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Preparation of gold nanoparticles using hydroquinone derivatives

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ABSTRACT

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1. Introduction

Over the past few decades, gold nanoparticles (GNPs) with unique physico-chemical properties have been intensively studied and found to be useful in many disciplines such as catalysis [1], biology [2] and SERS [3]. It is now well-known that the size, the distribution of sizes, shape, and composition of nano-materials can dramatically affect their physical and chemical properties, and plenty of efforts have been made to control the particles sizes [4]and shapes [5]. Jana et al. prepared gold nanoparticles with sizes between 5 and 40 nm using cetyl-trimethylammonium bromide (CTAB) as the stabilizer and sodium borohydride as the reductant [6].

Quinones/hydroquinones (Q/HQ) are an important class of prototypical redox molecules that play a variety of vital roles in life science, particularly in electron transfer and energy conservation systems. And there are some efforts to use quinones as a reductant to obtain GNPs. Perrault reported spherical GNPs in the size range of 50–200 nm in diameter synthesized by using the weak reductant hydroquinone [7].

In this work, we first use an electrochemical method to study hydroquinone and its non-ionic and ionic derivatives and the influence of the resulted GNPs; we hope to establish a correlation between chemical structure of reductant and the quality and shape of the resulted GNPs, and we believe that the influence of differences in chemical structure can supply new ideas in this field and shed light on the points that are still unresolved.

2. Experimental

This work first focuses on the growth procedures of gold nanoparticles using HQ, MHQ, TBHQ and PHQS

as reducing agents through a seed-mediated growth approach. It was found that the activation energy of

the hydroquinone and its derivatives are in the order PHQS > TBHQ > MHQ > HQ. The morphology of

GNPs synthesized with HQ, MHQ, and TBHQ is quasi-spherical and the size is 10-20 nm, while PHQS are

of several kinds of morphologies, such as rods and triangular prisms; PHOS could be a weak shape-

directing agent. We speculate that it resulted from the electric field asymmetry of its ionic side group.

In a typical synthesis, a gold seed solution was prepared by first combining HAuCl₄ solution (5.5 mL, 0.293 mM), deionized water (5.0 mL) and sodium citrate (0.05 mL, 0.05 M). This was followed by the addition of a freshly made aqueous solution of NaBH₄ (0.25 mL, 0.05 M) and agitated with ultrasound. After the solution turned pink, the ultrasound was stopped, and the as prepared seed solution was further aged for 12 h (more detailed experimental protocol is found in electronic Supplementary information).

3. Results and discussion

A series of experiments were performed to investigate the effect of hydroquinone (HQ), tert-butylhydroquinone (TBHQ), methylhydroquinone (MHQ) and potassium hydroquinone sulfonate (PHQS) concentration on the properties of the synthesized GNPs through a seed-mediated procedure. The concentration varied from 0.1 mM to 0.5 mM while the concentration of HAuCl₄ was kept at 0.15 mM. TEM images of the GNPs synthesized at 0.4 mM are shown as Fig. 1, and insets are HRTEM images. The morphology and size distribution of GNPs synthesized with HQ, MHQ, and TBHQ are shown in Fig. 1a, b and c respectively; they are guasi-spherical and polycrystalline and their diameters are in the range of 10–20 nm. Fig. 1d shows the TEM image of GNPs prepared with PHOS; there are a variety of morphologies such as rods and triangular prisms. The resulted GNPS are polycrystalline and the fringe spacing measured from the HRTEM images is 0.21 nm which corresponds to the spacing between the (111) planes of fcc gold. Fig. 2 shows UV-vis spectrum and cyclic voltammogram of GNPs synthesized at concentrations of 0.1 mM





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Fig. 1. TEM images and size histograms of gold nanoparticles synthesized by (a, a1) HQ, (b, b1) MHQ, (c, c1) TBHQ, and (d, d1) PHQS. Insets are the HRTEM images.

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