we

conjecture that it may be swept into the interior during the SEM characterization.

A possible formation mechanism of **R-Micro** is proposed as shown in Fig. 2D. **TANI**-EB can be doped and soluble in HAc. However, **TANI** in the HAc-doped emeraldine salt state is less soluble (HAc-**TANI** molecules) in the excess HAc and partly precipitate (HAc-**TANI** particles) from solution. Therefore, the initial system consists of a mixture of cyclohexane, excess HAc, HAc-soluble HAc-**TANI** molecules and some precipitated HAc-**TANI** particles. At the beginning of dialysis process, with the water diffusing into the system, considerable oil-in-water emulsions form. At this time, due to its amphiphilic behavior (the doped HAc-**TANI** ES consists of the hydrophobic conjugated backbone and hydrophilic-COOH groups), HAc-**TANI** particles served as surfactants coat the oil droplet-water interface to reduce the total interfacial energy. i.e., forming the Pickering emulsion (Fig. 2a) [27].

In order to verify that Pickering emulsifiers consist of HAc-**TANI** particles, the microcapsules and nanocapsules obtained in the control experiments are analyzed. In our previous report [6], without the addition of the precipitated granular and cyclohexane, HAc-**TANI** molecules can self-assemble into nanocapsules in virtue of the dialysis process (**F-Nano**) (Fig. 3b and c). Compared with the **F-Nano**, a great quantity of smaller solid particles, i.e. HAc-**TANI** particles, are obtained for **R-Nano** (Fig. 3a and c). Accordingly, compared to microcapsules with relative smooth shell (**F-Micro**) self-assembled by HAc-**TANI** molecules on the oil-in-water emulsion interface without HAc-**TANI** particles [21], the smaller solid HAc-**TANI** particles, served as the Pickering emulsifiers, adsorb on the interface of oil-in-water emulsion in **R-Micro**.

As dialysis continues, a volume of HAc are replaced with water, resulting in HAc-soluble, water-insoluble HAc-**TANI** molecules precipitate (Fig. 2b) and self-assemble (Fig. 2c) on the Pickering emulsion surfaces. Some reports indicate that well-defined
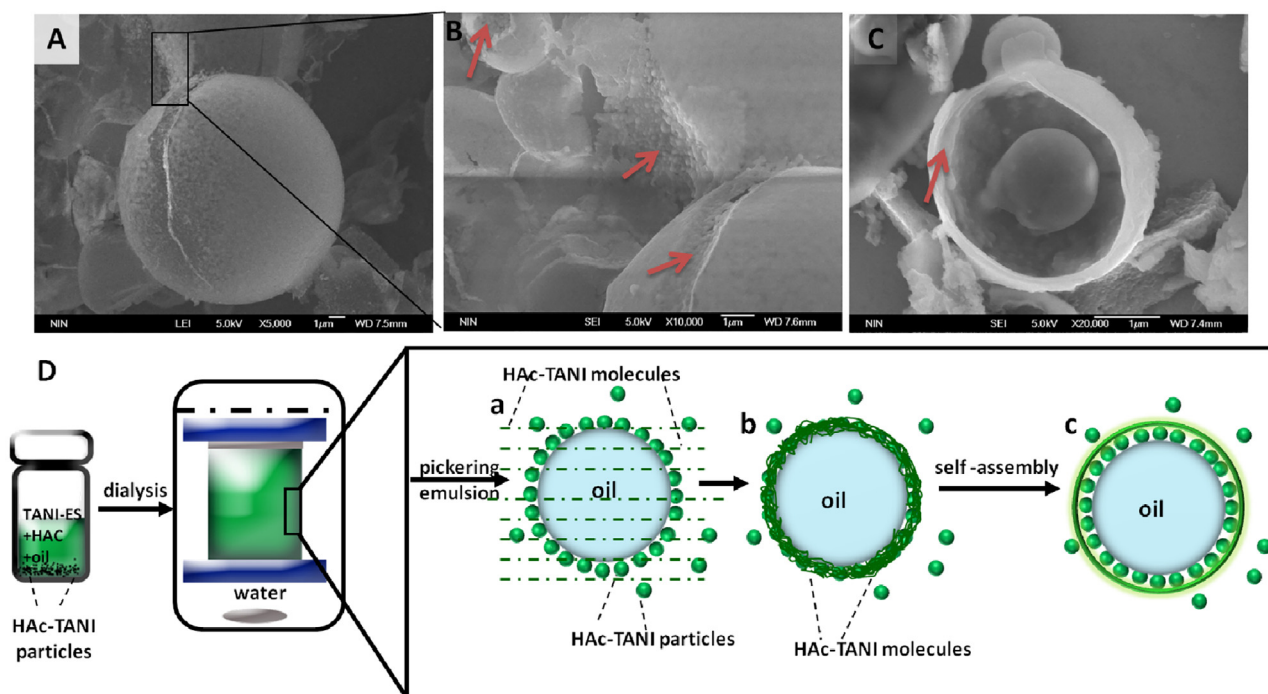

