CuS nanotubes for ultrasensitive nonenzymatic glucose sensors†

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CuS nanotubes made up of nanoparticles were successfully prepared in large quantities in an O/W microemulsion system under low temperature; the as-prepared CuS nanotube modified electrode was used as an enzyme-free glucose sensor.

Diabetes mellitus is a group of metabolic diseases afflicting about 200 million people worldwide. For these patients, frequent testing of physiological glucose levels is critical to confirm that treatment is working effectively and to avoid a diabetic emergency. The rising demand for glucose sensors with high sensitivity, high reliability, fast response, and excellent selectivity has driven tremendous research efforts for decades.[1,2] Amperometric glucose biosensors are one such promising methodology. Most previous studies on this subject involved the use of the enzyme glucose oxidase (GODx),[3–8] which catalyzes the oxidation of glucose to gluconolactone. Owing to the nature of enzymes, the most common and serious problem with enzymatic glucose sensors lies in their lack of long-term stability. For instance, the activity of GODx can be easily affected by temperature, pH value, humidity and toxic chemicals.[9] To solve this problem, nonenzymatic glucose sensors have also been explored in the hope of improving the electrocatalytic activity and selectivity towards the oxidation of glucose, such as noble metal-based and alloy-based[10–14] amperometric glucose sensors. However, these kinds of electrodes have displayed the drawbacks of low sensitivity, poor selectivity, high cost and loss of their activity quickly by adsorbed accumulation of intermediates[10] and chloride ions,[14] which can result in electrocatalyst surface poisoning.

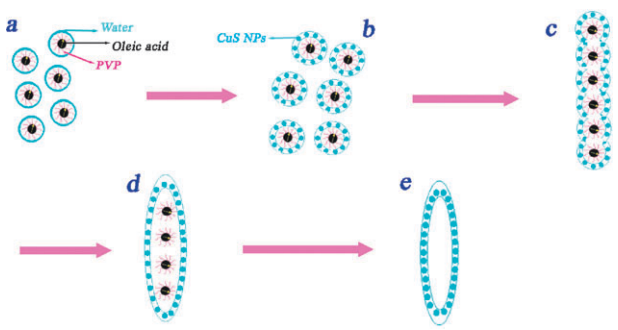
Recently, CuS was found to show interesting properties including metal-like electrical conductivity,[15] which may have potential application as electrochemical sensors. The synthesis of nanotubes has drawn much attention in recent years because these unique one-dimensional (1D) nanostructures have excellent electrochemical properties as well as special applications as electrochemical sensors.[16–19] There are several methods reported for the synthesis of CuS nanotubes.[20–23] However, these methods are complicated and high cost, and furthermore, the conventionally prepared tubular CuS structures have fewer electron transfer passages resulting in low sensitivity and so are limited in application, particularly, in biosystems and biomedicine. Therefore, a facile and cheap method for the large scale synthesis of uniform CuS nanotubes made up of nanoparticles are highly valuable.

In this work, CuS nanotubes made up of nanoparticles were successfully prepared in large quantities in an O/W microemulsion system under low temperature. The prepared materials which show more electron transfer passages were successfully applied as an enzyme-free glucose sensor. By comparison, the electrochemical catalytic activity of the sensor toward glucose oxidation is better than that of conventionally prepared CuS nanotubes.

The CuS nanotubes were solvothermally prepared by reduction of copper nitrate and sodium thiosulfate at 150 °C for 12 h in a Teflon lined stainless steel autoclave with a capacity of 60 mL using a microemulsion system (see ESI†). The yield can reach up to 90 wt%.

The synthesis procedure is shown in Scheme 1. First, oleic acid, water and poly(vinylpyrrolidone) (PVP) formed the microemulsion system. In this microemulsion system, oleic acid was used as a core and water as a shell (Scheme 1(a), Fig. S1, ESI†) With the reaction prolonged for 2 h, CuS nanoparticles were synthesized in the water phase and was composed of hollow CuS nanospheres (Scheme 1(b), Fig. S2, ESI†) When the reacting time was increased to 6 h, those hollow CuS nanospheres were further assembled to a tubular structure (Scheme 1(c), Fig. S3, ESI†) After 12 h, oleic acid/CuS nanotubes with core/shell structure were obtained (Scheme 1(d)). Finally, after washing with ethanol to remove the oleic acid template, the CuS nanotubes were obtained (Fig. 1).

