Electrochimica Acta 99 (2013) 145–151

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Sacrificial template-assisted fabrication of palladium hollow nanocubes and their application in electrochemical detection toward hydrogen peroxide

Guangdi Nie, Xiaofeng Lu*, Junyu Lei, Liu Yang, Xiujie Bian, Yan Tong, Ce Wang*

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 4 February 2013
Received in revised form 11 March 2013
Accepted 11 March 2013
Available online 22 March 2013

Keywords:
Sacrificial template
Palladium hollow nanocubes
Electrochemical catalysis
Hydrogen peroxide

ABSTRACT

Pure Pd hollow nanocubes assembled with uniform nanoparticles were successfully fabricated via a one-step redox reaction by using Cu_2O nanocubes as both sacrificial templates and the reducing agents. Almost no residual Cu_2O cores remained in the final Pd cubic nanoshells which were composed of nanograins with an average diameter of approximately 6.5 nm. A wide liner range (0.1–24.0 mM), a relatively high sensitivity (287.7 mA M^{-1} cm^{-2}) and a comparable detection limit (7.4 μM, S/N = 3) were observed in the electrochemical experiments, indicating that the obtained Pd hollow nanocubes as enzyme-free catalysts possessed excellent electrocatalytic activity to the reduction of H_2O_2.

1. Introduction

It is generally known that hydrogen peroxide (H_2O_2) as important oxidant, bleach, disinfectant and dechlorination agent is widely used in textile, food, comprehensive ecological improvement, electronic and chemical industry. Moreover, it has appeared as very common intermediate in many chemical and biological reactions. Consequently, it becomes more and more necessary to detect H_2O_2 rapidly and accurately. To our knowledge, even though various approaches have been developed at present for the determination of H_2O_2 [1–4], only electrochemical methods among them have been regarded as a highly effective way because of their rapid response, low detection limits and simple devices [5]. Particularly, despite of the fact that enzyme modified electrodes exhibit super selectivity and responsiveness toward H_2O_2 [6–8], the enzymes which usually require harsh conditions and complicated immobilization process are restricted in the practical application. By contrast, noble metals including silver (Ag), gold (Au), palladium (Pd) and platinum (Pt) etc., which possess good stability and excellent sensitivity, are appropriate as novel non-enzyme catalysts for the detection of H_2O_2 [5,9–13].

Noble metal nanomaterials with special morphologies such as nanocubes, nanotubes, nanostars, nanoplates, nanorods and so on, have always been the focus in scientific research field due to their prominent catalytic, electronic, optical, photonic and gas sensing properties [14–18]. In the last few years, hollow metal nanostructures have attracted extensive attention for their remarkable chemical and physical characters which are attributed to the special construction and composition [19–23]. Further, the tiny component units like nanoparticles, nanocubes and nanosheets, which assemble the porous walls of hollow structures, endow them with distinguished performance resulting in widespread potential applications [24–27]. For instance, NiO hollow nanospheres assembled with nanograins revealed high electrocatalytic activity for glucose [24]. Porous TiO_2 hollow nanospheres composed of nanoparticles presented high surface area, good thermal stability and enhanced photodegradation ability toward methyl orange comparing with commercial P25 in the presence of Cr (VI) [25]. In addition, dendrite-shaped CuO hollow micro/nanostructures comprised of nanocubes outside were demonstrated to be an outstanding anode material for lithium-ion batteries [26]. Hierarchically nanostructured α-Fe_2O_3 hollow spheres assembled by nanosheets are promising to be applied in water treatment [27]. Absolutely, numerous efforts have been made to synthesize hollow nanostructures of noble metals. A plenty of techniques, such as soft or hard template methods, Ostwald ripening and Kirkendall effect, have come into being accordingly [28]. Above them, template method, which has advantages on general versatility, narrow size distribution of the prepared products and availability in a wide range of sizes and materials with well-defined shapes, is considered

* Corresponding authors. Tel.: +86 431 85168292; fax: +86 431 85168292.
E-mail addresses: xflu@jlu.edu.cn (X. Lu), cwang@jlu.edu.cn (C. Wang).

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http://dx.doi.org/10.1016/j.electacta.2013.03.066

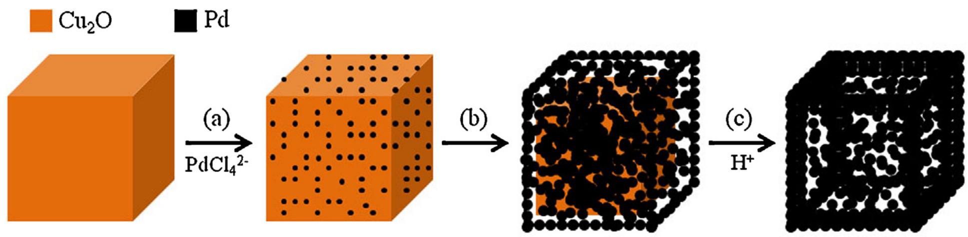

Fig. 1. Schematic illustration of the growth mechanism of Pd hollow nanocubes.

as a powerful means to synthesize hollow nanostructures [28,29]. Commonly employed templates mainly include monodispersed silica, polystyrene, carbon and metal nanoparticles [30–33].

