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

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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 varying 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 nanotubes, 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 locations along the nanohelices by UV reduction makes it possible for the application of superlong helical nanofibers in catalysis and material science.
performed that the supramolecular assemblies of lithocholic acid (LCA) ranged from straight, coiled, and helical tubes to single and double fan-like bundles in response 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-micro-structures 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 assembled 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 as 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 be served as an eco-friendly alternative to prepare excellent materials to meet the increasing global needs for environment protection, development of new fuel cells.

2. Experimental section

2.1. Materials

Sodium cholate (SC, A.R.), NaH2PO4 (A.R.) and Na2HPO4 (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 Kemiu 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 performed that the supramolecular assemblies of lithocholic acid (LCA) ranged from straight, coiled, and helical tubes to single and double fan-like bundles in response to the variation of pH, which can be applied as tunable templates to prepare silica replicas [24].

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 PIXel1D 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 HITACHI-U-4100 spectrophotometer (Hitachi, Japan) with a scan rate of 600 nm min−1. Thermogravimetric 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 CHI660E electrochemical workstation (CH Instruments, Shanghai Chenghua Co.) with a standard 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-assembly when their size increases to the meso- or macro-scale [39]. Fig. 2A, B exhibited the optical microscopy images of
the precipitate of bundles of ultralong SC/MB nanobelts. It can be seen that the nanobelts had a length about 212–295 μm and it is very flexible which made the length of the fans in the range from 425 to 590 μm. Fig. 2C shows the optically birefringence of nanobelts bundles aggregates illuminated with plane polarized light, tilted by an angle of 90° between the pictures, which indicated the long-range ordered structures of the nanobelts bundles and the molecular orientation of the macroscopic nanobelts bundles [40,41]. From TEM and SEM (Fig. 2D-H, Fig. S1 B) observations, it can be observed that the precipitates formed by SC/MB consist of the bundles of the ultralong nanobelts with a visible seeding center, which can form into single and double fans. The majority of the nanobelt bundles were found with double fans. The enlarged SEM image (Fig. 2F) demonstrated the inside of the nanobelt was solid. Moreover, CLSM was used to investigate the fluorescent properties of the nanobelt bundles. The CLSM image (Fig. 2I) displayed that the nanobelt bundles were characterized with green emission, indicating the intense fluorescent property of ultralong SC/MB nanobelts. All of these results clearly evidence that after the co-assembly of SC and MB, one-dimensional nanobelts were reconstructed. Thus, it can be concluded that the self-assembly of SC and MB into ultralong 1D nanobelts structures is a poor solvent mediated process because of the formation of SC/MB complexes through ISA strategy.

3.2. FTIR, XRD and TGA analysis

In order to get more information about the supramolecular assembly, FTIR spectroscopy was used to characterize the structural alteration and the interactions between SC and MB. As shown in the FTIR spectrums (Fig. 3A), the absorbance peak in 1580 and 1406 cm\(^{-1}\) corresponds to anti-symmetric and symmetric stretching modes of carboxyl group in SC respectively, and the asymmetric and symmetric methylene stretching bands are located at 2933 and 2859 cm\(^{-1}\), respectively [22]. The characteristic absorption peaks of MB are located at 1593 cm\(^{-1}\), 1487 cm\(^{-1}\) (aromatic rings stretching), 1386 cm\(^{-1}\) (C=N symmetric stretching), 1325 cm\(^{-1}\) (–CH\(_3\) symmetric stretching) [33,42]. When 5 mmol L\(^{-1}\) MB was added into the system, similar peaks appear in the spectra of the SC/MB bundles of nanobelts. However, the carboxyl group in SC has a red shift to 1561 and 1405 cm\(^{-1}\), and vibrations of the aromatic ring at 1593 cm\(^{-1}\) for MB has got shifted to 1600 cm\(^{-1}\). All of these results confirm that electrostatic interaction between SC and MB is the main driving force. Furthermore, for pure SC and SC/MB nanobelts, they show a wide peak at the region of 3483–3354 cm\(^{-1}\), indicating the formation of intermolecular hydrogen bond between the –OH groups on the concave α-face of SC [43,44].

