Fabrication and characterization of nanostructured ZnO thin film microdevices by scanning electrochemical cell microscopy†

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Scanning electrochemical cell microscopy (SECCM) was proven to be a prospective microfabrication method for the in situ synthesis and multiscale assembly of functional nanomaterials into microdevices. Nanostructured ZnO thin film was synthesized and assembled by SECCM, which has excellent electrochemical capacitance and electronic I–V properties.

Scanning electrochemical cell microscopy (SECCM) is a technique derived from scanning electrochemical microscopy (SECM) by replacing the ultramicroelectrode (UME) tip with a microcapillary tip.1,2 As shown in Fig. 1a, when in contact with a conductive substrate through an electrolyte microdrop with a volume of pico- or femto-liters, the microcapillary acts as not only the electrolytic cell but also as the scanning probe. In general, the working electrode is the local contact part of the substrate while the reference and counter electrode are placed in the microcapillary. When the microcapillary probe scans, the whole electrochemical microsystem is moving. The spatial resolution depends mainly on the size of the microcapillary orifice. Moreover, the electrolyte contamination to the whole substrate can be avoided because only the local contact part of the substrate is exposed to the electrolyte. SECCM has been proven to be a powerful method in investigations on local corrosion,3–6 underpotential deposition (UPD) on a single crystal electrode,7 surface analysis and imaging,8–13 electrocatalysis14–16 and electron transfer kinetics.17,18 Similar to SECM, SECCM is also a valuable method for electrochemical microfabrication. Yu and coworkers succeeded in electrodepositing copper and platinum nanowire and circuit bonds.19–22 In our previous work, single microcrystals of iron hexacyanides/NaCl solid solution were in situ synthesized and assembled on a microchip, which showed excellent all-in-solid-state electrochemical properties.23

ZnO is a direct wide bandgap (≈3.3 eV at 300 K) material with a large exciton binding energy of 60 meV, stimulating its applications in sensors, light-emitting diodes, supercapacitors, varistors and solar cell devices.24,25 ZnO nanomaterials can feasibly be synthesized through the hydrothermal method, magnetron sputtering, the metal–organic vapor phase epitaxy method, chemical vapor deposition and electrochemical deposition.26–30 Although the growth of patterned or aligned ZnO nanostructures is important for device applications, the miniaturization and multiscale assembly of ZnO nanomaterials into microdevices still remains a challenge. Here, a SECCM microfabrication method was proposed for the in situ synthesis and multiscale assembly of nanostructured ZnO thin films and their behaviour as electrochemical capacitors and varistors was characterized.

The borosilicate glass microcapillaries with μm sized orifices were prepared by a programmed laser puller (PS-2000, Sutter Co.).31 An aqueous solution containing 1.0 mol L−1 Zn(NO3)2 and 0.01 mol L−1 hexamethylene tetraamine (HMT) was injected into a microcapillary with an 50 μm diameter orifice. A platinum wire was inserted into the microcapillary as both counter and reference electrodes. The microcapillary was fixed on an ITO glass slide (the working electrode) to form the

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Fig. 1 (a) Schematic diagram of SECCM, a microcapillary acts as both scanning probe and electrolytic cell, the reference and counter electrodes are inserted in the capillary while the substrate is the working electrode. (b) SEM image of the ZnO thin film arrays synthesized through SECCM on a ITO substrate, accelerating voltage 15.0 kV, scale bar 50 μm. (c) SEM image of the nanostructure of the ZnO thin film synthesized through SECCM on a ITO substrate, accelerating voltage 15.0 kV, scale bar 10 μm. (d) Raman spectrum of the nanostructured ZnO thin film.
SECCM microsystem. To avoid the evaporation of water and the salt out of the electrolyte, the microsystem was placed in a chamber with a humidity of 85%. When the potential of the ITO substrate was held at $-1.5$ V, nitrate ions were reduced into nitrite anions. In the meantime, hydroxyl anions were produced on the local surface of the ITO substrate. As a result, Zn(OH)$_2$ was precipitated and transformed into ZnO. This mechanism was fully reviewed as follows:

\[
\begin{align*}
\text{NO}_3^- + \text{H}_2\text{O} + 2e^- & \rightarrow \text{NO}_2^- + 2\text{OH}^- \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn}($\text{OH})_2 \\
\text{Zn}($\text{OH})_2 & \rightarrow \text{ZnO} + \text{H}_2\text{O}
\end{align*}
\]

