Colloids and Surfaces B: Biointerfaces 83 (2011) 284–290

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

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

A novel biological strategy for morphology control of $PbWO_4$ crystals in *tomato* extract

Yuhua Shen [a,b,*], Yan Zhang [b], Yiqing Chen [a], Shikuo Li [b], Qingfeng Zhang [b], Anjian Xie [b]

[a] *School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China*
[b] *School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, China*

ARTICLE INFO

Article history:
Received 16 December 2009
Received in revised form
24 November 2010
Accepted 25 November 2010
Available online 2 December 2010

Keywords:
Tomato extract
Lead tungstate
Crystal
Fluorescence spectra

ABSTRACT

$PbWO_4$ crystals were readily synthesized by reacting lead oxide (PbO_2) with sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) at room temperature in the presence of *tomato* extract. Biomolecules such as vitamins, proteins in the extract played both the roles of reductant and template. The size and morphology of the $PbWO_4$ crystals could be controlled by adjusting the concentration of the reactants. When the concentration ratio of PbO_2 and Na_2WO_4 was increased, the morphologies of the products varied from spherical to fusiform. Room-temperature fluorescence spectra indicated the products had a slight blue shift compared to the solid structure, which may be due to the structure defects in the crystals. The possible mechanism of $PbWO_4$ crystal growth in *tomato* extract was discussed.

1. Introduction

Lead tungstate ($PbWO_4$) is a suitable candidate for high-energy physics applications because of its high density (8.3 g/cm^3), short decay time, high irradiation damage resistance, and has been widely used in the fields of electromagnetic calorimetry, excitonic luminescence, thermoluminescence and stimulated Raman scattering behavior [1–3]. Since the structure sensitivity of $PbWO_4$ and its luminescence is remarkably affected by the structure defects in the crystals, improving its scintillating properties through changing and controlling its morphology has become one of the principal focus in the research of $PbWO_4$ crystal [4,5].

Various approaches are available for the morphology-controlled synthesis of $PbWO_4$ crystals, for example, wet chemical routes, hydrothermal preparation, AOT-microemulsions [6–9] and sonochemical synthesis [10,11], the Czochralski [12] and Bridgeman methods [13], etc. However, it is still very important to develop more facile methods in mild reaction conditions. Recently green chemistry has been widely investigated for the synthesis of nanomaterials, because the previous methods involved a large amount of hazardous byproducts [14]. As an alternative to conventional methods, biological methods are considered green and ecologically sound for the micro- or nano-material fabrication [15]. People have used purified natural materials to prepare noble metal nanoparticles, for example, Nadagouda and Varma have synthesized gold and platinum nanoparticles with interesting morphologies using vitamin B_2 [16]. Our group has fabricated monodisperse silver and gold composite thin films by vitamin E [17,18]. And we have also synthesized silver and selenium nanoparticles using *Capsicum annuum L.* extract [19,20].

Lead oxide is a toxic substance which can be absorbed into the body by inhalation and ingestion. The substance may have serious effects on the blood, bone marrow, central nervous system, peripheral nervous system and kidneys, resulting in anaemia, encephalopathy (e.g., convulsions), peripheral nerve disease, abdominal cramps and kidney impairment. It causes toxicity to human reproduction or development. Bioaccumulation of this chemical may occur in plants and in mammals [21]. These heavy metal oxides are present in industrial (e.g., in the waste battery) and municipal effluents. Therefore, it is of great scientific and practical interest to reveal the possible removal and recycling of lead oxide from wastewater using low-cost treatments. *Tomato* is inexpensive and ready available natural product. In addition, *tomato* extract is no toxicity, compared to other reducing agents, which makes it an ideal multifunctional agent for the production of crystals. Herein, the *tomato* extract was used as reductant for PbO_2 to direct the formation of $PbWO_4$ crystals in an aqueous solution. This synthesis procedure is simple, economical, convenient, and the hazardous PbO_2 can be changed into a useful functional material. To the best of our knowledge, the use of *tomato* extract at room temperature for the synthesis of $PbWO_4$ crystals from PbO_2 has not been reported.

* Corresponding author at: School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, China. Tel.: +86 551 5108090; fax: +86 551 5108702.
E-mail address: s_yuhua@163.com (Y. Shen).

