Mesoporous Indium Oxide for Nonenzymatic Uric Acid Sensing

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Abstract. Mesoporous indium oxide has been successfully obtained by a simple nanocasting method. The characterization indicated that the powders havea good crystalline structure, and the synthesis was successfully controlled in nanoscale (meso-structure). The elcctrochemicalsensor based on mesoporousindium oxide exhibit good uric acid sensing properties, and a possible mechanism was also given.

Introduction

Uric acid (2,6,8-trihydroxypurine) is a metabolite of purines, nucleic acids and nucleoproteins which is found in blood, serum, urine, or biological fluids, and it excreted by the human body. Abnormal level of uric acid can lead to several diseases, for example gout, physiological disorder, hyperuricaemia, myocardial infarction, and Lesch-Nyhansyndrome[1]. Therefore, the accurate detection of uric acid levels is essential for human health. Clack and Lyons first proposed the concept of biosensor based on the biological activity of the specificenzyme. In recent decades, enzyme sensor technology has been tremendous progress in uric acid detection. However, enzymes can only work effectively under proper conditions, and it is not conducive to a wide range of applications[2, 3]. In contrast, nonenzymatic biosensors were advocated, such as amperometric uric acid sensors, which is based on metal oxide.

Recently, mesoporous materials have gained extensiveinterests for the sensing application, due to their large specific surface area and pore volume. Among them, mesoporous indium oxides have considerable attention in different fields because of its low toxicicty, electronic structure and structural stability. They have been extensively studied for applications in the areaof lithium ion-battery, functional glass, solar cells andgas sensor. However, the application in nonenzymaticuric acid sensingof mesoporous metal oxide has scarcely been reported.In this paper, we present a simple and effective method for the synthesis of mesoporous indium oxide material with crystalline wall. The sensor based on mesoporous In_2O_3 showed good uric acid sensing properties, and a possible mechanism was also given.

Experimental

The detailed procedure of mesoporous silica SBA-15 was synthesized as follow: 0.8 g of triblock copolymer P123 (Aldrich) and 0.8 g of glycerol were dissolved in 30 g 2M hydrochloric acid solution, which was stirred at 37 °C for 8 h to get a transparent solution. Then, 1.8 g of TEOS was added to the above solution under vigorous stirring. After stirring for 5 min, the mixture was kept in static conditions at the same temperature for 24 h, followed by aging at 100 °C for another 24 h [4]. The solid product was filtered and washed with ethanol. Then the as-synthesized white powder was dispersed into a mixture of 12 ml concentrated HNO_3 and 5 ml H_2O_2 (30 wt %) in a Teflon vessel followed by digesting under 1.3 MPa for 2 min. Then the powder was filtered, washed with distilled water and dried at room temperature. And then, mesoporous In_2O_3 was prepared with SBA-15 as hard templateaccording to the prior lierature [5].

Characterization and electro chemical experiments

The powder XRD patterns were tested on a D8 Tools X-ray diffraction instrument.Cyclic voltammetric (CV) and amperometric (i–t) measurements were performed using CHI 660E Electrochemical Workstation (CH Instruments, USA). Ag/AgCl (3 M KCl) electrode and Pt wire were used as the reference electrode and the counter electrode, respectively.Bare glassy carbon electrode (GCE, dia. 3 mm) was polished with1 μm and 0.05 μm alumina slurries, and then successively sonicated in ethanol, and deionized water followed by drying at room temperature. An appropriate volume of In_2O_3/ethanol suspension (5 mg/mL) was dropped on the surface of GCE. 5 mL of NaOH with an appropriate concentration was applied as the electrolyte in the study[6].

Results and discussion

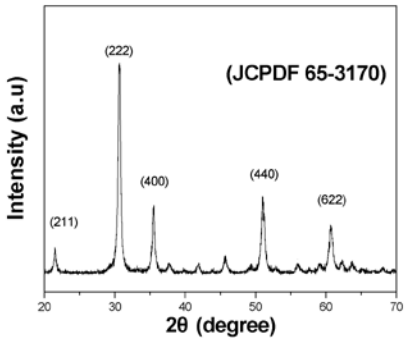

Fig. 1 Wide-angle XRD patterns of the sample.

