Solid State Communications 149 (2009) 1755–1759

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Direct growth of silver nanostructures on zinc substrate by a modified galvanic displacement reaction

Sa Lv[a], Hui Suo[a], Xu Zhao[b], Chunxu Wang[a], Shengyu Jing[a], Tieli Zhou[a], Yanan Xu[a], Chun Zhao[a,*]

[a] *Joint State Key Laboratory on Integrated Optoelectronics, Jilin University, Changchun 130012, People's Republic of China*
[b] *College of Chemistry, Jilin University, Changchun 130012, People's Republic of China*

ARTICLE INFO

Article history:
Received 12 May 2009
Received in revised form
20 June 2009
Accepted 18 July 2009 by F. Peeters
Available online 23 July 2009

PACS:
73.61.At
79.60.Jv

Keywords:
A. Metals
A. Nanostructures
E. Galvanic displacement

ABSTRACT

This paper reports a modified galvanic displacement approach for the synthesis of Ag nanostructures with different morphologies. During the process, $AgNO_3$ as starting material is reduced using zinc foil and this is followed by suitable thermal treatment. The reaction time, concentration of the $AgNO_3$ aqueous solutions and thermal treatment temperature directly influence the morphologies of Ag nanostructures. X-ray diffraction (XRD), field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and UV–visible spectra are used to characterize the products obtained. Furthermore, a representative experiment using rhodamine (R6G) as the probe molecule confirms that the Ag nanostructure shows strong surface-enhanced Raman scattering (SERS) activity.

1. Introduction

In recent years, metal nanostructures have attracted considerable attention on account of their widespread potential applications in electronics, photography, catalysis, magnetism and information storage [1,2]. In particular, Ag nanostructures continue to arouse intense scientific interest due to their practical uses in ultra-trace chemistry, biological sensing, surface plasma resonance (SPR) and surface-enhanced Raman scattering (SERS) [3,4]. The intrinsic properties of metal nanostructures are associated with their shape and size [5]. Therefore, substantial efforts have been focused on modifying the synthesis strategies that could provide the desired control of the morphology of Ag nanostructures. So far, Ag nanowires, nanobelts, nanorods, nanocubes, nanodendrites and nanoplates have been constructed by a variety of approaches, including seed-mediated growth, the polyol process, electrochemical deposition, use of soft templates and photochemical synthesis, etc. [6–10]. Most recently, galvanic displacement as a facile, efficient method has been widely adopted for depositing Ag nanostructures directly on solid substrate. Galvanic displacement is a type of electroless deposition process that utilizes the difference of the standard electrode potentials of various elements, leading to spontaneous reaction without using any additives or complicated procedures. However, most galvanic displacements involve the reduction of silver salts with metal or semiconductor substrate by immersing the substrate into the silver salt solution at room temperature. The reaction is inevitably effected by many external conditions, such as temperature, immersion rate, ultrasonic vibration and concentration gradient, which usually lead to uneven deposition [11]. To resolve these problems, Sun et al. have employed a method of dropping the $AgNO_3$ solution on the surface of the substrate to directly grow Ag nanostructures at room temperature [3,12,13]. In our previous work, we made a detailed comparison of the growth processes and mechanisms for Ag nanostructures prepared by solution-dropping and solution-immersion routes. The results confirmed that it was difficult to control the deposition rate in the solution-immersion route. Moreover, a reaction rate that is too fast is unfavorable for anisotropic growth of Ag nanostructures [14]. In this communication, we describe the employment of a modified galvanic displacement reaction to directly grow Ag nanostructures on zinc substrate, which was realized by dropping $AgNO_3$ solution on zinc surface followed by suitable thermal treatment. Furthermore, the Ag nanostructure obtained, as SERS substrate material, was also investigated by using rhodamine (R6G) as the probe molecule.

---

[*] Corresponding author. Tel.: +86 431 85168241; fax: +86 431 88499134.
E-mail address: zchun@jlu.edu.cn (C. Zhao).

