



Synthesis and assembly of oligoaniline for hierarchical structures within stable and mild acid system



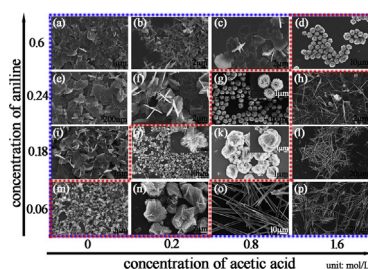
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HIGHLIGHTS

- Simple approach to fabricate OANI superstructures with controllable morphology.
- Stable pH value to form the uniform morphologies.
- Investigate the forming mechanism for the complex morphologies of OANI.

GRAPHICAL ABSTRACT



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ABSTRACT

Oligoanilines (OANI) with hierarchical structures were synthesized via chemical oxidative polymerization within a stable weak-acid system. Acetic acid was used as the buffer and dopant, and low concentration of ammonium peroxydisulfate (APS) and aniline were added to tune the pH value and to obtain different morphologies. With the pH value varied from 4.26 to 4.11 to 3.26, flake-like structure, flower-like morphology consisted of dozens of nanoflakes and lath-like structure composed of parallel alignment of nanorods are produced, respectively. Under different reaction conditions, OANI with different chemical structures are formed and simultaneously assemble into hierarchical structures. The formation mechanism of these hierarchical structures is proposed. These hierarchical OANI were used as support to load Mo catalyst and flower-like OANI/Mo catalyst shows a good property in epoxidation of cyclooctene.

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1. Introduction

Polyaniline (PANI) shows excellent performances in the electronic devices [1,2], biological researches, sensor development [3], and studies on catalysis [4]. However, poor processability limits its application. An effective solution is to colloidize PANI with various structures, such as nanofiber [5], nanotube [6], and nanoparticle [7], which have been widely reported in the last decade. As research progressed, PANI with more complex morphologies [8,9], such as

leaf-like [10], flower-like [11,12], sea urchin-like [13,14], tower-like [15], have also been synthesized.

The conventional chemical oxidative polymerization of aniline is carried out in a strong acidic solution and initiated by APS. Recent studies find that the pH value of the polymerization reaction has significant influence on the morphologies and structures of obtained PANI/OANI due to protonation of the primary and secondary amines [16]. The OANI with different functional group such as phenazine, quinone-imine etc., could be acquired under alkali, neutral and mild acidic conditions [17]. These initial OANI play a decisive role in the formation of plenty of micro/nanostructures. Various chemical structures and various intermolecular interactions (such as hydrogen bonds, π - π stacking interaction, ionic interaction, hydrophobic interaction, etc.) of OANI

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lead to different micro/nanoscale morphologies [18]. The properties of micro/nanomaterials are dependent on their morphology. Understanding the formation mechanism of micro/nanoscale morphology of PANI/OANI will be helpful in improving its synthetic reproducibility, tailoring its properties and expanding its applications [19]. The pH value of weak acid, especially ranging from 4.6 to 2.5, is the key to investigate the formation mechanism of various PANI morphologies [20].

In this paper, a weak organic acid, acetic acid, was taken as buffer and dopant to control the pH value of the reaction system, and the dilute APS concentration was used to maintain the pH value of the reaction system in the scope of the mild acidic conditions. The obtained typical morphologies of OANI were analyzed in detail. The influence of reaction conditions on the morphology of the product was studied. The formation mechanism was proposed. These micro/nanostructure OANI has large specific surface area and can be used as catalyst support.

2. Experimental

2.1. Materials

Aniline (98%, Beijing Chemical Reagent Company, Beijing) was distilled under reduced pressure before use. Ammonium peroxydisulfate (98%, Alfa) was used as the oxidant. Acetic acid (99%, Beijing Chemical Reagent Company, Beijing) was used as the buffering agent and doping acid as well.

2.2. Synthesis of oligoaniline

In a typical synthesis, 5 mL (87.5 mmol) acetic acid and 0.273 mL (3 mmol) of aniline was dissolved in 30 mL deionized water under ultrasound. Then, 20 mL 0.05 M APS aqueous solution was added into the mixture. The reaction was kept at 25 °C for 12 h. The product was centrifuged, washed with 30 mL deionized water and 30 mL ethanol for three times, and finally lyophilized. Other OANI samples were prepared under the same procedure except for the concentration of acetic acid and aniline.

2.3. Preparation and catalytic test of OANI/Mo

OANI/Mo catalysts were prepared via the ligand exchange method [21]. In brief, $\text{MoO}(\text{O}_2)_2(\text{DMF})_2$ was first prepared according to the original reported [22]. Then, 0.1 g as-synthesized OANI was dispersed into 30 mL acetonitrile, and 0.2 g $\text{MoO}(\text{O}_2)_2(\text{DMF})_2$ was added into the solution. After stirring at 60 °C for 24 h, the PANI/Mo catalysts were obtained by filtration, washed with 30 mL deionized water and 30 mL ethanol, and finally dried at 40 °C for 24 h.

