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New insights into the formation mechanism of gold nanoparticles using dopamine as a reducing agent

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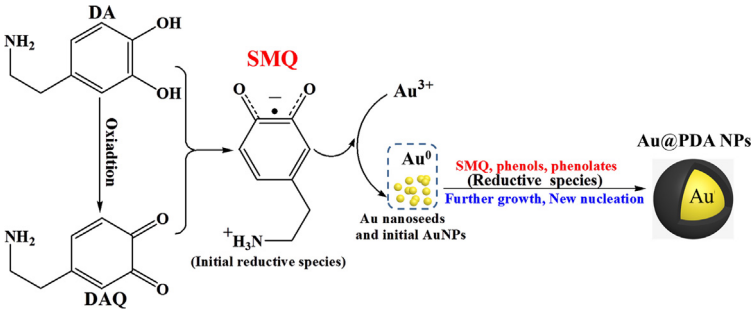
GRAPHICAL ABSTRACT



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ABSTRACT

Dopamine (DA), a simplified mimic of mussel proteins, can be employed as a reductant in the preparation of Au nanoparticles (AuNPs) due to its inherent catechol building block. The widely accepted mechanism of AuNP formation using DA as the reductant assumes that the reduction of Au(III) ions involves the two-electron oxidation of DA, where the corresponding phenol and phenolates serve as the reductive species to yield quinone. We herein report a novel insight into the mechanism of formation of AuNPs using DA as the reductant. We demonstrate that the synthesis of AuNPs requires the prior oxidation of the DA to form quinone units, which then catalyze the formation of semiquinones. These semiquinone radicals (SMQs) reduce the Au(III) ions to form the initial AuNPs, and further growth is then catalyzed by the first AuNPs, with nucleation occurring where the SMQs, phenols, and phenolates can serve as reductive species. In addition, DA oxidizes and polymerizes to form a polydopamine capping layer on the AuNPs. We therefore expect that the novel mechanism proposed herein may promote us to furthermore explore the production of noble metal NPs using other polyphenols.

1. Introduction

Recently, gold nanoparticles (AuNPs) have received significant attention in the areas of biomedical devices [1], biosensors [2], catalysis [3], and pharmaceuticals [4], due to their fascinating optical, electronic, and chemical properties [1–4]. To date, a variety of methods and techniques have been reported and reviewed for the preparation of AuNPs, including chemical [5–14], sonochemical [15], and photochemical [16] approaches. However, the chemical reduction method is the most common synthesis route for AuNPs due to its simplicity. This method is based on the chemical reduction of gold precursors by a reductant [5–14].

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In this context, the commonly used mussel protein mimic, dopamine (DA) [17,18], has been found to be an effective reductant in the synthesis of AuNPs [8–13]. Besides its reducing ability, DA and the generated polydopamine (PDA) can also be used as binding agents [17,18], which help stabilize the produced NPs [14]. In these reports, the authors considered that the initial reductive species are the phenols or phenolates of DA, and they also propose that the reduction of Au ions involves a two-electron oxidation of DA to yield the quinone [10–13].

Moreover, the oxidation mechanism of DA remains controversial [19]. Many researchers have reported that the oxidation of DA is a two-electron reaction, which produces the corresponding dopamine-quinone (DAQ) [20–22]. However, DA has also been reported to undergo one-electron oxidation, wherein semiquinone radicals (SMQs) are the main intermediates [23,24]. On the other hand, SMQs also form via disproportionation involving DA and DAQ [25,26]. This lack of consensus encourages us to further explore the formation mechanism of AuNPs using DA as the reductant.

Herein we present new insights into the formation mechanism of AuNPs using DA as the reductant. We consider that the initial reductive species is not the phenol group itself, but rather the SMQs formed by electron transfer from o-quinone to the catechol units [25,26]. In particular, we propose that the DA-based synthesis of AuNPs requires that DA is first oxidized to form quinone units, which then catalyze the formation of SMQs [25,26].

