Materials Research Bulletin 46 (2011) 929–936

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Preparation of dendritic-like Ag crystals using monocrystalline silicon as template

Yanlin Wei, Yashao Chen *, Linjing Ye, Pengmei Chang

Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, School of Chemistry and Materials Science, Xi'an 710062, China

ARTICLE INFO

Article history:
Received 14 September 2010
Received in revised form 12 January 2011
Accepted 14 February 2011
Available online 18 February 2011

Keywords:
A. Structural materials
B. Chemical synthesis
B. Crystal growth
D. Microstructure

ABSTRACT

Symmetric dendritic silver structures with controlled morphology were successfully synthesized by a solvothermal method with the assistance of monocrystalline silicon. The morphology and structure of the dendritic silver were characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and scanning electron microscopy (SEM). It was found that the architecture of silver crystals could be controlled via simply adjusting the experiment parameters: $AgNO_3$ concentration, reaction time and temperature. Moreover, structural characterizations suggested that the dendritic silver structures preferentially grew along (1 1 1) and (2 0 0) directions, leading to the formation of dendritic structures with 1–2 μm in stem diameter and 10–50 μm in length. Additionally, the formation process of the dendritic silver structures was studied, and a possible formation mechanism was proposed based on the experimental results.

1. Introduction

Morphology-controlled synthesis of metal nanostructures has been rapidly developed into a promising field in material chemistry. It is generally accepted that the morphology (including dimensionality and shape) of the nanostructure can effectively tune their intrinsic chemical and physical properties, e.g., tailoring the surface-enhanced Raman scattering and catalytic properties of functional materials [1–4]. Among various metal nanostructures, nanostructured silver, as a typical noble metal nanomaterial, has been gained particular interest for the biocompatibility and low toxicity, important applications in catalysis [5], surface-enhanced Raman scattering as excellent substrates [6], DNA sequencing [7], etc. in recent years. The manipulation of the size and shape of silver materials at the nanoscale has great potential to influence the electronic and optical properties. Up to now, a range of technically important silver nanostructures with specific structural features, have been successfully prepared by various strategies including templated and templatless synthesis, such as zero-dimensional spheres and tetrahedral quantum dots, one-dimensional nanorods, nanowires [8–12] and nanobelts [13–15], two-dimensional nanoplates [16,17] and triangular plates [18–20], and three-dimensional (3D) nanocages [21] and branched multipods [22,23].

However, it remains a great challenge to develop facile, mild and effective methods to creating hierarchical, 3D silver nanostructures, together with well-controlled dimensions and morphologies, such as silver nanostructures with 3D dendritic morphology. Such 3D dendritic silver structures, which can provide high surface area and supply more absorption sites for reactant molecules to increase performance in catalytic applications, is a type of higher level 1D nanomaterial with a hierarchical structure. Recently, much effort has focused on the development of technique to produce silver nanostructures with dendritic morphology. For example, Wu et al. synthesized unique dendritic silver nanostructure, with stems, branches, and leaves via a simple electroless metal deposition method [24]. Ding et al. reported a work on the synthesis of dendritic silver nanostructure with a well-defined shape by a replacement reaction at the room temperature [25]. With the Reney nickel as template and reducing agent, Xie et al. synthesized dendritic silver structures [26]. Naka et al. produced dendritic silver structures from the reduction of silver ions via tetrathiafulvalene (TTF) in acetonitrile [27]. Based on sonoelectrochemistry with the assistance of poly(*N*-vinylpyrrolidone) (PVP), Meng et al. synthesized dendritic silver structures [28]. Guo and Fan reported a simple wet chemical route using L-ascorbic acid as a reductant in mixed surfactant solution consisting of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl benzyl sulfonate (SDBS) at room temperature to synthesize dendritic silver structures [29]. Yang et al. produced nanodendritic silver structures using finely dispersed Zn microparticles as a reducing agent without using any templates or surfactants [30]. Very recently, Pearson et al. propose a new approach, the potential of an ionic liquid, as an elegant solvent medium to perform galvanic replacement reactions, leading to shape transformation of spherical Ag nanoparticles into dendrite-like hierarchical flat Au–Ag nanostructures [31], which is the first time that the

* Corresponding author. Tel.: +86 29 85303725; fax: +86 29 85307774.
E-mail address: yschen@snnu.edu.cn (Y. Chen).