Fig. 2. SEM images of ruptured microcapsules (A, B, C) and schematic of the electroactive **R-Micro** formation by self-assembly of HAc-**TANI** molecules on Pickering emulsion surfaces (D).
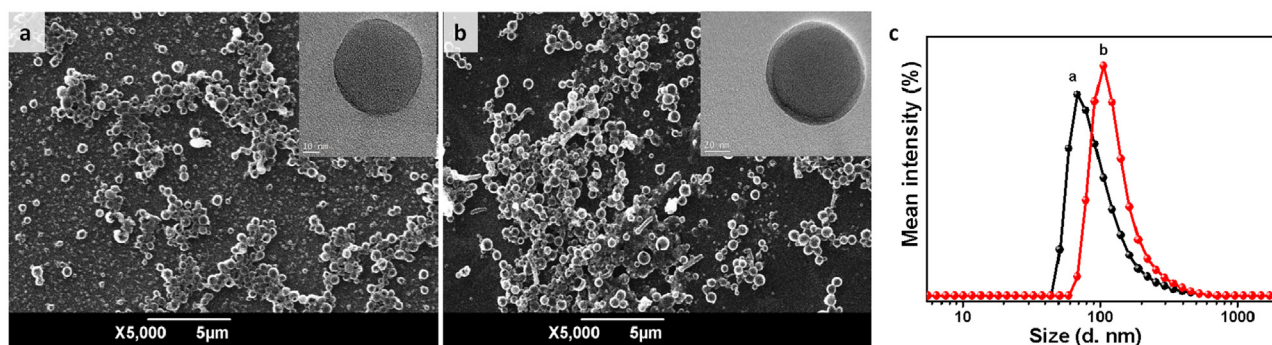
Fig. 3. SEM images of **R-Nano** (a) and **F-Nano** (b) and particle size distribution of them (c). Insets: TEM images of nanoparticles with the average diameter of 50 nm in **R-Nano** and **F-Nano**.
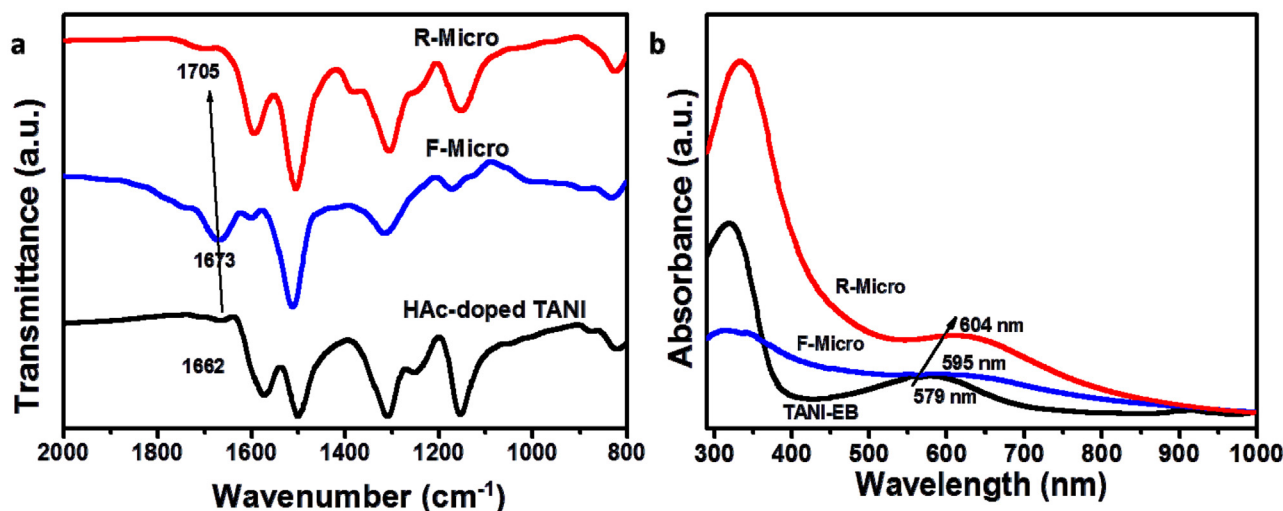

