



## Synthesis, density functional theory, molecular dynamics and electrochemical studies of 3-thiopheneacetic acid-capped gold nanoparticles

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### ABSTRACT

Gold nanoparticles capped with a bifunctional ligand, 3-thiopheneacetic acid (3-TAA) were synthesised by borohydride reduction at room temperature. The transmission electron microscopy (TEM) analysis showed that the particle aggregates and had semi-linear partial linkages that could be attributed to multi-modal binding of the ligand with various gold nanoparticles through the terminal thioether (–S–) group and oxygen of the carboxylic (–COOH) group. This bimodal interaction led to limited stability of the resultant nanoparticles when tested using highly electrolytic media. To investigate further, density functional theory (DFT) quantum chemical and molecular dynamic calculations were conducted. The energetically favorable binding modes of the ligand to gold nanoparticle surfaces using the Gaussian program were studied. The DFT results showed kinetic stability of Au–3-TAA–Au interactions leading to inter-particle coupling or aggregation. Electrochemical analysis of the resultant nature of the capping agent revealed that 3-thiopheneacetic acid did not form a polymer during the preparation of Au–3-TAA. The cyclic voltammograms of Au–3-TAA nanoparticles coated glassy carbon electrode showed a typical gold character with the oxidation and reduction peaks at 1.4 V and 0.9 V, respectively.

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### 1. Introduction

The synthesis of nanosized materials, especially metal nanoparticles, requires considerable control of their composition, size, shape, stability and dispersion properties owing to applications in various scientific fields. This has led to a plethora of investigations relating to the property exploitation of these entities as biomolecular conjugates, metallics, thin films and semiconductors [1–6]. Many different protocols have been developed for the synthesis of gold and other noble metal nanoparticles, with the bulk-precipitation-based Turkevich method [7] and the biphasic Brust et al. [8] method at the forefront. The preparative methods are devised such that there is a capping agent that binds to the surface atoms of the nanoparticle, thus controlling the particle sizes and preventing particle aggregation, which tends to reverse the unique nanoparticle properties back to bulk. These approaches use citrate as both a reducing agent and capping agent or the biphasic method of direct reduction in the presence of a ligand. The choice of ligand can also introduce a secondary functionality to the nanoparticle surface. Bifunctional ligands are usually equipped with a thiol head-group (–SH) which attaches to the gold

or other metal nanoparticle surface and a secondary group, either carboxyl (–COOH), amine (–NH<sub>2</sub>), hydroxyl (–OH) or other organic moieties depending on the desired application.

The interaction between gold and sulfur has, for a long time, eluded clear-cut explanations and undermining the significant developments in spectroscopy. Lack of reproducibility in single-crystal growth had been identified as the single biggest difficulty for such techniques as X-ray crystallography [9]. Recent work by Jadzinsky et al. [10] successfully demonstrated the mode of attachment of gold to sulfur by growing a single crystal of Au<sub>102</sub>(p-MBA)<sub>44</sub> (MBA – mercaptobenzoic acid). The binding group was observed to interact weakly with the surface atoms of the “grand core”, which is a truncated 79-atom cluster having gold–gold bonds resembling those of a bulk metal. The gold–sulfur bond showed that gold formed a homolytic bond with bond strength in the order of ca. 50 kcal/mol. This observation agreed well with prior theoretical predictions [11]. Further experimental and DFT work on the Au<sub>n</sub>MBA<sub>n</sub> system by Mpourmpakis et al. proposed a mechanism implicating the solvent contributions on the stability and growth of the clusters [12]. Other literature of importance on this subject has been published elsewhere [13] and on DFT studies of AuNPs [14,15]. The practical usefulness of sulfur based ligands as effective capping agents for metal nanoparticles has been well demonstrated [16,8,17]. The fate of the hydrogen of

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