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Short Communication

Fabrication and characterization of urchin-like polyaniline microspheres using lignosulfonate as template

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ABSTRACT

An urchin-like conducting microsphere was fabricated by synthesizing polyaniline, PANI, with lignosulfonate, LGS. FESEM images showed that this special PANI structure was controllably formed because the pure PANI presented only a nanofiber formed mat, and the PANI/LGS mixture with the ANI/LGS ratio (%) at 36/1 and 18/1 formed spheres while the PANI nanofibers lied on spherical surface, and only at 9/1 led the PANI nanofiber to stand on sphere surface in the urchin-like structure. Taking the pure PANI as a reference, the urchin-like PANI/LGS microsphere has been found to have enhanced conductivity and thermal stability.

1. Introduction

Polyaniline, PANI, has received great attention due to its excellent environmental stability, ease synthesis, tunable properties and low production cost [1–3]. Yet the PANI has been successfully fabricated in various forms, e.g. micro-/nanotubes [1–5], micro-/nanofibers [6] and micro-/nanospheres [7]. The formation of PANI in urchin-like microsphere has been recently continuously reported by some groups due to this structure benefitting drug loading [7–10]. However, it was found that all reported cases using non-biomaterials [7–10]. Since the drug delivery systems expected the biomaterials, to fabricate biomaterials-based urchin-like PANI microsphere is obviously required.

The aim of this work is to apply the biomaterial, lignosulfonate (LGS) as a template to synthesis of urchin-like PANI conducting microsphere. In terms of our previous studies, LGS has negative charges and low surface tension [11] and capable to dope PANI [12,13]. However, yet without any report on PANI/LGS formed urchin-like structure.

2. Experimental

2.1. Materials

As previous used and described in detail, the aniline, ANI, (99%) and ammonium peroxodisulfate, APS (99%) both in analytical grade reagents were used as received and all of them obtained from the Sinopharm Chemical Reagent Co., Ltd. located at Shanghai, China [4,5,12,13]. A commercial LGS-Na from Jiangmen Sugar Cane Chemical Factory, Guangdong of China, was used as received. This LGS particle has been used and introduced previously with a known averaged diameter at about 611 ± 50 nm [11]. All used chemicals were purchased from a local chemical store at Shanghai and used as received. Lab made distilled water was always used through the whole work.

2.2. Fabrication of urchin-like conducting microspheres

PANI/LGS mixture solution polymerized using 0.45 g ANI and varied LGS, e.g. 0.01–0.05 g. Initially, the ANI and LGS were subsequently dissolved in 190 ml water to form a mixed solution, then 3 ml of hydrochloride solution was

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controlled added within 15 min at 25 °C. After that, the solution polymerization was started by adding 10 ml APS solution rapidly less 30 s. After polymerization, the formed samples were dried in an oven at 100 °C for 24 h similarly as previously [4,5,12,13].

2.3. Characterization

Field emission scanning electron microscopy, FESEM, images are prepared by a JEOL JSM-6700-F field emission SEM microscope.

Transmission electron microscopy, TEM, images are performed by JEOL, JEM-2100F.

Ultraviolet–visible, UV–vis, spectra are recorded using a Lambda 35 UV–vis spectrometer, Perkin Elmer, USA.

X-ray diffraction, XRD, patterns are recorded by the Rigaku D/Max-2550 PC instrument (Rigaku, USA).

Thermal stability is characterized by NETZSCH STA-409PC (NETZSCH, Germany).

Conductivity is measured using a SDY-4 Four-Point Probe Meter (Four Dimensions, Inc. USA).

3. Results and discussions

3.1. Morphology and conductivity of PANI/LGS microsphere

The morphologies of pure PANI nanofiber and three PANI/LGS mixtures in relation to different ANI/LGS ratios were presented in Fig. 1, respectively. Observe the pure PANI appeared only a mat structure where the formed nanofibers crossed each other (Fig. 1a). Three PANI/LGS mixtures have been found to present the microsphere structure, however, the ANI/LGS ratio at 36/1 and 18/1 both showed sphere with lied PANI nanofibers on the sphere surface (Fig. 1b and c) and only at 9/1 showed a urchin-like structure because the PANI nanofibers vertical stand on the sphere surface (Fig. 1d1 and d2). This urchin-like PANI/LGS microsphere was furthermore characterized by immersing the sample in water to allow the LGS dissolved then being removed from the sphere. TEM images of this PANI microsphere were showed in Fig. 1d3 and d4. It was found that this urchin-like PANI microsphere has hollow structure. This thus indicated that the LGS is exactly a template for formation of this urchin-like hollow microsphere due to it formed the core to allow polymerized PANI nanofibers self-assembled on its surface.