Fig. 4. (a) FT-IR spectra of **R-Micro**, **F-Micro** and pure HAc-doped **TANI** and (b) UV–vis spectra of **R-Micro**, **F-Micro** and as-synthesized **TANI**-EB.

nanostructures and hierarchical microstructures can be formed by self-assembly of oligo(aniline)s, i.e. π-conjugated molecules, via intermolecular interactions, such as ionic interactions, π-π stacking, and hydrogen bonds [28]. As shown in Fig. 4a, the main peaks in the FT-IR spectrum of **R-Micro** at 1593 and 1504 cm^{-1} are ascribed to C=C stretching vibrations of quinone and benzene ring in **TANI**-EB, respectively [22]. The peak located at 1662 cm^{-1} in the pure HAc-doped **TANI**, attributing to the stretching vibrations of the carbonyl group, is shifted by $\Delta k = 11\ cm^{-1}$ and 43 cm^{-1} in the **F-Micro** and **R-Micro**, respectively. It suggests that more carboxylic ions acted as dopant counter ions exist in **R-Micro** sample, i.e. more electrostatic interactions form [21]. In addition, as shown in Fig. 4b, the main characteristic bands in the UV–vis spectrum of **R-Micro** located at 331 nm and 604 nm are corresponded to π-π* transitions of the benzene ring and the benzenoid to quinoid (π_B-π_Q) excitonic transition in **TANI**-EB, respectively [22]. The π_B-π_Q absorption band of the obtained **R-Micro** locates at 604 nm, which is bathochromic shifted by $\Delta\lambda = 9$ nm and 25 nm compared with that of **F-Micro** and as-synthesized **TANI**, respectively. It indicates that π-π stacking interaction in **R-Micro** sample is stronger than that in **F-Micro** sample because more HAc-**TANI** Pickering emulsifiers exist in **R-Micro** sample [22].

4. Conclusions

In summary, a novel and efficient strategy has been developed to prepare electroactive and rigid liquid core-**TANI** shell microcapsules in a simple dialysis process. Firstly, HAc-**TANI** particles served as Pickering emulsifiers absorb on oil-in-water emulsions and then are cross-linked by the self-assembly of HAc-**TANI** molecules. The formed robust electroactive microcapsules have great potential to be applied for encapsulating hydrophobic actives for many industrial uses. Furthermore, the proposed method is being explored to fabricate other conducting oligomers based microcapsules. The release strategy is also an interesting issue under investigation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.synthmet.2017.02.019.

References

[1] G.J. Summers, U.S. Waware, M.R. Maduwa, C.A. Summers, Conducting polyaniline nanorods doped with aromatic carboxyl chain end functionalized polystyrene, Synth. Met. 209 (2015) 251–261.

[2] K. Krukiewicz, A. Katunin, The effect of reaction medium on the conductivity and morphology of polyaniline doped with camphorsulfonic acid, Synth. Met. 214 (2016) 45–49.

[3] D.S. Correa, E.S. Medeiros, J.E. Oliveira, L.G. Paterno, L.H.C. Mattoso, Nanostructured conjugated polymers in chemical sensors: synthesis, properties and applications, J. Nanosci. Nanotechnol. 14 (2014) 6509–6527.

[4] I. Shown, A. Ganguly, L.C. Chen, K.H. Chen, Conducting polymer-based flexible supercapacitor, Energy Sci. Eng. 3 (2015) 2–26.

[5] Y.Y. Zhao, Z.M. Zhang, L.M. Yu, Corrosion protection of carbon steel by electrospun film containing polyaniline microfibers, React. Funct. Polym. 102 (2016) 20–26.

[6] I. Kulszewicz-Bajer, I. Rozalska, M. Kurylek, Synthesis and spectroscopic properties of aniline tetramers. Comparative studies, New J. Chem. 28 (2004) 669–675.

[7] I. Rozalska, P. Kulyk, I. Kulszewicz-Bajer, Linear 1,4-coupled oligoanilines of defined length: preparation and spectroscopic properties, New J. Chem. 28 (2004) 1235–1243.

[8] Z. Wei, C.F.J. Faul, Aniline oligomers-architecture, function and new opportunities for nanostructured materials, Macromol. Rapid Commun. 29 (2008) 280–292.

[9] Y. Wang, H.D. Tran, L. Liao, X. Duan, R.B. Kaner, Nanoscale morphology dimensional control, and electrical properties of oligoanilines, J. Am. Chem. Soc. 132 (2010) 10365–10373.

[10] Y. Wang, J. Liu, H.D. Tran, M. Mecklenburg, X.N. Guan, A.Z. Stieg, B.C. Regan, D.C. Martin, R.B. Kaner, Morphological and dimensional control via hierarchical assembly of doped oligoaniline single crystals, J. Am. Chem. Soc. 134 (2012) 9251–9262.

