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Ionic self-assembly of bundles of ultralong SC/MB nanobelts with enhanced electrocatalytic activity for detection of ascorbic acid

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ABSTRACT

The formation of bundles of ultralong nanobelts by an anion biological surfactant sodium cholate (SC) and a cationic dye (MB) through ionic self-assembly approach was obtained. The nanobelts possess smooth surfaces, flat end facets and solid internal structure. This one dimensional self-assembly is dominated by the π–π stacking interactions between MB molecules in concert with the hydrogen bonding between SC molecules. The shape and length of the bundles of SC/MB nanobelts could be easily controlled by changing the SC concentration and the aging temperature. Moreover, the electrocatalytic properties of the SC/MB nanobelts modified electrode were also investigated and the results indicated that the bundles of ultralong SC/MB nanobelts exhibited efficient electrocatalytic activity towards L-ascorbic acid (AA) in phosphate buffer solution (pH = 7.0). In addition, the electrostatic interaction between AA and MB also facilitates the electrons transfer on the surface of the GCE and promotes the oxidation of AA. The present work provides an alternative way to design and fabricate the ultralong 1D nanobelt structures with tunable sizes using small organic molecules. This system may also open up a way for the design and development of optical and electronic devices in the potential bio-applications and electrocatalyst for fuel cells.

1. Introduction

The self-assembly of electronically and optically active small organic molecules into well-defined nanostructures especially into one-dimensional (1D) nano/microstructures has attracted extensive research attention to the researchers. Most of the 1D nano/microstructures have a controlled and predictable fashion, such as wires, rods, belts and tubes [1–4]. The fabrication of the 1D nano/microstructures has been considered to be an important way to produce the electronic devices with next generation nanoscale, which have potential applications due to their high surface-to-volume ratios and rationally designed surfaces [5–10]. Recently, the fabrication of ultralong organic 1D nano/microstructures with the average length varing from micrometer up to millimeter scale, has been reported [7]. Surprisingly, the apparent increase in the aspect ratio of ultralong organic 1D nano/microstructures is testified to have advantage in terms of single device fabrication, which expands their applications in fields such as optical waveguides, organic light emitting diodes, photoswitching devices [11–13].

Noncovalent interactions, such as hydrogen bonding, van der Waals, π–π stacking, and electrostatic interactions, often drive the self-assembly of different kinds of organic molecules to form ultralong organic 1D nano/microstructures [14,15]. Self assembly of biomolecules into these types of functional nanostructures has been identified as an efficient way to create nanoarchitectures with potential applications in biomimetics, biomedicine, optical waveguides and bionanotechnology [16–18]. For example, Li et al. obtained the peptide of diphenylalanine (FF) microrods, nanofibers, microtubes by manipulating the fabrication conditions [19]. The characterization of a single FF microrod indicates that the FF microrod can act as an active optical waveguide material with the introduction of Rhodamine B (RhB). Among various biomolecules, bile salts, belonging to cholic acid derivatives, possess a special steroidal backbone with an amphiphilic structure which can create unique physiochemical properties. The self-assembly behavior of bile salts is different from those of conventional surfactants with a linear hydrocarbon chain. These bile salts can also self-assemble to peculiar nanostructure including nantubes, nanofibers and nanohelices [20–22]. Li et al. investigated the superlong helical nanofibers with left- and right-handed orientations produced by tuning the concentration of glutathione (GSH) and sodium deoxycholate (NaDC) [23]. The controlled growth of Ag nanoparticles at arranged lacations along the nanohelices by UV reduction makes it possible for the application of superlong helical nanofibers in catalysis and material science. Zhang et al.

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performed that the supramolecular assemblies of lithocholic acid (LCA) ranged from straight, coiled, and helical tubes to single and double fan-like bundles in respond to the variation of pH, which can be applied as tunable templates to prepare silica replicas [24].

Thus, the bile salts is a good candidate to develop the 1D nano/microstructures and the employing of bile salts and charged dyes with the efficient electrocatalytic property through ionic self-assembly (ISA) strategy will enrich the range and content of the self-assembly chemistry [25,26]. Methylene blue (MB), which is one water-soluble dye possesses fine electrochemical properties. It has been widely used in basic electrochemical studies and applications, such as electrocatalysis, solar cells, and biosensors [27–29]. The assembly of MB molecule into the 1D nanobelts has also overcome the disadvantage of its solubility in water and enabled the stability of the biosensors [30–32]. The electron mediator assemblied with MB could also markedly decrease the overpotential necessary for the oxidation of biomolecules, such as L-ascorbic acid (AA), dopamine (DA), nicotinamide adenine dinucleotide (NADH) [33–35]. Among them, AA has been proposed as a biologically friendly compound for use in fuel cells [36–38]. Therefore, development of efficient electrochemical material possessing electrocatalysis towards AA is also of great interest. And the investigation of the electrocatalytic oxidation of AA will also accelerate the development of the new fuel cells.