In a typical catalytic test, 0.05 g of the as-synthesized OANI/Mo catalyst, 0.46 mL cyclooctene, 5 mL acetonitrile and 2.5 mL H_2O_2 were added into a 25 mL round-bottom flask equipped with a condenser. The mixture was stirred at 60 °C for 12 h. After centrifuging the mixture, the supernatant was identified by Anilent 7890/5975C-GC/MSD.

2.4. Characterization

The morphologies of the products were characterized by SEM analysis. The samples were ion-sputtered with carbon and characterized with a field emission scanning electron microscopy (FESEM, SUPRA-55). Fourier transform infrared (FTIR) spectrum was measured on KBr pellets at 32 scans per spectrum at 1 cm^{-1} resolution by using a Nicolet Impact 6700. For ultraviolet–visible (UV–Vis) spectroscopy, the OANI *m*-cresol solution was measured using a

Shimadzu UV-2550 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were made on a Thermo Escalab 250Xi with a monochromatic Al $K\alpha$ X-ray source (photo energy of 1486.6 eV). Powder X-ray diffraction (XRD) measurement was carried out on a M21X X-ray diffract meter with Cu- $K\alpha$ wavelength of 0.154 nm, operating at 40 kV and 40 mA, scanning from 5 to 90 at 5° min^{-1} .

3. Results and discussion

3.1. Typical morphologies of OANI

The hierarchical structures OANI were synthesized by chemical oxidative polymerization using APS as the oxidant in the presence of acetic acid. Under different concentrations of aniline, it made a big difference in the self-assembled hierarchical structures. Fig. 1 shows the scanning electron microscopy (SEM) images of three typical structures. At high concentration of aniline (0.6 M), nanoflakes are acquired (Fig. 1a and b). These flakes are approximately 50 nm in thickness, 6–10 μm in width and length. When the concentration of aniline is reduced to 0.24 M, the flower-like microspheres are obtained (Fig. 1c and d). The microspheres are about 6 μm in diameter, and they are consisted of 20–40 pieces of nanoflakes with 80 nm in thickness. These nanoflakes randomly crossed, but all passed through the center of the microsphere. The extra-long lath-like structure is synthesized at lower aniline concentration (0.06 M, Fig. 1e and f). They are 6 μm in width, 4 μm in thickness, 90 μm in length and made up of orderly stacked nanorods (200 nm in length, 50 nm in diameter, marked with green lines in Fig. 1f).

An insight into the chemical structures of OANI samples is obtained from FTIR spectroscopy. The FTIR spectra of as-synthesized samples are presented in Fig. 2. The region between 1000 and 1700 cm^{-1} shows several characteristic peaks: 1583 cm^{-1} and 1510 cm^{-1} (C=C stretching vibrations of quinoid and benzenoid rings, respectively), 1442 cm^{-1} (skeletal C=C stretching vibration of substituted aromatic ring), 1297 cm^{-1} (C–N stretching vibration of the benzenoid ring), 1176 cm^{-1} (aromatic C–H in-plane bending vibration) [23]. The lath-like sample appears stronger absorption and a red shift at the C=C stretching vibrations of quinoid ring (1565 cm^{-1}), indicating more quinoid ring is produced. The strong peak at 1249 cm^{-1} is associated with the C–N⁺ stretching vibration in a polaron structure, indicating the much higher protonation level of the lath-like sample [24]. The peak at 1041 cm^{-1} is due to the S=O symmetric stretching, which is related with sulfate anions in the protonated formed PANI [25]. The flower-like sample and the flake sample have similar spectra. The peaks at 1413 cm^{-1} and 1209 cm^{-1} are assigned to the totally symmetric stretching of the phenazine heterocyclic ring. The shoulder at 1625 cm^{-1} is attributed to the hydrogen bonded C=O stretching vibration [26].

The peaks at 696 cm^{-1} is due to the ring out-of-plane deformation of mono-substituted phenylene ring. The peaks at 740 (flake-like, flower-like)/753 cm^{-1} (lath-like) is due to the C–H out-of-plane bending of mono-substituted phenylene ring. These indicate the samples are oligomers. The peaks at 861 (flake-like, flower-like) and 848 cm^{-1} (flower-like, lath-like) are associated with the C–H out-of-plane bending on 1,2,4-substituted rings and 1,4-substituted rings, respectively.

The peaks at 3268 cm^{-1} and 3198 cm^{-1} can be attributed to the hydrogen-bonded N–H stretching vibrations of the secondary amine owing to different types of intra- and inter-molecular hydrogen bonds, respectively. The lath-like sample has the stronger peak at 3198 cm^{-1} than 3268 cm^{-1} , indicating the presence of inter-molecular hydrogen bonds. The peaks at 3427 cm^{-1} and shoulder at 3345 cm^{-1} correspond to asymmetric and symmetric free N–H stretching vibrations, respectively. The strong peaks at 3427 cm^{-1}

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