The conductivity of the pure PANI nanofiber and the PANI/LGS microsphere was compared also in Fig. 1. Observe the urchin-like PANI/LGS microsphere presented the highest conductivity as compared with others suggesting the role of LGS played is also a dopant. This is known from our previous studies [12,13] and expected for application of PANI [1–3].

In terms of FESEM and TEM images (Fig. 1), a related mechanism on formation of this urchin-like conducting microsphere was therefore ascribed in Fig. 2, where the LGS particle is a seed and the PANI nanofibers were in situ synthesized and self-assembled on the LGS surface to form the urchin-like microsphere.

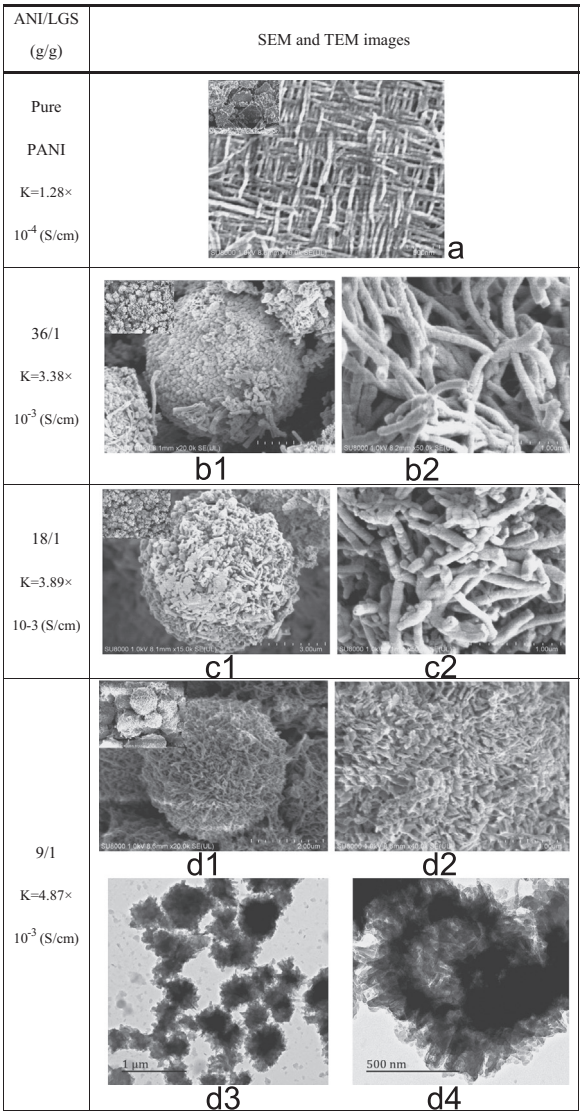

Fig. 1. SEM and TEM images of PANI/LGS conducting microspheres in relation to various ANI/LGS ratios and each related conductivity.

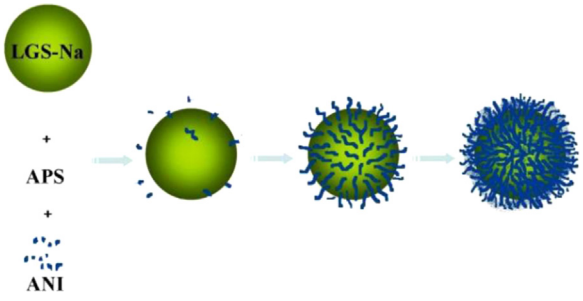

Fig. 2. Mechanism on formation of urchin-like PANI/LGS conducting microspheres.

3.2. Structure of PANI/LGS mixture

In order to understand the reason why the formed urchin-like PANI/LGS microsphere has the highest