In this article, the ultralong 1D nanobelts self-assembled by an anion biological surfactant sodium cholate (SC) and a cationic dye (MB) can be operated easily through ISA strategy. Consequently, the ultralong 1D nanobelts self-assembled with SC and MB could be used to be a biosensor towards AA. The ISA strategy of the fabrication of ultralong 1D nanobelts with good electrocatalytic activity could avoid complex organic synthesis and have attracted widespread attention due to its universality, cheapness, and simplicity. This novel system can been served as an eco-friendly alternative to prepare excellent materials to meet the increasing global needs for environment protection, development of new energy resources and resource sustainability.

2. Experimental section

2.1. Materials

Sodium cholate (SC, A.R.), NaH_2PO_4 (A.R.) and Na_2HPO_4 (A.R.), L-ascorbic acid (AA, A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. Methylene blue (MB, A.R.) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. The structures of SC and MB are shown in Fig. 1. Ultrapure water with a resistivity of 18.25 MΩ cm was obtained using a UPH-IV ultrapure water purifier (China).

2.2. Sample preparation

Ultralong SC/MB nanobelts were obtained by a simple and efficient method through ISA strategy. The required amounts of the raw powder of SC and MB were dissolved in a certain volume of ultrapure water. And the samples were prepared by mixing the SC and MB solutions together to a final certain concentration. The bundles of nanobelts were collected by filtration and washed three times with ultrapure water before freeze-drying in vacuum at −55 °C for 24 h.

2.3. Characterization

Optical microscopy measurements were performed with "Axio SCOP. A1" A Pol (ZEISS, Germany) microscope fitted with AxioVision SE64. Field-emission scanning electron microscope (FE-SEM) images were recorded on a Hitachi SU8010 ultra high resolution scanning microscope with an acceleration voltage of 5.0 kV, and the samples were loaded on the silica surface, previously sputter-coated with a homogeneous platinum layer for charge dissipation during SEM imaging. Powder X-ray diffraction (XRD) patterns of the samples were obtained using a PANalytical B.V. X'pert3 powder diffractometer (40 kV, 40 mA), using Cu Kα radiation (λ = 0.15406 nm). Data was collected by a PIXcel1^D detector in the 0.5–15° 2θ range with an acquisition time of 4 min. Fourier transform infrared (FTIR) spectra in KBr pellets were recorded on a VERTEX-70/70v spectrophotometer. Confocal laser scanning microscopy (CLSM) images were recorded using an inverted microscope (model IX81, Olympus, Tokyo, Japan) equipped with a high numerical-aperture 60× oil-immersed objective lens (PlanApo, Olympus, Tokyo, Japan), and a 16 bit thermoelectrically cooled EMCCD (Cascade 512B, Tucson, AZ, USA). Imaging acquisition and data analysis were performed using MetaMorph software (Universal Imaging, Downingtown, PA, USA) at the excitation wavelength of 535–565 nm. UV — vis measurements were performed using a HITACHIU-4100 spectrophotometer (Hitachi, Japan) with a scan rate of 600 nm min^{-1}. Thermal gravimetric analysis (TGA) was performed on a Universal V3.6 TA Thermal Analysis Q5000 system. The samples were deposited in an platinum crucible and heated in a continuous flow of nitrogen gas with a ramp rate of 10 °C min^{-1} from room temperature to 800 °C. The electrochemical measurements were performed on a CHI 660E electrochemical workstation (CH Instruments, Shanghai Chenghua Co.) with a stangdard three-electrode cell. A Pt foil serves as the counter electrode. Ag/AgCl (3 M KCl filled) was used as the reference electrode. The working electrodes (modified-GCE) were prepared by coating 5 μL ultralong SC/MB nanobelts aqueous suspension (2.5 mg mL^{-1}) on GCE. After the solution was dried, the electrode was coated with 5 μL of Nafion solution (0.2 wt%). The modified GCEs were dried naturally before use.

3. Results and discussion

3.1. Synthesis and characterization of ultralong SC/MB nanobelts

Firstly, the self-assembled nanostructures formed by SC and MB was investigated. The TEM image showed that the pure 100 mmol L^{-1} SC formed vesicles with the diameter ranged from 45 to 150 nm (Fig. S1A). Interestingly, when 5 mmol L^{-1} MB was added to the 100 mmol L^{-1} SC solution, the aggregate transformed from vesicles to precipitate. It is well-known that the solution based mixed self-assembly inspires that the aggregates could precipitate out from the solution of the mixed self-assemblies when their size increases to the meso- or macro-scale [39]. Fig. 2A, B exhibited the optical microscopy images of

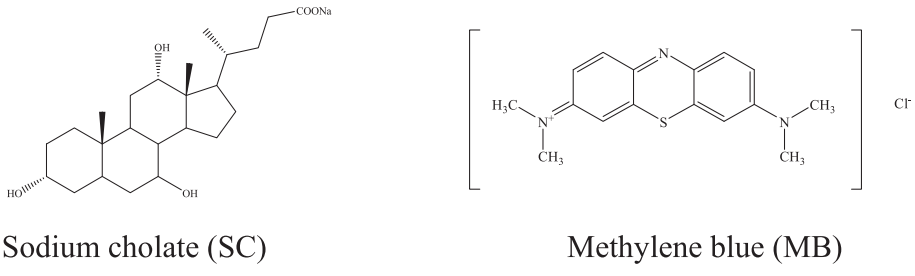

Fig. 1. The structures of SC and MB.