XRD measurements were performed to ascertain the presence of crystallization within the self-assembled nanostructures. And the difference in the XRD patterns could demonstrate the change of the molecules packing mode of the samples [8]. The XRD patterns of SC and MB raw powders and SC/MB bundles of nanobelts are shown in Fig. 3B. As the XRD patterns depict, the sharp peaks of SC and MB patterns demonstrate that their raw powders are crystalline. Compared with the pure SC and MB, the SC/MB bundles of nanobelts exhibits an XRD pattern with a broad diffraction peak of the amorphous characteristic of the materials, indicating the molecules are arranged in an disorder manner. Combining the SEM image of the nanobelts, it can be deduced that molecules are assembled into nanobelts with impaired crystallinity [45].

The UV/Vis spectroscopy (Fig. 3C) is performed to study the conformation of MB in the aggregate of the nanobelts. It can be seen from Fig. 3C (b) that two major absorbance peaks of methylene blue can be seen at 290 and 664 nm due to benzene ring and heteropoly aromatic linkage [46,47], characteristic of the MB monomer in solution. The shoulder at 617 nm was ascribed to the absorbance of the MB dimer corresponding to the 0–1 vibronic transition, which is attributed to the π–π stacking of...
the aggregate of MB molecules [42,48]. There is no difference between spectral property of solution of 0.25 mmol L\(^{-1}\) MB (Fig. 3C (b)) and nanobelts of 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB (Fig. 3C (a)), which demonstrated that the conformation of MB in the self-assembly still existed as monomer and dimer and didn’t changed compared with MB solution.

Furthermore, the thermal stability of bundles of ultralong SC/MB nanobelts has been investigated by TGA technique under nitrogen atmosphere (Fig. 3D). For pure MB, the first weight loss below 120 °C (5.0%) is due to the release of water. The second weight loss, above 250°C, corresponds to the decomposition of the MB dye, which can be divided into two steps: the Cl atoms dissociate and some cyclization also takes place by liberation of N atoms in the first step, while in the second step the molecule gets fragmented mostly by breakage of C–S bonds. For bundles of ultralong SC/MB nanobelts, the first weight loss is also attributed to the vaporization of water, and the second loss from 300 to 490 °C (53.7%) is ascribed to the decomposition of SC and MB. It can be seen that the MB decomposes at higher temperatures when assembled in the SC/MB nanobelts. Therefore, the thermal stability of the MB is improved by the self-assembly of SC and MB.

3.3. Formation of bundles of ultralong SC/MB nanobelts with different incubation time

The time-dependent morphology change for the self-assembly of 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB system has also been investigated to elucidate the pathway responsible for the assembly (Fig. 4), from which the mechanism for the self-assembly process of bundles of ultralong nanobelts can be speculated. According to the experimental

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**Fig. 3.** (A) FTIR curves of (a) SC, (b) MB and (c) 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelts. (B) XRD curves of (a) SC, (b) MB and (c) 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelts. (C) The UV/Vis spectroscopy of the samples of nanobelts of 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB systems (a) and solution of 0.25 mmol L\(^{-1}\) MB (b). (D) TGA curves of (a) SC, (b) MB and (c) 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelts.

**Fig. 4.** Optical microscopy images showing time-dependent assembly of bundles of ultralong nanobelts for 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB systems.
Scheme 1. Schematic representations of (A) the formation of bundles of ultralong nanbelts with the aging time and (B) the molecular packing mode for 100 mmol L$^{-1}$ SC/5 mmol L$^{-1}$ MB systems.

Fig. 5. SEM microscopy images (A, D), POM images (B, E, H), CLSM images (C, F, I), TEM (G, H). The MB concentration is fixed at 5 mmol L$^{-1}$ for all samples. The SC concentration is varied from 10 mmol L$^{-1}$ (A, B, C), to 75 mmol L$^{-1}$ (D, E, F), to 125 mmol L$^{-1}$ (G, H, I).
nanobelts, such as the concentration, aging temperature and pH. Thus, the self-assembly process is crucial to control the length of the nanobelts with the general information was obtained. Small bundles of nanobelts with the length about 70 μm were observed primarily (15 s), then the nanobelts elongated and branched with the time going on (60–180 s). 300 s later, the nanobelt bundles grew up to about 240 μm, which finally form the bundles of ultralong nanobelts.