0038-1098/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2009.07.026

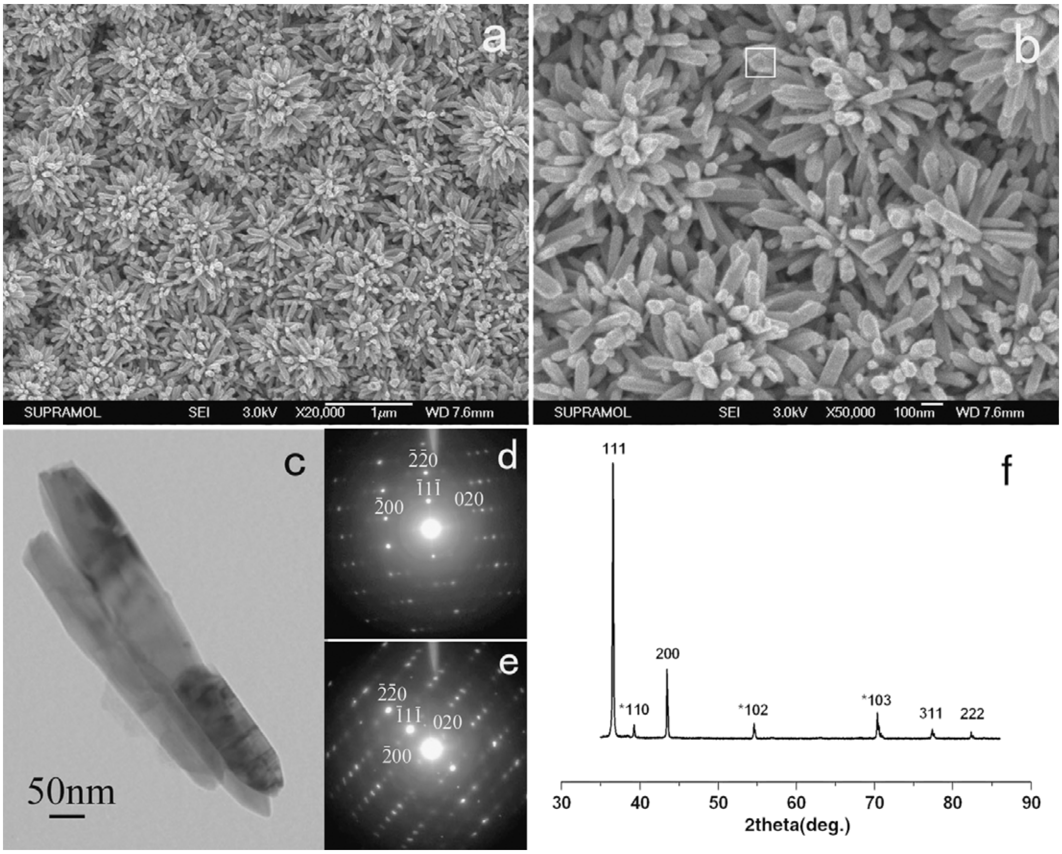

Fig. 1. (a) Low magnification and (b) high magnification FE-SEM images; (c) a TEM image; ((d), (e)) SAED patterns; (f) the XRD pattern of the Ag nanoflowers.

2. Experimental section

In a typical procedure, $AgNO_3$ aqueous solution (0.02 M) was preheated at 50 °C for 10 min, then a droplet of the above $AgNO_3$ solution was dropped onto the surface of the previously cleaned zinc foil. After that, the zinc foil was transferred into a sealed container with a black cap to minimize the effect of light illumination and water evaporation. The whole reaction process was kept at 50 °C for 5 h. The resulting zinc foil was then thoroughly rinsed with ethanol and deionized water and dried under nitrogen. The products obtained were characterized using X-ray diffraction (XRD, Shimadzu XRD 6000, Cu Kα radiation), a scanning electron microscope (SEM, JEOL FESEM JEM-6700F), a transmission electron microscope (TEM, HITACHI H-8100), selected area electron diffraction (SAED), UV–visible (Shimadzu UV-2550) and Raman spectrometers (Renishaw 1000, excited with a 514.5 nm Ar^+ laser).

3. Results and discussion

In our experiments, Ag nanostructures were prepared by reduction of $AgNO_3$ with Zn according to the reaction equation $Zn^0_{(s)} + 2Ag^+_{(aq)} \rightarrow 2Ag^0_{(s)} + Zn^{2+}_{(aq)}$. The reaction principle was discussed in our previous paper [14]. Fig. 1 shows the characterized images of typical product obtained by a procedure of dropping 0.02 M $AgNO_3$ solution onto zinc substrate followed by thermal treatment at 50 °C for 5 h. As revealed by a low magnification SEM image (Fig. 1(a)), highly uniform Ag nanoflowers are distributed on the zinc substrate over a large area. Fig. 1(b) is a corresponding magnified image, clearly showing that the nanoflowers are constructed from many nanorods with a mean diameter of 60 nm. The area outlined in Fig. 1(b) is a representative image of the end of the nanorods, which exhibits a pentagonal crystalline structure. The results are further confirmed in Fig. 1(c) using TEM by scraping off the black films on the zinc foil and ultrasonic dispersal in ethanol. The corresponding SAED patterns shown in Fig. 1(d) and (e) are taken at the tip and root sections of the nanorods, respectively. The appearance of the ($\bar{1}1\bar{1}$), (020) and ($\bar{2}00$) facets indicates that the Ag rods have twinning structure. Combining with the SEM result as shown in Fig. 1(b), it can be concluded that the Ag nanorods should be of fivefold-twinned structure bounded by five {111} facets, with the growth direction indexed to be along [110] as reported in the literature [15]. Fig. 1(f) shows a representative XRD pattern of the Ag nanoflowers. As can be seen, all of the peaks can be readily indexed to face-centered cubic (fcc) Ag (JCPDS card no. 04-0783), in addition to the peaks marked with asterisks being attributed to the zinc substrate (JCPDS 04-0831). No characteristic peaks of other impurities are observed, indicating high purity of the samples.

The temporal evolution of the Ag nanoflowers was investigated and the corresponding SEM images of the samples synthesized from 10 min, 1 h, 5 h, and 9 h are presented in Fig. 2. During the early reaction stage (10 min), the structures obtained were spherical aggregates of nanoplates with the thickness of 25–35 nm (Fig. 2(a)). When the reaction time was increased to 1 h, Ag microspheres consisting of many short branches with sharpened tips were achieved (Fig. 2(b)). Further increasing the reaction time to 5 h resulted in highly uniform and dense Ag nanoflowers on a large scale (Fig. 2(c)), and the inset in Fig. 2(c) gives a magnified representative image of individual Ag nanoflowers comprising many nanorods, also evident from Fig. 1(a) and (b). With the reaction time extended to 9 h, it is observed from Fig. 2(d) that numerous Ag nanoparticles with diameter of about 30 nm formed net-like structures.

The effect of the $AgNO_3$ concentration on the morphologies of Ag nanostructure was further examined. When the $AgNO_3$ concentration is 0.2 M under otherwise identical conditions, dendritic Ag