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Electrochemical potential-responsive tetra(aniline) nanocapsules *via* self-assembly

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A simple and effective approach is developed to obtain electroactive TANI nanocapsules *via* self-assembly. The carboxylic acid doped TANI molecules can self-assemble into nanocapsules through a simple dialysis process. The average diameter of the nanocapsules can be tuned using hydrophilic dopant acids with different alkyl lengths. Furthermore, those electroactive nanocapsules can be disrupted by applying a reducing voltage at -0.1 V.

Introduction

Recently, polymeric vesicles and nanocapsules prepared by selfassembly techniques have attracted considerable attention in the applications of active ingredient encapsulation and release, ranging from delivery and release of drugs or bioactive agents,¹⁻³ diagnostic imaging,⁴ nanoreactors,^{5,6} electrical energy storage,7 and so on. One of the most attractive advantages of polymer vesicles and nanocapsules is their stimuli-responsive properties, including pH-,8 thermo-,9 redox-,10 photoresponse,11 etc. Among them, the redox-responsive disruption or reorganization of polymeric vesicles and nanocapsules can be achieved by either the addition of redox chemical additives12 or the application of electric potentials.13 Compared with the former, electrical stimulus is more favorable for application in industry and biological systems without changing the chemical composition, concentration, volume, or temperature.

Oligo(aniline)s, as the good model compounds for studying the optical, electronic, magnetic and structural properties of polyaniline (**PANI**),^{14,15} have drawn increasing academic interest in the construction of responsive polymer vesicles and nanocapsules. This interest mainly stems from the fact that the oligo(aniline)s retain the unique redox chemistry of **PANI** and possess the relatively high conductivity.¹⁶ At the same time, the well-defined chemical structure of oligo(aniline)s provides molecular engineering possibilities for design and synthesis of multiblock polymers or oligomers with oligo(aniline)s sub-units exhibiting unique electrochemical redox property.¹⁷

Among these oligo(aniline)s, phenyl-NH₂ end-capped tetra(aniline) (Ph/NH₂ TANI) is the shortest oligomer that can represent the emeraldine oxidation state. Park and co-workers18 reported electrical switching between vesicles and micelles using redox-responsive self-assembly of an amphiphile, TANI block with poly(ethylene glycol). In aqueous solution, the self-assembled vesicles could be burst to form pucklike micelles by an oxidizing voltage at 0.2 V, while the collapsed micelles could regenerate vesicles upon the application of a reducing voltage at -0.5 V. This interesting electrochemical potentialresponsive behavior could be attributed to the changes in packing density of TANI units upon oxidation to the emeraldine base (EB) state from the leucoemeraldine base (LEB) state. Another kind of voltage-responsive vesicle obtained from a diblock polymer, TANI block with poly (N-isopropylacrylamide), could be destructed completely by applying an oxidizing voltage at 0.6 V.19 A TANI-containing triblock, TANI-PEO-TANI, molecular architecture was also developed by Yang etc.²⁰ This rod-coil-rod triblock copolymer exhibited pH-dependent selfassembly behavior in water to yield vesicles with a low conductivity. Another triblock oligomer containing TANI and ethylene could also self-assemble into electroactive vesicle in THF.21

By far, reports on the electroactive vesicles and nanocapsules mainly use the self-assembly of multiblock polymers or oligomers. Unfortunately, the complex procedures for the synthesis of copolymer and the attachment of large structural (*i.e.*, functionless) blocks diluting the electroactive functionality within the bulk material make it difficult to achieve its potential application requiring a high density of electroactivity.²² Besides, few articles focus on that the amphiphilic nature of doped **TANI** molecules can make it possible to self-assemble into electroactive nanocapsules. We show that electroactive liquid core–**TANI** shell microcapsules can be obtained *via* the self-assembly of carboxylic acid doped **TANI** molecules on the

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interface of oil-water droplet in our previous report.²³ In this communication, according to the amphiphilic nature of doped Ph/NH_2 **TANI**, we report that the carboxylic acid doped **TANI** molecules can self-assemble into the electrochemical nanocapsules directly through a simple dialysis process without the addition of the oil. The average size of nanocapsules is dependent on the length of alkyl chain in the doped acid. Also, the effect of voltage on the electroactive nanocapsules is investigated.