3.4. Formation mechanism of bundles of ultralong SC/MB nanobelts

From the experimental results mentioned above, it seems that the transition from molecularly dispersed MB and SC to higher assembled SC/MB complex is instantaneous and it can be concluded that the SC/MB complexes show spontaneous nucleation, interfacial control, and one-dimensional growth kinetics to form nanobelts with a fan-like structure. The formation mechanism of bundles of ultralong SC/MB nanobelts was described in Scheme 1. Scheme 1A showed the formation of bundle of nanobelts for 10 mmol L$^{-1}$ SC/5 mmol L$^{-1}$ MB systems with the aging time. Initially, a single fiber is formed by homogeneous nucleation [49], which subsequently branches in the opposite directions with large spacing in the third dimension. During the growth process, the fibers exhibit repeated tip splitting, leading to bundles of ultralong nanobelts morphology.

During the process of self-assembly, the additional direction is provided by the hydrogen bonding between protonated carboxylic acids of SC to control over the lateral association of the molecule along with inherent π-stacking interaction of MB. The electrostatic interaction between the opposite charged molecules of SC and MB promotes the formation of SC/MB complexes. Thus, the driving forces for the assembly of bundles of ultralong SC/MB nanobelts incorporate deprotonation–protonation of carboxylic acid groups of SC, strong π–π stacking, hydrogen-bond interaction and electrostatic interaction between SC and MB. The possible molecular packing mode for formation mechanism of bundles of ultralong SC/MB nanobelts was described in Scheme 1B. The ionic self-assembly approach is supposed to provide a new way to construct 1D microstructures, which possesses optical and electrocatalytic properties due to the directional arrangement of the molecules [6].

3.5. The influence of concentration on the morphology of SC/MB assemblies

The self-assembly process is crucial to control the length of the nanobelts, such as the concentration, aging temperature and pH. Thus, a series of relevant experiments were done to investigate the differences between them. Firstly, the influences of the concentrations of SC and MB on the produced nanobelts were investigated. As shown in Fig. 5, when the concentration of SC was varied while the concentration of MB is fixed at 5 mmol L$^{-1}$, the dimension of the nanobelts with different morphologies was changed gradually. For the sample of 10 mmol L$^{-1}$ SC/5 mmol L$^{-1}$ MB, the average diameter of the SC/MB spherulites is around 41 μm (Fig. 5A). As the concentration of SC further increases (75 mmol L$^{-1}$), SC/MB spherulites (Fig. 5D) evolved into dumbbell-like nanobelts and the length increased accordingly. With the enhancement of SC concentration, more molecules will be accelerated to accelerate the seed formation and the crystallization rate, which is closely related to nanobelt length and degree of dispersion [50]. However, as the concentration of SC increased to 125 mmol L$^{-1}$ or higher concentration, the hydrogel was obtained. This behavior may be attributed to high hydrogen bonding ability of SC, which forms stable intermolecular hydrogen bonds with SC molecules, leading to the formation of hydrogel [44]. The POM images (Fig. 5B, E, H) revealed that all the aggregates displayed anisotropy, which means all the assembled structures are in good order. In addition, the CLSM images (Fig. 5C, F, I) with green fluorescence demonstrated the intense fluorescent property of SC/MB aggregates.

Then, the morphologies of SC/MB assemblies with varying the content of MB from 1 mmol L$^{-1}$ to 10 mmol L$^{-1}$ were investigated when the SC concentration was fixed at 100 mmol L$^{-1}$. It can be observed from Fig. S2 that the number of fiber bundles increases with the enhancing of MB from 1 mmol L$^{-1}$ to 10 mmol L$^{-1}$, and then the nanobelts involve into 3D network with the appearing of the hydrogel with the increasing of the MB concentration. The reason for the formation of hydrogel may be the increase of the strength of the electrostatic interaction between SC and MB.

Based on the above results, it can be deduced that the simple variations in concentrations of SC and MB could tune the dimensions of the nanocrystals, and influence the self-assembly morphologies by changing the speed of crystallization. This is because that for the formation of bundle of ultralong SC/MB nanobelts, higher concentrations of SC and MB were adopted to induce a large number of solid rod-like composites forming in the solution and make the whole assemblies lack water. Therefore, the hydrogen bond interactions between water and SC molecules are reduced. In addition, the growth along the wall is almost the same as that in the middle of the nucleated clusters [19,51].
And the steric hindrance of the molecules is also one of the factors affecting the aggregation direction. As a consequence, the SC/MB nanobelts assembled into more complicated microstructures with fan-like shape.