The XRD pattern (Fig. S4, ESI†) shows that all the diffraction peaks can be indexed to the hexagonal phase of the covellite structure (JCPDS no. 6-464) with the $P6_3/mmc$ space group and a primitive hexagonal unit cell with $a = 3.792$



Scheme 1 The formation of CuS nanotubes.

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† Electronic supplementary information (ESI) available: Detailed experimental procedures, characterization, XRD, HRTEM, TEM, SEM, EIS, CV, CA data. See DOI: 10.1039/b814725f

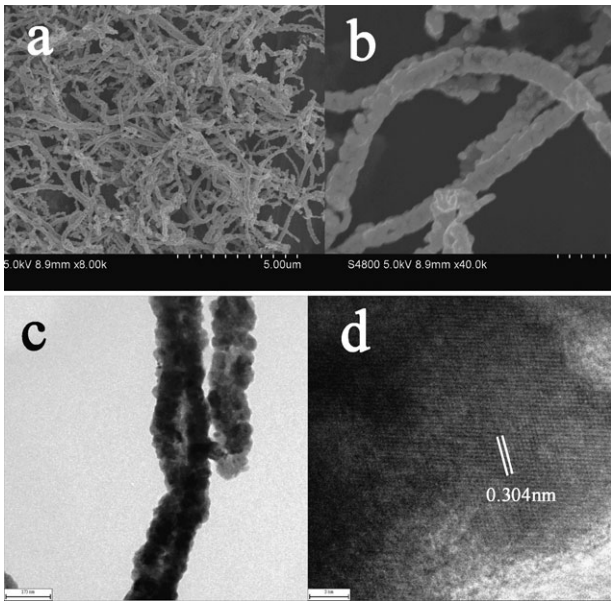

Fig. 1 (a and b) FESEM images with different magnification, (c) TEM image, (d) HRTEM image of the as-prepared CuS nanotubes.

and $c = 16.344$ Å. No other impurities, such as $Cu_{1.8}S$, Cu_7S_4, $Cu_{1.96}S$, Cu_2S, oxides, or organic compounds related to the reactants, were detected. The TEM image in Fig. 2(c) clearly shows that all of the particles are straight tubular nanotubes with 30–90 nm inner diameter and 40–80 nm in thickness. The walls of these nanotubes, which are made up of nanoparticles of *ca.* 30 nm, are coarse, which is consistent with the evaluation of the broadened diffraction peaks indicated by the XRD pattern.