Fig 1 shows the XRD pattern of the sample. It shows clearly several well-resolved peaks which can be indexed to(211), (222), (400), (440), (622), and so on. These peaks were in agreement with In_2O_3 (JCPDF 65-3170), andthe relatively strong diffraction peaksindicating that the prepared indium oxide has highly crystalline walls.

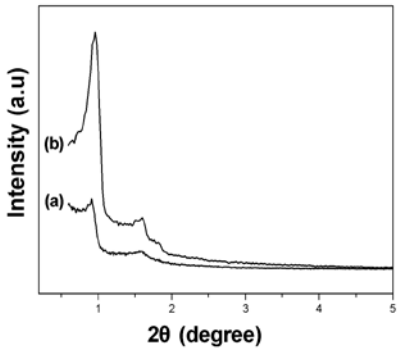

Fig. 2 Small-angle XRD patterns of (a) indium oxide and (b) SBA-15.

The small angle XRD patterns of prepared indium oxide and hard template SBA-15are given in Fig. 2. The curve of indium oxide showed more than two well-resolved diffraction Bragg peak, resulting that the mesoporous structure of the hard template SBA-15 was well duplicated. The $d_{(hkl)}$ value ratios of the first two peaks is about 2: $\sqrt{3}$, revealed that the original mesostructure of the 2-D hexagonal space group (P6mm) of hard template was successfully nanocasted by mesoporousindium oxide.

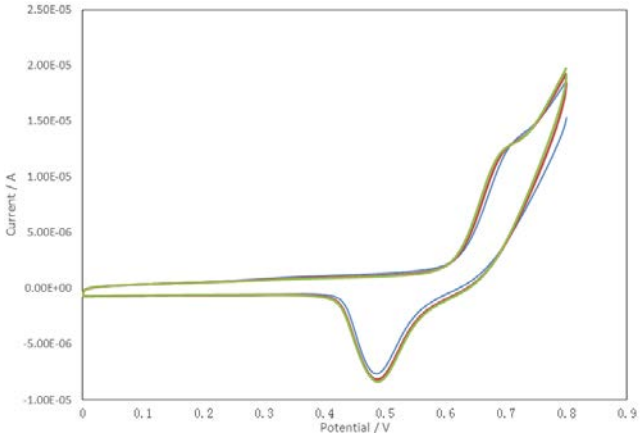

Fig. 3CVs of the In_2O_3/GCE composed of different scan numbers (1-6) in the presence of 1 mMuric acidcontaining0.1 M NaOH solution at a scan rate of 50 mV/s

The results characterized indicated that the synthesis was successfully controlled in nanoscale (meso-structure), and mesoporous indium oxide has a good crystalline structure.The CVs of theelectrochemical sensors which base on as-prepared In_2O_3wasinvestigated in presence of 1 mM uric acid containing0.1 M NaOH solution in the range from 0to 0.8 V vs. Ag/AgClat a scan rate of 50 mV/s. The first cycle needs higher oxidation potential.In the next cycles, the anodic peaks shiftto lower potentialsand the cathodicpeaks shiftto higher potentials in the firstcycle. It is a progressive oxidation of theIn_2O_3 as the scan cycles increase.The oxidation rate of $In_2O_3$is slowed, anda pair of redox peak tends to stabilize with anodic peak at about 0.7 V andcathodic peak at about 0.48 V in Fig.3, the wide positive work potentialwindow of is favorable for the In_2O_3/GCE electro-oxidation of uric acid. Yielding an ΔE_pvalue of0.22Vwhere the anodic potential is much greater thanthe cathodic potential,shows that the electrode surface occurs larger polarization.