0927-7765/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfb.2010.11.034

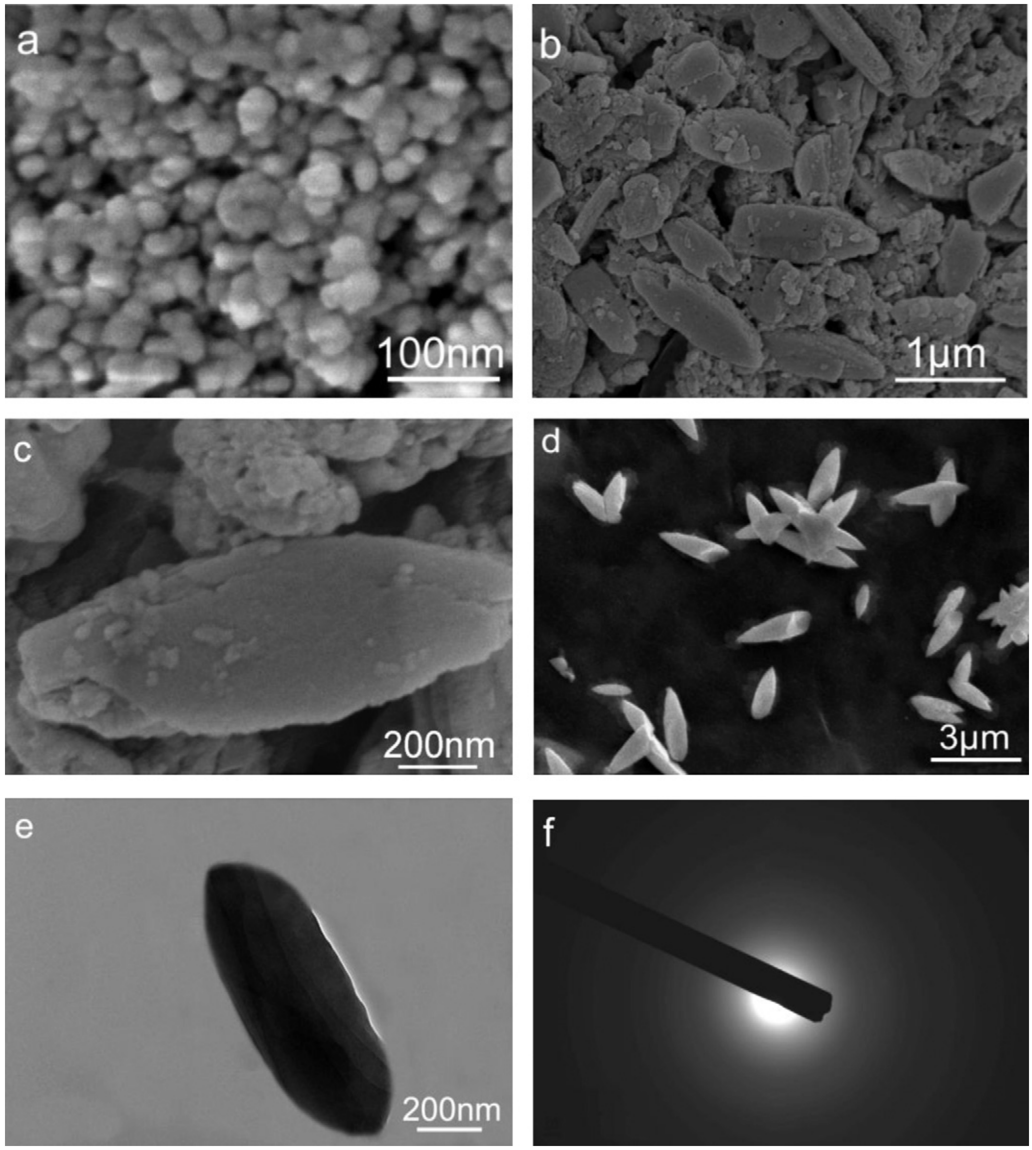

Fig. 1. SEM images of the products I (a), II (b, c) and III (d), TEM image (e) of the product II and SAED pattern (f) of the product II from e, pH = 4.5. The reaction time is 20 h.

2. Experimental

2.1. Materials

Sodium tungstate ($Na_2WO_4 \cdot 2H_2O$), and lead oxide (PbO_2) were purchased from Shanghai Reagent Company (China). Absolute ethanol was from Shanghai first revitalization chemical industry factory (China). All the reagents were of analytical purity and used without any further purification. The water used in this experiment was double distilled water. The *tomato* was fresh and was purchased from the Anhui University supermarket.

2.2. Synthesis of $PbWO_4$ crystals using tomato extract

Prior to the experiment, the *tomatoes* (ca. 120 g) were washed thoroughly with double distilled water to ensure that no impurities were attached to them. They were then placed in an extract extractor (*PHILIPS-HR1861*, *China*) for extraction. The extract was then separated by centrifugation at 2000 rpm for 5 min to remove insoluble fractions and macromolecules, and finally a light red extract was collected for further experiments.

In a typical procedure, 20 mL of a 5.002 mmol/L aqueous Na_2WO_4 solution was added to 50 mL of the *tomato* extract. Another 2.855 mmol/L PbO_2 was introduced into the above mixture. The pH value of the solution was adjusted to 4.5, which was kept stirring rapidly at room temperature for 20 h (I). The deposit was collected by eccentricity at 12,000 rpm for 4 min, and washed with double distilled water, absolute ethanol for several times, and then dried in vacuum until a constant weight was achieved and the final sample was called product (I). For preparation of systems (II), (III) and products (II), (III), the same procedures were repeated, but concentrations of Na_2WO_4 and PbO_2 were adjusted to 25.01 mmol/L and 14.27 mmol/L (II), 50.02 mmol/L and 28.55 mmol/L (III), respectively.

To further study the effect of pH value on the products, the synthesis of $PbWO_4$ crystal was also carried out at pH 6.0. The experiments were similar to the systems (I–III), the obtained products were labeled as (IV–VI). All the products were collected in the same way as the characterization mentioned above.