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Microwave-assisted synthesis of high aspect ratio ruthenium nanorods

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Abstract

Poly (*N*-vinyl-2-pyrrolidone) (PVP)-stabilized ruthenium nanorods with high aspect ratio by refluxing ruthenium(III) chloride in n-propanol have been successfully prepared by means of a facile and rapid microwave heating for the first time. The structure and morphology of the obtained products were characterized by transmission electron microscopy (TEM), select area electron diffraction (SAED), ultraviolet–visible spectrophotometry (UV–vis), X-ray photoelectron spectroscopy (XPS) and Fourier transform spectroscopy (FT-IR). XPS analysis reveals that the nanorods were in the metallic state. TEM images showed that ruthenium nanorods had an obvious one-dimensional structure with the aspect ratio ranged from 5 to 40 nm and length up to 600 nm. SAED patterns indicated that the nanorods were single-crystalline with a hexagonal structure.

Keywords: Poly (*N*-vinyl-2-pyrrolidone); Ruthenium; Nanorods; Microwave

In recent years, one-dimensional nanostructures, such as nanotubes, nanowires, nanorods and nanobelts, have been attracting considerable attention from both fundamental and applied research, mainly due to their unique structural nature and electronic, magnetic, optical and/or catalytic properties, which depend highly on their size and shape [1–5]. Compared with the zero-dimensional structure, the shape anisotropy of the one-dimensional structure also provides a better model system to study the dependence of electronic, optical, catalytic and magnetic properties on size confinement and dimensionality [6].

As an important member of the group of platinum metals, ruthenium nanoclusters have been known to show very unique and interesting activities as the catalyst [7–9]. Accordingly, much emphasis has focused on developing diverse methods to obtain size controllable ruthenium colloids [10]. However, all these methods are difficult to control the morphology of ruthenium nanoclusters. While the other novel metals, such as silver, platinum and palladium nanoclusters, have colorful shapes [11–13]. Although different methods have been developed to prepare spherical nanoparticles with different sizes, the morphology control of ruthenium still remains a preparative challenge. Up to now, only a few groups have reported the special morphologies of ruthenium nanoclusters. For example, Zhang *et al.* reported a shuttly like ruthenium particles with the aspect ratio enlarged from 4.5 to 5.0 [14]. Harpeness *et al.* synthesized rodlike ruthenium nanoclusters with the aspect ratio of only 1.6 by a microwave-polyol process [15].

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Microwave irradiation method often has been widely applied to produce one-dimensional nanostructures due to its quick, uniform and energy efficient heating method. In this paper, we explored microwave heating method to prepare ruthenium nanorods with high aspect by refluxing ruthenium(III) chloride in n-propanol using PVP as capping agent.

1. Experimental

The typical synthesis is as follows. First, PVP (0.1387 g, 2.5×10^{-2} mol, as monomeric unit) and $RuCl_3$ (0.0327 g, 2.5×10^{-3} mol) were dissolved in *n*-propanol (50 mL) in a 250 mL round-bottomed flask at room temperature under magnetic stirring to form a dark red solution. Then the solution was irradiated to reflux by a modified domestic microwave oven (800 W, 2.45 GHz) with a refluxing apparatus. After the mixture was refluxed for a certain period of time, the color of the solution changed from dark red to deep purple. In all the experiments the microwave over is employed at 100% power. The resulting product could be collected by centrifugation and washed three times using ethanol, then dried 10 h under vacuum at 50 °C.

2. Results and discussion

It is well known that UV–vis absorption spectra have been regarded as an effective method to illustrate the evolution of metal species in the preparation of colloidal metal clusters. Fig. 1 presents the UV–vis spectra of a PVP-stabilized solution before and after Ru^{3+} ions reduction by MW irradiation at different reaction intervals. As shown in Fig. 1, there was a peak at 340 nm assigned to the Ru^{3+} ions in the UV–vis spectrum of the original solution (0 h). As the irradiation time was prolonged, the peak at 340 nm decreased gradually and a broad absorption centered at 509 nm attributed to the Plasmon band of Ru was detected. After about 180 min of MW irradiation, the absorption peak at 340 nm disappeared completely, which indicated that Ru^{3+} ions were entirely reduced to Ru(0) metal. The increasing scattering absorbance at 509 nm with time revealed the formation of ruthenium (0) colloids. Additionally, the color of the solution turned from dark red to deep purple, which also indicated ruthenium ions were reduced and the metal particles were formed.

In order to further confirm the formation of metallic ruthenium nanostructures, XPS measurements were employed to determine the oxidation state of PVP-stabilized ruthenium nanostructures (spectra not shown). The binding energies of Ru $3d_{5/2}$ at 280.0 eV, Ru $3p_{1/2}$ at 483.8 eV and Ru $3p_{3/2}$ at 461.2 eV in the PVP-coated ruthenium nanostructures were consistent with those of ruthenium metal [16], respectively. The combination between ruthenium and PVP was investigated by spectroscopic measurement. In comparison the FT-IR spectra of PVP-stabilized ruthenium nanoclusters with pure PVP employed in the preparation, the absorption band at 2960 cm^{-1}, 1660 cm^{-1}, 1280 cm^{-1}, and 1070 cm^{-1} were assigned to the vibration models of C–H, C–O, N–OH, and C–N, respectively, indicating PVP

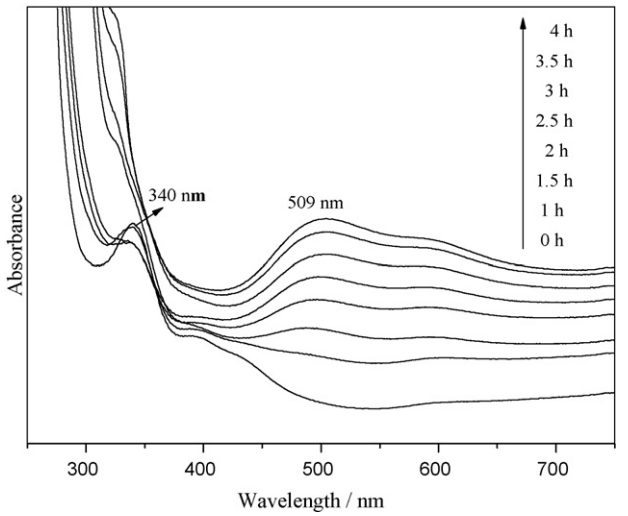

Fig. 1. UV–vis absorption spectra of ruthenium colloids stabilized by PVP at different reaction stages.