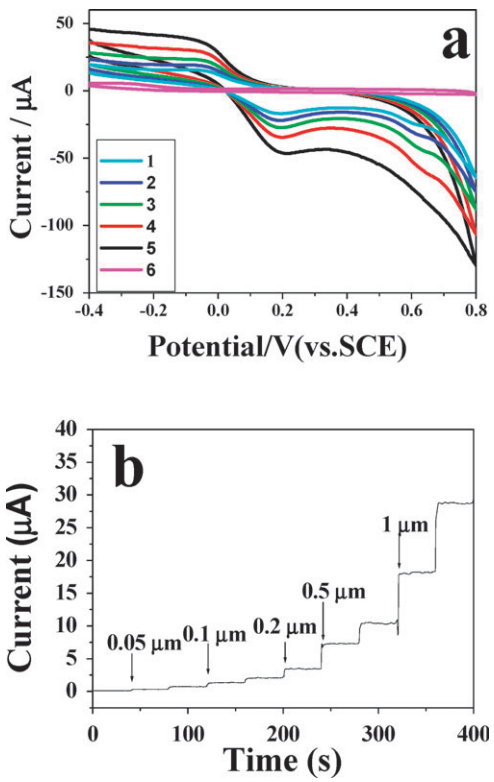

Fig. 2 (a) CV performance of as-prepared CuS nanotube/Nafion-modified GC electrodes in the presence of the same amount of glucose in 50 mmol L^{-1} PBS (pH 9.2) at a scan rate of 50 mV s^{-1}. (scans 1–5 correspond to 1, 2, 3, 4, 5 μmol L^{-1} glucose in 50 mmol L^{-1} PBS, respectively, scan 6 corresponds to 5 μmol L^{-1} glucose in 50 mmol L^{-1} PBS on the bare GC electrode); (b) CA response of as-prepared CuS nanotube/Nafion-modified GC electrodes at 0.2 V upon subsequent addition of glucose solution.

The impedance spectroscopies of different electrodes were observed to study the electron transfer capacity. As Fig. S5, ESI† shows, the semicircle diameter of EIS (R_{et}) of conventionally CuS nanotube modified electrode (curve c) is larger than the as-prepared CuS nanotubes (curve b) modified electrode, which means, the electron transfer ability of our sample is better than for the conventionally prepared CuS nanotubes. This may be attributed to the structure of the materials. The as-prepared CuS nanotubes were made up of CuS nanoparticles, providing both a larger surface area and more active points as well as better electron transfer passage than that of the conventionally prepared CuS nanotubes, which led to the electrochemical probe communicating with the surface of the electrode easily.

For the development of an amperometric biosensor for glucose, the as-prepared CuS nanotubes were dispersed in Nafion, a perfluorosulfonated polymer, to facilitate the modification of the GC electrode surface. As shown in Fig. 2(a), curve 6, glucose shows no redox peak at a bare GC electrode. However, the as-prepared CuS nanotube exhibits strong electrocatalytic activity in response to glucose oxidation. One oxidation waves in the anodic sweeping and one anodic wave in the cathodic sweeping indicate the high catalytic ability of the electrode towards glucose oxidation. From the CV profiles (Fig. S6b, ESI†) we find that the conventionally CuS nanotube also exhibits catalytic response towards glucose oxidation. However, with the same amount of glucose added, the peak current increase of the as-prepared CuS nanotube is larger than that of the conventionally CuS nanotubes. All these appearances mean that the response of glucose on our sample is better than that on conventionally CuS nanotube modified electrodes.

The above phenomenon implies that our sample can greatly improve the electron transfer between glucose and the GC electrode, which should be a direct result of the novel structure. The above electrochemical experiments also underscored the results of the EIS. For amperometric sensing application, electrodes are generally evaluated by measuring current response at a fixed potential with the analyte added. Fig. 2(b) displays the amperometric response (at +0.20 V) at the as-prepared CuS nanotube modified electrode to the successive addition of 1 mM glucose in PBS (pH = 9.2). As expected from the voltammetric data (Fig. S7b, ESI†), the CuS nanotube modified electrode showed good linear response to the changes of glucose concentration, producing steady-state signals within 10 s. The as-prepared CuS nanotube modified electrode gives a linear dependence ($R = 0.994$) in the glucose concentration range of 0.05–5 μM with a sensitivity of 7.842 μA μM^{-1}, as depicted in Fig. S7b, ESI.† Exhilaratingly, the as-prepared CuS nanotube modified electrode also shows high stability and reproducibility in detection of glucose, with a relative standard deviation about 1.8% in more than 20 measurements.

In summary, an enzyme-free glucose sensor based on the CuS nanotube modified electrode was synthesized. Compared to the conventional CuS nanotubes, the as-prepared CuS nanotubes display high electrocatalytic activity towards the oxidation of glucose, showing significantly lower overvoltage and a linear dependence ($R = 0.994$) in the glucose concentration up to 5 μM with a sensitivity of 7.842 μA μM^{-1}. Thus, the as-prepared CuS nanotubes holds promise for being developed as a nonenzymatic glucose sensor at low cost.

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