The scanning electron microscopy (SEM) image of the synthesized ZnO microspots was shown in Fig. 1b. The average diameter of the ZnO microspots was in harmonious accordance with the orifice size of the microcapillary. Fig. 1c shows the higher resolution SEM image of the ZnO spot, in which a thin film nanosheet network can be observed. The EDS results show that the atomic percentage ratio of O/Zn is 53:47 (see S2, ESI†). The nonstoichiometric ratio of O/Zn predicts lattice defects of the ZnO nanostructure and its applications in energy storage devices and electronic components. The confocal Raman spectrum (Fig. 1d) shows the specific peaks for ZnO at 415 nm, 550 nm and 1070 nm, which were in a linear relationship with the scan rates. (c) Charging and discharging curve of the nanostructured ZnO thin film in the first 1000 cycles. (d) The mass specific capacity of the nanostructured ZnO thin film in the first 1000 cycles.

After the microsynthesis of the nanostructured ZnO thin film, its electrochemical capacity was investigated by using a new microcapillary containing an aqueous solution with only 0.1 M NaCl (see S6, ESI†). Since the microcapillary was fixed right on the nanostructured ZnO thin film, the background of the Au substrate could be well excluded. Fig. 2a shows the cyclic voltammograms of the nanostructured ZnO thin film on a bare Au substrate. Well-shaped charging and discharging current responses of the electric double layer were obtained, which were in a linear relationship with the scan rates (Fig. 2b). The electrochemical capacity can be obtained by the following equation:

\[
C = \frac{dQ}{dE} = \frac{I dt}{dE} = \frac{I}{v}
\]

Where, $C$ is the electrochemical capacity, $Q$ is double-layer charge, $E$ is potential, $I$ is the charging or discharging current, $v$ is the scan rate. From the slope of the line in Fig. 2b, the electrochemical capacity of the nanostructured ZnO thin film was 34.6 nF. The constant-current charging and discharging behavior was shown in Fig. 2c, where the charging and discharging current was 0.9 nA with a period of 5 seconds. Since the nanostructured ZnO thin film has a diameter of about 4.0 V, the nonlinear coefficient, $x$, is obtained as 3.0 from the following equation:

\[
x = \frac{|d\lg J/d\lg V|}{a}
\]

where $V$ is the applied electric field intensity and $J$ is the resulting current density. The $x$ value was pretty low because the nanostructured ZnO thin film hasn’t undergone ceramic treatment. In order to improve the $I$–$V$ property of the ZnO micro-varistor, we prepared new microchips where a silicon nitrate membrane was used as the insulator. Then, the nanostructured ZnO thin film assembled on the micro-varistor was sintered at 400 °C for 30 minutes. The $I$–$V$ behavior was promoted obviously as show in Fig. 3c. The region of the

![Fig. 2](image-url)
breakdown tension is about 10.0 V and the nonlinear coefficient, $x$, is obtained as 7.9. On one hand, heat treatment can lead to higher crystallinity of the ZnO film and promote electronic properties. On the other hand, the breakdown of the electron transfer barrier caused by the Schottky junction between the gold microwire and nanostructured ZnO thin film decreases dramatically. This can be verified by the three orders of magnitude difference of current response between the cases without and with heat treatment. All the results predict that the nanostructured ZnO thin film fabricated by SECCM can be applied in microelectronic components such as diodes, varistors and so forth.24,37

In conclusion, SECCM proves to be a prospective and competitive microfabrication method for in situ synthesis and assembly of nanostructured functional materials in micro-devices. Moreover, nanostructured ZnO thin films prepared through SECCM have excellent electrochemical capacitance and electronic properties. The authors are thankful for the financial support of the National Science Foundation of China (NSFC 20973142, 21061120456, 21021002), the National Basic Research Program of China (2012CB932900, 2011CB933700), and the National Project 985 of High Education.

Notes and references


Fig. 3 The $I$–$E$ behaviour of the nanostructured ZnO thin film in all-in-solid-state micro-devices: (a) without heat treatment and (c) sintered at 400 °C for 30 minutes; and the logarithmic relationship between the current density and applied electric field intensity in the breakdown region: (b) without heat treatment and (d) sintered at 400 °C for 30 minutes.