3.6. The influence of the aging temperature on the morphology of SC/MB assemblies

In order to demonstrate whether the aging temperature is also crucial to the formation of SC/MB assemblies, the influence of the aging temperature on the morphology of SC/MB assemblies were investigated. For example, the average length of the SC/MB nanobelts is almost several millimeters at an aging temperature of 60 °C, which is visible to the naked eye. However, the average length of the SC/MB bundle of nanobelts reduces with the decrease of aging temperature (Fig. 6A-C). It can be seen that the average SC/MB nanobelts length decreases to 0.5 mm at an aging temperature of 20 °C, and only a small number of irregular butterfly-like aggregates with hundreds of micrometers appeared at the aging temperature of 4 °C. According to the influence of the aging temperature, it can be speculated that when the temperature is raised, the hydrogen bonds between the molecules of SC and between SC and water are weakened, resulting in the lower hydrophilicity and the aggregation of the SC/MB nanobelts [44]. That is, the ability of the self-assembly of SC-MB is promoted due to the decrease of the hydrophilicity, and longer SC/MB nanobelts can be formed at higher temperature. Thus, these results showed above indicated that the aging temperature is of great importance to form the SC/MB belt-like structures.

3.7. The influence of pH on the morphology of SC/MB assemblies

Fig. 6(D-F) showed the different morphologies of 100 mmol L⁻¹ SC/5 mmol L⁻¹ MB system at different acidity-alkanity by adding HCl or NaOH. It can be seen that addition of small amounts of acid in the form of dilute HCl (0.001 mol L⁻¹ HCl), the bundles of nanobelt still exist but become shorter and more dispersed. Further addition of HCl resulted in gelation of 100 mmol L⁻¹ SC/5 mmol L⁻¹ MB system (0.01 mol L⁻¹ HCl). This implies that the hydrogen bonding between the carboxylic acid groups is crucial to gel formation. However, as the basicity of the SC/MB system increases, the length and width of the nanobelt increase accordingly (0.001 mol L⁻¹ NaOH) which indicated the deprotonation of the carboxy group enhances the electrostatic interaction between SC and MB, inducing the growing up of the bundle of nanobelts.

3.8. Electrocatalytic activity of bundles of ultralong SC/MB nanobelts

There are many studies to verify the electrochemical behavior of MB immobilized in substrate, which makes it widely used in basic electrochemical materials and applications [33–35,42,52,53]. Firstly, in order to demonstrate the electrocatalysis behavior of SC/MB nanobelts towards AA in the present study, a series of contrast experiments about the electrocatalysis activity of the nanobelts produced at different
concentrations and temperature have been performed (Fig. S3A). From these experiments, we draw the following conclusion: the nanobelts fabricated with 100 mmol L\(^{-1}\) SC and 5 mmol L\(^{-1}\) MB (named as ultralong SC/MB nanobelts) is the optimal material to make the modified electrode materials due to its excellent electrochemical property. The typical cyclic voltammograms of the ultralong 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelts modified GCE in 0.1 mol L\(^{-1}\) phosphate buffer solution (PBS, pH = 7.0) at different scan rates were shown in Fig. S3B. It can be seen that the peak potential is independent of the scan rate varying from 20 and 400 mV s\(^{-1}\). The pair of well-defined and broad redox waves were displayed with the modified electrodes. The calibration plots shows that the anodic and cathodic peak current are linearly proportional to the scan rate (ν\(^{1/2}\)) (Fig. S3C), which demonstrates the electrochemical behavior of bundles of SC/MB nanobelt onto the GCE electrode is a adsorption confined redox process \([52,54,55]\). Thus, from these results, it is confirmed that 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelts have good electrochemical reversibility.

Then, the electrode modified with 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelt was used as the mediated oxidation of ascorbic acid (AA) in neutral media. The CV curves of the modified GCE and bare GCE in 1 mmol L\(^{-1}\) AA (0.1 mol L\(^{-1}\) PBS, pH = 7) at 50 mV s\(^{-1}\) were displayed in Fig. 7A. There is an irreversible oxidation peak locating at 0.48 mV for the bare GCE. A small peak-potential shifts towards negative direction to 0.254 mV and the oxidation peak current increases for the modified GCE, which indicates that the ultralong SC/MB nanobelts have the catalytic activity for the oxidation of AA efficiently \([33]\). The cyclic voltammograms of the 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelts modified GCE in 1 mmol L\(^{-1}\) AA (0.1 mol L\(^{-1}\) PBS, pH = 7) at different scan rates were also performed in Fig. 7B. The inset plots in Fig. 7B shows that the oxidation peak current increases linearly with the square root of the scan rate (ν\(^{1/2}\)), suggesting that the electrocatalytic activity of SC/MB nanobelts modified GCE towards AA is controlled by the diffusion of AA in the solution \([56,57]\). In addition, as the AA is negatively charged in neutral aqueous solution (p\(K_a\AA = 4.1\)), the electrostatic interaction is expected between AA and MB of the bundles of ultralong SC/MB nanobelts, which would also facilitate the oxidation of AA \([57–59]\). Thus MB can effectively promote the electrons transfer at the base GCE surface and decrease the overpotentials of AA as it possesses high electroactivity.