Experimental section

Synthesis of TANI

N-Phenyl-1,4-phenylenediamine (98%) was purchased from Aldrich chemical Co. Ltd. and other chemicals were from Tianli Chemical Reagent Co. Ltd. All reagents were used as received. The synthetic route of Ph/NH₂ **TANI** in emeraldine base (EB) state (**TANI**-EB) has been reported in our previous literature.²³ MALDI-TOF-MS *m/z*: $[M + H]^+$ calcd for C₂₄H₂₀N₄, 366.2; found: 366.14. IR (KBr): 3373 (s, ν_{N-H}), 3023 (m, ν_{C-H}), 1593 (s, $\nu_{C=C}$ of quinone rings), 1502 (s, $\nu_{C=C}$ of benzenoid rings), 1301 (s, ν_{C-N}), 815 (m, δ_{C-H}).

Electroactive TANI nanocapsules via self-assembly

In a typical preparation process, 2.0 mg of fine **TANI-**EB powder was dispersed in 4.0 ml of glacial acetic acid (HAc) under ultrasonic irradiation for 5 min. Then the mixture was centrifuged at 4000 rpm for 5 min. The supernatant was collected and placed into a dialysis bag (3500 MW cutoff, Viskase). The sealed bag was suspended within a 1000 mL beaker containing deionized water under stirring to allow the acid to diffuse out of the dialysis bag until the pH of the outer deionized water stabilized at 7. The outer deionized water was renewed every 2 h for the first 10 h and then every 7 h for the remaining period of time.

Characterization

Matrix-assisted laser desorption ionization time-of-fight mass spectrometry analysis (MALDI-TOF MS) was performed on an Applied Biosystems 4700 Proteomics Analyzer. UV-Vis spectra were recorded on an Agilent 8453 instrument. FT-IR spectra of the dried samples were obtained on a Bruker, TENSOR37 infrared spectrometer with KBr pellets. Dynamic light scattering (DLS) and zeta potential measurements were carried out by using a Malvern Zetasize Nano ZS90 apparatus. SEM images were taken in JEOL JSM-6390A Field Emission Scanning Electron Microscope. The samples were prepared by casting a drop of the final solution on a silicon wafer. Transmission electron microscopy (TEM) was performed on a JEM model 2100 electron microscope. The samples were prepared by drop-casting 1 to 2 drops of the nanocapsules dispersion onto the carbon-coated copper grids and allowed to dry in air. Cyclic voltammetry (CV) was performed on a CHI 660D electrochemical work station with a conventional three electrode cell, using Ag/AgCl (3 M KCl) as the reference electrode and Pt foil as the counter electrode. The working electrode was prepared by simple

dropping the final vesicles solution onto the surface of the FTO glass. The loading of **TANI** vesicles solution on the FTO glass was 0.3 ml cm⁻². The FTO glass was obtained from Pilkington (Toledo, USA) (14 Ohm per square, thickness of 2.2 mm). CV investigations were carried out in 1.0 M H₂SO₄ solutions (degassed for 30 minutes with high purity N₂) in the range from -0.2 to 1.0 V at a scan rate of 100 mV s⁻¹.

Results and discussion

Electroactive TANI nanocapsules via self-assembly

As shown in Fig. 1, the as-synthesized **TANI-EB** powder with aggregated morphology (Fig. 1a) dissolved in HAc assembled into vesicles with average diameter of 250 nm by dialyzing the mixture against deionized water. The broken nanocapsules observed in SEM images (the arrows in Fig. 1b) and the strong contrast between the pale edge and the dark center in the TEM image (Fig. 1c) are evidence for their hollow nature. The average walls of nanocapsules are approximately 30 nm thick. Those nanocapsules collapse occurred in thinner shell area when exposed to high vacuum and energy during SEM and TEM characterization (Fig. 1b and c and 5b and c).²⁴ Therefore, it seems that the size in SEM images is slightly larger than that of hydrodynamic radius determined from DLS (Fig. 1d).