In the past few years, it has been reported that a series of hollow micro/nanostructures of noble metals and their alloys have been fabricated using cuprous oxide (Cu_2O) crystals as chemical template [29,34,35]. This strategy with the features of low cost and simple synthesis can accomplish the controlled preparation of hollow architectures under facile conditions. Nevertheless, the formation process of hierarchical Pd nanocages by this protocol

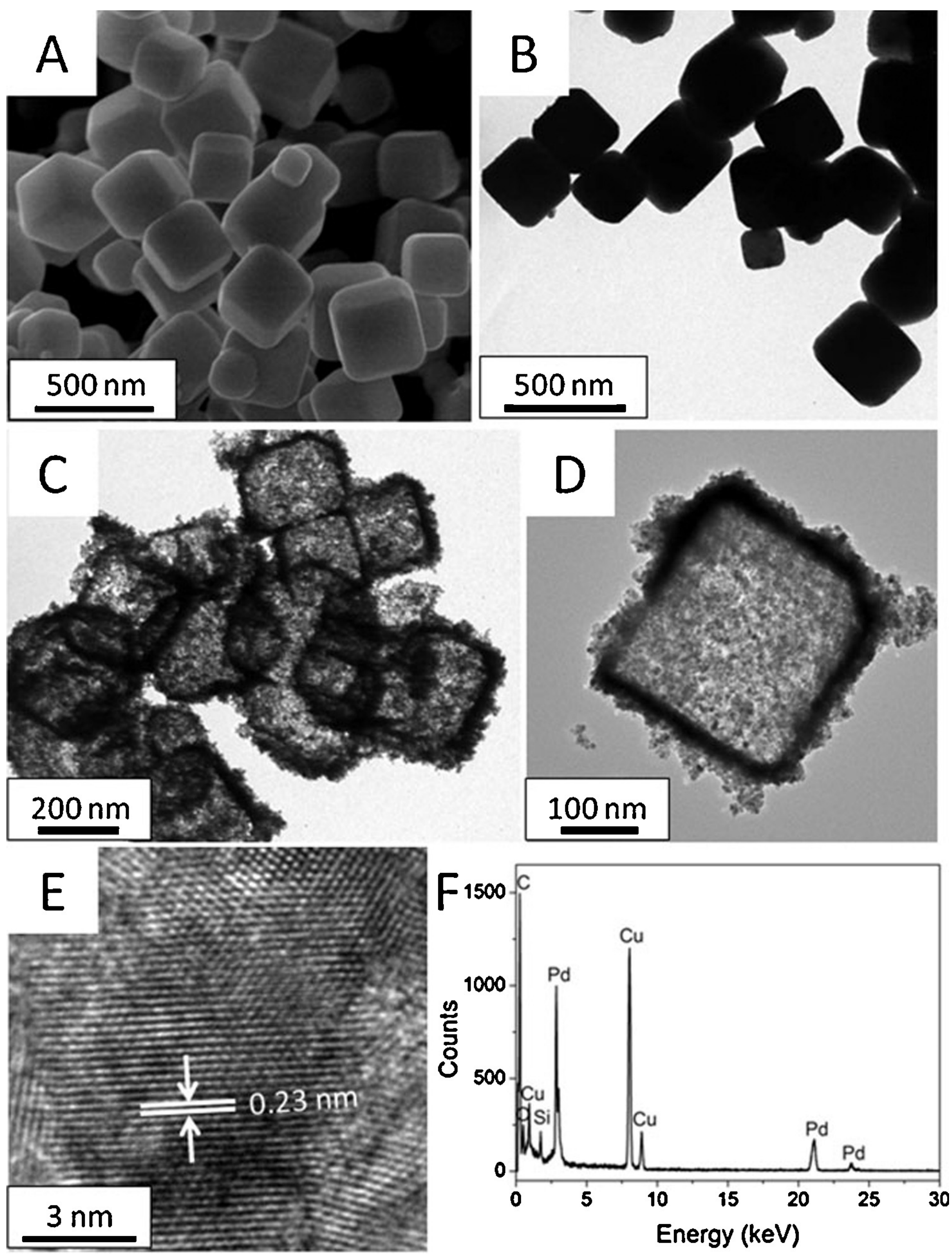

Fig. 2. (A and B) SEM and TEM images of the as-prepared Cu_2O nanocubes. (C and D) TEM images of Pd hollow nanocubes at different magnifications. (E) HRTEM image of the obtained Pd nanoshells. (F) EDX spectrum of the Pd hollow nanocubes.