Cyclic voltammograms of the 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelts modified GCE was scanned continuously at 100 mV s\(^{-1}\) for 100 cycles in 1 mmol L\(^{-1}\) AA (0.1 mol L\(^{-1}\) PBS, pH = 7). There was no obvious change in the shape of the waves (Fig. S4A). The evolution of the oxidation peak current (I) of the ultralong SC/MB nanobelts modified electrode was shown in Fig. S4B. The peak current of the ultralong SC/MB nanobelt modified GCE decreased slightly with a loss of about 17% of its initial activity, indicating the electrode is stable \([60,61]\). The repeatability was studied with cyclic voltammograms of three ultralong SC/MB nanobelts modified electrodes in 1 mmol L\(^{-1}\) AA (0.1 mol L\(^{-1}\) PBS, pH = 7) (Fig. S4C). All the three ultralong SC/MB nanobelts modified electrodes exhibited almost the same current responses. The relative standard deviation (RSD) of the peak current was 5.4%. This behavior revealed that the electrochemical behavior of the SC/MB nanobelts modified electrode was highly repeatable.

Next, the influence of the concentration of AA on the catalytic behavior was investigated. Fig. 7C exhibits the DPV curves of 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelt modified electrode in 0.1 mol L\(^{-1}\) PBS (pH = 7) with different concentration of AA at a fixed scan rate of 50 mV s\(^{-1}\). The anodic peak current increases with positive shifts when the concentration of AA is increased. A linear relationship between log \(I_{pa}\) and log \(c_{AA}\) is found within the concentration range of 0.025–10 mmol L\(^{-1}\), as shown in the inset of Fig. 7C. The regression equation is \(log I_{pa} (\mu A) = 2.10393 c_{AA} (\text{mmol L}^{-1}) + 0.72466\). The correlation coefficient is as high as 0.99897 and the lowest limit of detection (LOD) for AA is calculated to be 8.477 mmol L\(^{-1}\) (based on S/N = 3). This value is lower than some previous report of MB-composites for sensing AA \([33,52]\).

In order to estimate the effect of structure and morphology on the electrocatalytic activity of the MB composites, the CV curves was performed on bare GCE and three other modified electrodes (100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelt, ruinate 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelts (Fig. S5), NaDc/MB fibers (Fig. S6)) (Fig. 7D). It is obvious that the modified GCE with bundles of ultralong SC/MB nanobelts displays the lower peak-potential and higher current intensity compared with the other three short fibers modified electrodes. It highlights that the structure of 100 mmol L\(^{-1}\) SC/5 mmol L\(^{-1}\) MB nanobelt provides an ideal morphology for anchoring bioactive molecules. The longer the nanobelt is, the more conducive the electron transfers. These results demonstrate that our bundles of ultralong SC/MB nanobelts can be used as an advanced electrode material, offering a new promising platform for application of ultralong 1D nanobelt compounds in electrochemistry, bioelectronics, and fuel cells.

4. Conclusion

In summary, the preparation of bundles of ultralong 1D nanobelts using theionic self-assembly of oppositely charged surfactant SC and dye MB was presented. And the morphologies of the SC/MB composites could be tuned by the preparation conditions such as temperature, concentration, or pH. Moreover, due to the combination of the hierarchical micro/nanostructures, characterization of the SC/MB composites indicates that the properties of the parent materials can be conserved and improved by the ISA strategy, such as the electrical activity of the MB molecule. Therefore, the bundles of ultralong SC/MB nanobelts display the fine electrocatalytic activity towards oxidation of AA in neutral media. These results illustrate the potential of the ISA strategy for the generation of the functional nano-materials with excellent electronic property in bio-applications and electrocatalysis.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi.org/10.1016/j.molliq.2018.01.134.

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