0025-5408/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2011.02.025

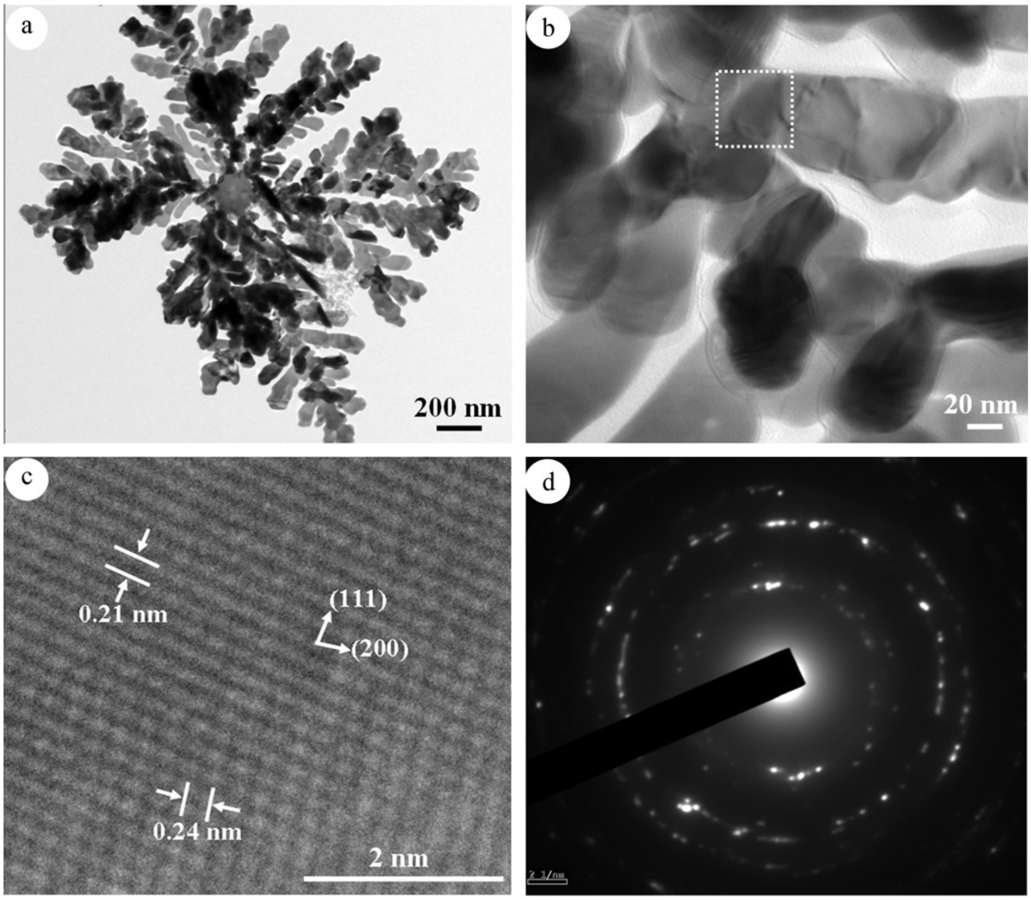

Fig. 1. (a) Low-magnification TEM image of synthesized dendritic silver structures; (b) higher magnification TEM image of the dendritic silver structures; (c) HRTEM image of the square area in panel b and (d) the SAED patterns.

nanodendritic structures are synthesized with a galvanic replacement reaction in the ionic liquid. We are interested in exploring a new method to prepare dendritic silver structures in aqueous solution, which could be helpful to reproducible and controllable synthetic route for technological applications.

In this paper, a very efficient template technique for synthesis of well-dispersed dendritic silver structures at high yield was proposed, which was carried out by simply reducing silver nitrate with ethylene glycol in the surrounding (1 1 1) silicon plate etched with hydrofluoric acid. The obtained dendritic silver structures exhibited good thermal stability, and the structural characterizations suggested that the unique dendritic silver structures preferentially intergrew along (1 1 1) and (2 0 0) crystal faces.

2. Experimental

All chemicals used were analytical grade without further purification.

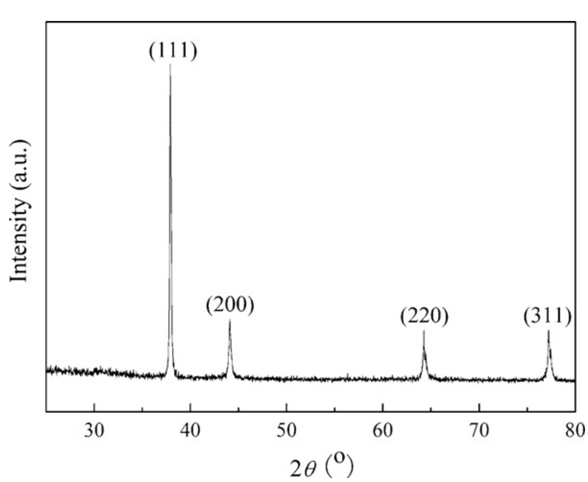

Fig. 2. XRD pattern of synthesized dendritic silver structures.

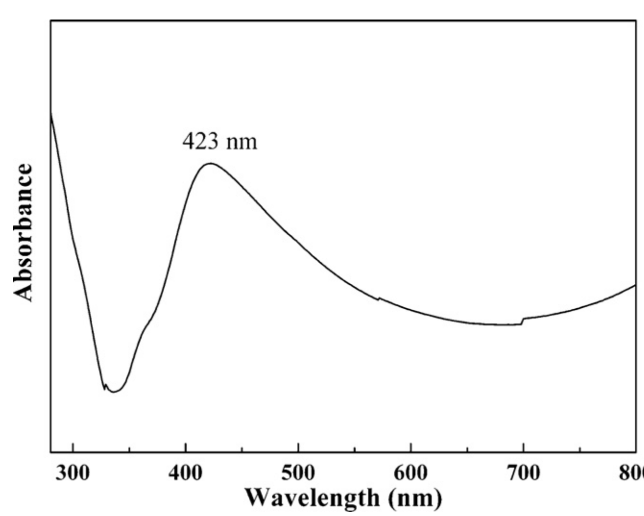

Fig. 3. UV–vis absorption spectrum of synthesized dendritic silver structures.