[11] O.A. Bell, G. Wu, J.S. Haataja, F. Brömmel, N. Fey, A.M. Seddon, R.L. Harniman, R. M. Richardson, O. Ikkala, X. Zhang, C.F.J. Faul, Self-assembly of a functional oligo(aniline)-based amphiphile into helical conductive nanowires, J. Am. Chem. Soc. 137 (2015) 14288–14294.

[12] W. Lyu, J. Feng, W. Yan, C.F.J. Faul, Self-assembly of tetra(aniline) nanowires in acidic aqueous media with ultrasonic irradiation, J. Mater. Chem. C 3 (2015) 11945–11952.

[13] C.U. Udeh, N. Fey, C.F.J. Faul, Functional block-like structures from electroactive tetra(aniline) oligomers, J. Mater. Chem. 21 (2011) 18137.

[14] J.O. Thomas, H.D. Andrade, B.M. Mills, N.A. Fox, H.J.K. Hoerber, C.F.J. Faul, Imaging the predicted isomerism of oligo(aniline)s: a scanning tunneling microscopy study, Small 11 (2015) 3430–3434.

[15] M. Karthikeyan, T. Ramachandran, Review of thermal energy storage of micro- and nanoencapsulated phase change materials, Mater. Res. Innov. 18 (2014) 541–554.

[16] B. Andrade, Z. Song, J. Li, S.C. Zimmerman, J. Cheng, J.S. Moore, K. Harris, J.S. Katz, New frontiers for encapsulation in the chemical industry, ACS Appl. Mater. Interfaces 7 (2015) 6359–6368.

[17] J. Shi, Y. Jiang, X. Wang, H. Wu, D. Yang, F. Pan, Y. Su, Z. Jiang, Design and synthesis of organic-inorganic hybrid capsules for biotechnological applications, Chem. Soc. Rev. 43 (2014) 5192–5210.

[18] H. Kim, S.M. Jeong, J.W. Park, Electrical switching between vesicles and micelles via redox-responsive self-assembly of amphiphilic Rod-coils, J. Am. Chem. Soc. 133 (2011) 5206–5209.

[19] Y. Wu, S. Liu, Y. Tao, C. Ma, Y. Zhang, J. Xu, Y. Wei, New strategy for controlled release of drugs. potential pinpoint targeting with multiresponsive tetraaniline diblock polymer vesicles: site-directed burst release with voltage, ACS. Appl. Mater. Interfaces 6 (2014) 1470–1480.

[20] W. Lv, J. Feng, W. Yan, Electrochemical potential-responsive tetra(aniline) nanocapsules via self-assembly, RSC Adv. 5 (2015) 27862–27866.

[21] W. Lv, J. Feng, W. Yan, C.F.J. Faul, Self-assembly and pH response of electroactive liquid core-tetra(aniline) shell microcapsules, J. Mater. Chem. B 2 (2014) 4720–4725.

[22] Z. Yang, X. Wang, Y. Yang, Y. Liao, Y. Wei, X. Xie, Synthesis of electroactive tetraaniline-PEO-tetraaniline triblock copolymer and its self-assembled vesicle with acidity response, Langmuir 26 (2010) 9386–9392.

[23] Z. Ao, Z. Yang, J. Wang, G. Zhang, T. Ngai, Emulsion-templated liquid core-polymer shell microcapsule formation, Langmuir 25 (2009) 2572–2574.

[24] Y. He, X. Yu, Preparation of silica nanoparticle-armored polyaniline microspheres in a Pickering emulsion, Mater. Lett. 61 (2007) 2071–2074.

[25] W. Chen, X. Liu, Y. Liu, H.-I. Kim, Novel synthesis of self-assembled CNT microcapsules by O/W Pickering emulsions, Mater. Lett. 64 (2010) 2589–2592.

[26] D. Chao, S. Wang, R. Yang, E. Berda, C. Wang, Synthesis and properties of multifunctional poly(amic acid) with oligoaniline and fluorene groups, Colloid Polym. Sci. 291 (2013) 2631–2637.

[27] L. Zhang, M. Wan, Self-assembly of polyaniline-from nanotubes to hollow microspheres, Adv. Funct. Mater. 13 (2003) 815–820.

[28] Y. Yan, R. Wang, X. Qiu, Z. Wei, Hexagonal superlattice of chiral conducting polymers self-assembled by mimicking β-Sheet proteins with anisotropic electrical transport, J. Am. Chem. Soc. 132 (2010) 12006–12012.