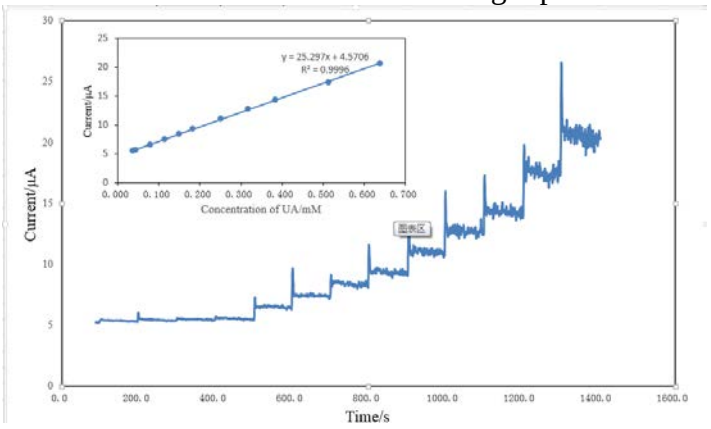

Fig. 4Aerometric response of the In_2O_3/GCE to successive addition of uric acid to 0.1 M NaOH. Inset shows its correspondingcalibration curve.

Fig.4 shows the amperometric responses at the applied potential of 0.5 V of the In_2O_3/GCE electrodes with successive increments of the uric acid concentration from 0 to0.64mM. The In_2O_3/GCE electrode responds rapidly to the changes in urea acidconcentration.The In_2O_3/GCE electrode shows an inferior detection limit. All the results indicated that the In_2O_3/GCE sensor had a better sensitivity and a lower detection limit for uric acid. The corresponding calibration curve (Fig. 4) is linear up to 0.64mM with a sensitivity of 361.4μA·mM^{-1}·cm^{-2} and a detection limit of 11μM (S/N = 3),but saturated at a higher uric acidconcentration. The obtained sensitivity is better than those of 24.72μA·mM^{-1}·cm^{-2} at anovel molecularly imprinted polymer thin film as poly(PD–BCD)[7].Sensors modified with In_2O_3 nanoparticles show good performances through increasing the surface area and enhancing the mass transport. Therefore, it is reasonable to expect that processing In_2O_3 into nanostructured materials could enhance its performance in the catalytic activity towards the electro-oxidation of uric acid.

Conclusions

Mesoporous indium oxide was successfully obtained through a simple and effective nanocasting method. The elcctrochemicalsensor based on mesoporousindium oxide exhibit good uric acid sensing properties with high sensitivity. And it could be seen as a promising candidate fordetecting low concentration of uric acidundernon-harsh conditions.

Acknowledgements

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References

[1]. Suresh R, Giribabu K, Manigandan R, Stephen A, Narayanan V. Fabrication of Ni–Fe_2O_3 magnetic nanorods and application to the detection of uric acid. *RSC Advances*. 2014;4: 17146.

[2]. Jiang LC, Zhang WD. A highly sensitive nonenzymatic glucose sensor based on CuO nanoparticles-modified carbon nanotube electrode. *Biosensors and Bioelectronics*. 2010;25: 1402-1407.

[3]. Li C, Su Y, Zhang S, Lv X, Xia H, Wang Y. An improved sensitivity nonenzymatic glucose biosensor based on a Cu_xO modified electrode. *Biosensors and Bioelectronics*. 2010;26: 903-907.

[4]. Wang Y, Zhang F, Wang Y, et al. Synthesis of length controllable mesoporous SBA-15 rods. *Materials Chemistry and Physics*. 2009;115: 649-655.

[5]. Wu Z, Yang Y, Gu D, et al. Silica-Templated Synthesis of Ordered Mesoporous Tungsten Carbide/Graphitic Carbon Composites with Nanocrystalline Walls and High Surface Areas via a Temperature-Programmed Carburization Route. *Small*. 2009;5: 2738-2749.

[6]. Zhang Y, Su L, Manuzzi D, et al. Ultrasensitive and selective non-enzymatic glucose detection using copper nanowires. *Biosens Bioelectron*. 2012;31: 426-432.

[7]. Chen PY, Vittal R, Nien PC, Liou GS, Ho KC. A novel molecularly imprinted polymer thin film as biosensor for uric acid. *Talanta*. 2010;80: 1145-1151.