In Fig. 2, the CV curve obtained from the bare FTO glass electrode exhibits no obvious peaks, while the CV curve of the obtained nanocapsules shows two stronger redox processes. There are two reduction peaks at 0.51 V and 0.21 V *vs.* Ag/AgCl, which are attributed to the transition from pernigraniline (PA) oxidation state to EB state and EB state to LEB state, respectively.²⁵ This indicates that the obtained nanocapsules exhibit the unique redox activity which is similar to that expected for simple **TANI** materials.¹⁶



Fig. 1 Scanning electron microscope (SEM) images of the as-synthesized **TANI**-EB powder (a) and the obtained nanocapsules (b), TEM image of the obtained nanocapsules (c) and particle size distribution (d) of the final **TANI** nanocapsules.



Fig. 2 Cyclic voltammetry of bare FTO glass and the final TANI nanocapsules in 1.0 M $\rm H_2SO_4.$

Proposed formation mechanism of the electroactive TANI nanocapsules

A possible formation mechanism of the electroactive nanocapsules is shown in Fig. 3. **TANI**-EB is soluble in HAc and can be doped in this environment at the same time. Some of the formed HAc-doped **TANI** precipitated from solution, which was removed by centrifugation. The remaining homogeneous solution (HAc-doped **TANI** dissolved in the excess HAc, Fig. 3A) was placed in the dialysis bag. During the dialysis process, the excess HAc was replaced with water, resulting in the formation of nanocapsules (Fig. 3B). The driven forces for the selfassembly can be divided into three parts. Firstly, due to its hydrophilic –COOH groups from HAc and its hydrophobic conjugated backbone of **TANI**, the HAc-doped **TANI** can form micelle.^{26,27} Under the slow exchange of HAc with the water, the hydrophilic environment promotes aggregation among the hydrophobic conjugated backbone to produce self-assembly,



Fig. 3 Schematic of electroactive TANI nanocapsules formation by the self-assembly process of the amphiphilic HAc-doped TANI molecules.

whereas the hydrophilic -COOH groups are solvated by the hydrophilic solvent. The resulting aggregated regions of the TANI conjugated backbone are possibly configured at the core of the self-assembled structure. Secondly, driven by $\pi - \pi$ stacking interactions, those hydrophobic conjugated backbones interact with each other to self-assemble into the shell of nanocapsules (Fig. 3C).^{23,28-30} It can be seen from Fig. 4A, the $\pi_{\rm B}$ - $\pi_{\rm O}$ absorption of the final nanocapsules is red shifted by $\Delta\lambda$ = 16 nm compared with that of as-synthesized TANI, indicating the existence of strong π - π stacking interaction.^{21,23} Besides, the electrostatic interactions introduced by the dopants can also serve as one of the important driving forces for the selfassembly.³¹ As shown in Fig. 4B, a strong peak attributed to the stretching vibrations of the carbonyl group is located at 1662 cm⁻¹ in the pure HAc-doped TANI, which is shifted to 1708 cm⁻¹ in the final nanocapsules.³² This indicates that the carboxylic groups exist in the final TANI molecules. Thus, the carboxylic ions act as dopant counter ions that reside near the positively charged nitrogen atoms during the dialysis process, leading to the formation of electrostatic interactions. When the dialysis finished, the TANI in emeraldine salt (ES) state was dedoped into EB state (Fig. 3D), as the UV-Vis and FT-IR characterization of the final nanocapsules shown in Fig. 4. Interesting, the carbonyl groups still exist in the molecular structure of final nanocapsules. Combined with the shift in the C=O stretching frequency in FT-IR spectra, we deduce that the double bond of the carbonyl groups are in conjugation with π -bonded system of TANI.³³

Size control of the nanocapsules

The diameter of the aggregates assembled nanocapsules can be readily tuned using different alkane length of carboxylic acid which is related to hydrophobicity of the dopant aliphatic chain. The average diameter of nanocapsules increases with the increase in the length of hydrophilic dopant acid (Fig. 5). The average diameter of nanocapsules obtained using acetic acid is