2. Results and discussion

We first examined the effect of the pH of the reaction system on the formation of the AuNPs using DA as a reductant. Initially, the pH of an aqueous DA solution was varied between 4.0 and 8.0 and allowed to stand under air for 30 min prior to the addition of a solution of $HAuCl_4$ (i.e., Au(III)). Ultraviolet–visible (UV–Vis) spectroscopy was then employed to monitor the reaction between the Au(III) ions and the DA solution at a range of pH values. For example, at pH 8.0, addition of the gold salt led to a rapid color change with surface plasmon resonances (SPR) centered at ~520 nm, which is consistent with the formation of AuNPs (Fig. 1A) [5]. As shown in the transmission electron microscopy (TEM) image of the obtained product (Fig. 1B), mainly spherical particles (in addition to a few anisotropic particles) exhibiting a uniform size distribution were observed. Upon decreasing the pH of the DA solution to 7.0, a broader SPR band was observed at ~600 nm (Fig. 1C). In this case, a small amount of larger and aggregated spherical AuNPs were clearly observed in the TEM image

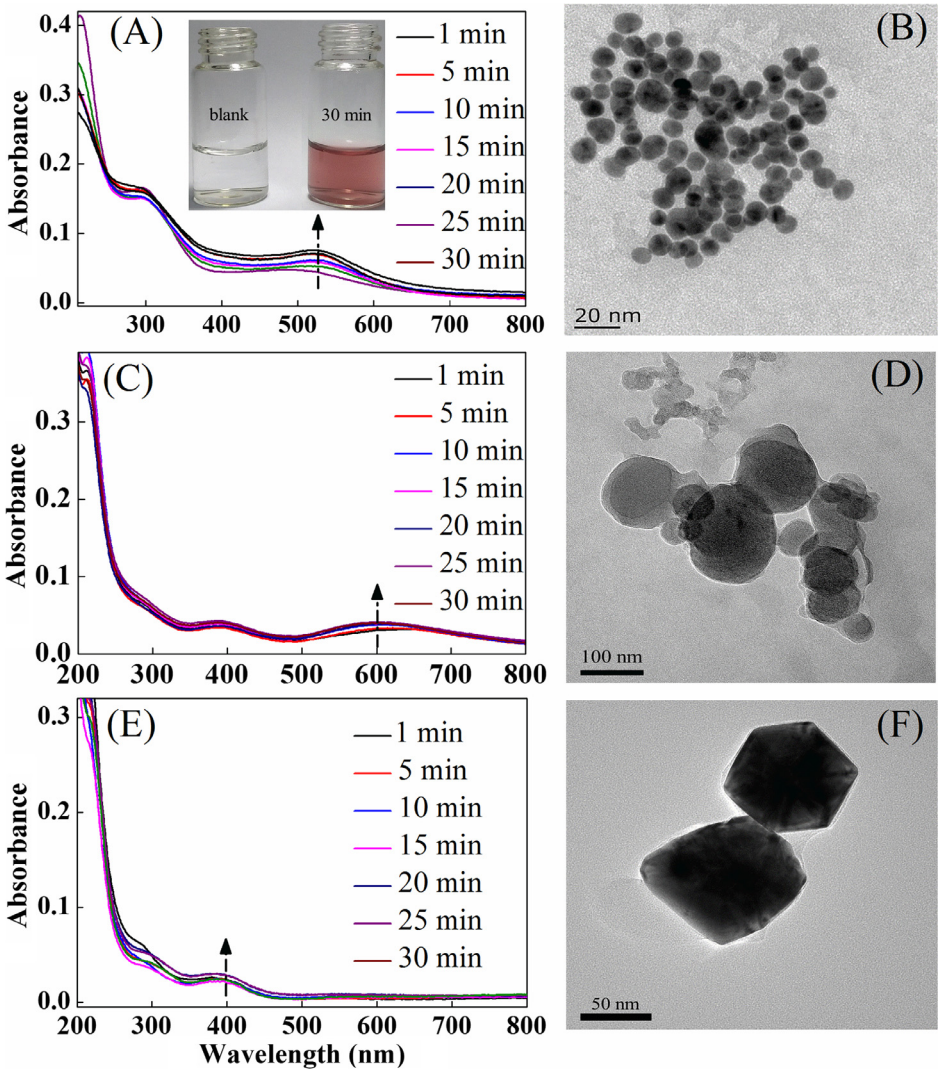

Fig. 1. Time dependent UV–Vis spectra of the AuNPs prepared at (A) pH 8.0, (C) pH 7.0, and (E) pH 4.0 via the reduction of $HAuCl_4$ by DA. The insets show the corresponding AuNP solutions after reduction. TEM images of the AuNPs prepared at (B) pH 8.0, (D) pH 7.0, and (F) pH 4.0.