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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

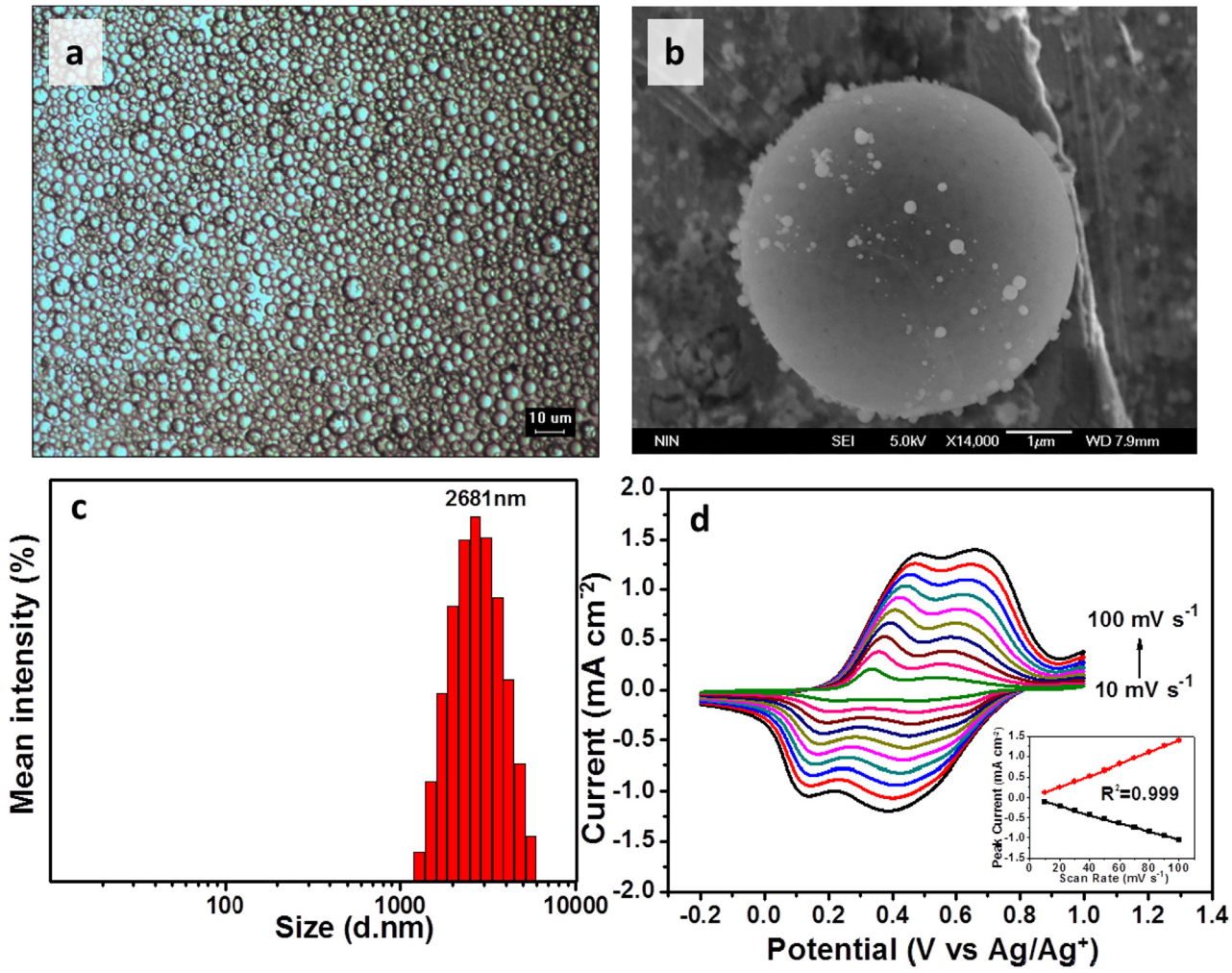

Fig. 1. Optical (a), SEM (b) images, particle size distribution (c), and cyclic voltammetry (in 1.0 M H_2SO_4 at different potential scan rates: 10–100 mV s^{-1}) of **R-Micro**, with inset showing the relationships between the oxidation and reduction peak current vs. potential scan rate (d).