Fig. 4 (A) UV-Vis spectra of (a) the final nanocapsules, and (b) as-synthesized TANI dissolved in dimethyl sulfoxide without the solvatochromism effect on the $\pi_B - \pi_{\Omega}$ absorption peak: in the UV-Vis spectra of final nanocapsules, the main characteristic bands located at 317 nm and 591 nm are ascribed to $\pi - \pi^*$ transitions of the benzene ring and the benzenoid to quinid ($\pi_B - \pi_{\Omega}$) excitonic transition in TANI-EB, respectively;²¹ (B) FT-IR spectra of the as-synthesized TANI-EB powder, the final nanocapsules and pure HAc-doped TANI: the main peaks in the FT-IR spectra of the final nanocapsules located at 1593 and 1502 cm⁻¹ are corresponded to C=C stretching vibrations of quinone and benzene ring in TANI-EB, respectively.²¹



Fig. 5 SEM images and particle size distributions of nanocapsules prepared using acetic acid (a), propionic acid (b) and butyric acid (c) as dopants.

around 250 nm. When propionic acid was used, nanocapsules with an average diameter of 325 nm were well dispersed in solution. The average diameter of nanocapsules furthermore increased to 483 nm when butyric acid was the dopants. This interesting phenomenon further supports the mechanism proposed above.

Electrochemical potential-responsive property of TANI nanocapsules

The electrochemical-responsive behavior of **TANI** nanocapsules were further investigated in both NaCl and H_2SO_4 aqueous solution. The final **TANI** nanocapsules were casted on the surface of FTO glass as the working electrode, Ag/AgCl as the reference electrode and Pt foil as the counter electrode. V_{red}



Fig. 6 CV curves of final TANI nanocapsules before (a) and after (b) being electrochemically reduced at -0.1 V for 4 h in 0.5 M NaCl (A) and 1.0 M H₂SO₄ (B) electrolyte; SEM images of TANI nanocapsules after being electrochemically reduced at -0.1 V for 4 h in 0.5 M NaCl (C) and 1.0 M H₂SO₄ (D).

(-0.1 V) was the static potential applied to the aqueous for 4 h. As we can see from the SEM images in Fig. 6, the nanocapsules being electrochemically reduced in both NaCl and H₂SO₄ aqueous were destroyed and partially collapsed to form disk aggregates (Fig. 6C and D). Literature report indicates that the conductivity of corresponding electrolytes system, *i.e.*, the individual ions, plays a curial role in electrochemical response.³⁴ It means that the doping of H⁺ makes TANI more electroactive than Na⁺, resulting in the differences of CV curves obtained in two different electrolytes. Moreover, TANI exhibits unique reversibly oxidation-reduction chemistry property in acid solution.14,16 Therefore, there are two redox pairs in the CV curve of the obtained nanocapsules in H₂SO₄ solution but one pair in NaCl electrolyte. Interestingly, a new irreversible oxidation peak (0.098 V in NaCl aqueous and 0.257 V in H₂SO₄ aqueous) appears in both CV curves obtained using two different electrolytes, which might due to the reduction of TANI nanocapsules. However, this new band could not be attributed to the transition from LEB state to EB state because there are still two pairs of redox peaks in H_2SO_4 aqueous (Fig. 6B). Unfortunately, there are no reports on this peak in the electrochemistry of oligo(aniline)s, and the possible mechanism is under investigation.

Conclusions

In summary, novel electroactive **TANI** nanocapsules can be obtained *via* self-assembly during a simple dialysis process. The amphiphilic feature, π -conjugation and electrostatic interactions of carboxylic acid doped **TANI** molecules make them self-assemble into nanocapsules for slow exchange of carboxylic acid with the water. The morphology of the obtained nanocapsules can be controlled by the alkyl length of carboxylic acid. In particular, without using any chemical additives, the electrochemical potential response makes nanocapsules a potential carrier for the burst release. Besides, this new strategy for electroactive nanocapsules *via* self-assembly may be applied to other conducting oligomers like oligo(pyrrole)s.

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