



# 1,2,4-Triazole-3-thiol-protected silver-nanoparticles as a platform for *ECE* electrochemical reaction<sup>☆</sup>



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## ARTICLE INFO

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## ABSTRACT

Incorporation of “green chemistry” principles into nanotechnology has become one of the key subjects for nanoscience researches. In this work, we report an electrochemical reaction with *ECE* mechanism on the surface of 1,2,4-triazole-3-thiol-protected silver nanoparticles (TATAgNPs) via electrochemical oxidation of catechol in the presence of TATAgNPs. The reaction proceeds via the nucleophilic 1,4-Michael addition of TATAgNPs to electrochemically generated *o*-benzoquinone in aqueous solution and at ambient temperature and pressure. The occurrence of *ECE* mechanism on the Ag nanoparticles was proved by cyclic voltammetric and controlled potential coulometry. Also functionalized AgNPs were characterized by UV-Vis spectroscopy, dynamic light scattering (DLS) and transmission electron microscopy (TEM) techniques.

## 1. Introduction

Due to the unique properties of noble metal nanoparticles which make them attractive for numerous promising applications, they are studied in various applications such as catalysis [1], energy conversion [2], sensing [3], photochemistry [4], medicine [5], biotechnology [6] and optoelectronics [7].

Generally, for these applications and also for the stability, introducing the appropriate ligand on the surface of nanoparticles is required. Nevertheless, introducing of appropriate functionality to the surface of nanoparticles (NPs) and understanding the chemistry of NPs environment have been a critical aspect for their use.

In the case of thiolate stabilized NPs, three main approaches have been used for introducing functionality: 1- Synthesis of NPs with the desired ligand which has some limitations such as sensitivity of functional groups of protecting thiols towards the NP synthesis conditions [8,9], 2- ligand-exchange reaction which is a versatile method but requires large excess of thiol with the desired functionality [10,11], and 3- post-synthesis via interfacial reactions of terminal functional groups on the surface of NPs which is often more desirable approach compared with the others [12–14]. For example, Workentin's research group has used Michael addition reaction for the incorporation of amine moiety

on to the AuNPs modified with maleimide functional group in high pressure condition and in organic solvents [15].

On the other hand, over the two past decades an increasing attention has been devoted to the topic of “green” chemistry in chemical processes [16–18]. In a green synthetic strategy, employing nontoxic chemicals, renewable materials and environmentally friendly solvents are some of the key issues that merit great consideration. Furthermore, in recent years, electroorganic synthesis as a typical environmentally benign process has attracted particular attention since electrons are clean reagents, the electrodes can be removed at the end of the electrolysis and also there is no need for oxidizing and reducing reagents [18]. On the other hand, when the solvents such as water, ethanol and ionic liquids are used, it becomes more ecologically friendly [18].

In previous studies, we have shown that catechol derivatives can be oxidized electrochemically to corresponding *o*-benzoquinones, and can further be attacked as Michael acceptors by a variety of nucleophiles [18,19]. Also, recently we have presented a novel electrochemical method for the modification of glassy carbon surface by catechol derivatives [20]. In this direction, here we present a novel and totally green approach for post-modification of AgNPs via Michael addition reaction on the surface of 1,2,4-triazole-3-thiol-protected silver nanoparticles by an *ECE* electrochemical mechanism in green conditions.

<sup>☆</sup> Urgency statement

In this work, the electrochemical modification of silver nanoparticles in the bulk of aqueous solution with pH = 7.0 is reported for the first time. For this purpose, synthesized 1,2,4-triazole-3-thiol-protected silver-nanoparticles were used as a nucleophile for 1,4-Michael addition reaction with electrochemically generated *o*-benzoquinone. The modification process was characterized using electrochemical techniques such as cyclic voltammetry and controlled potential coulometry as well as TEM, DLS, and UV-Vis spectroscopy.

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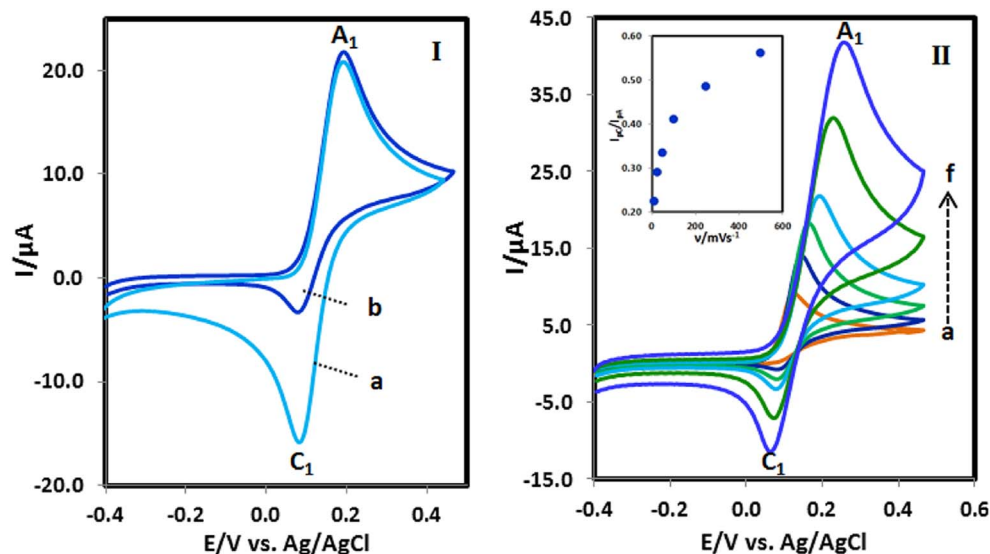
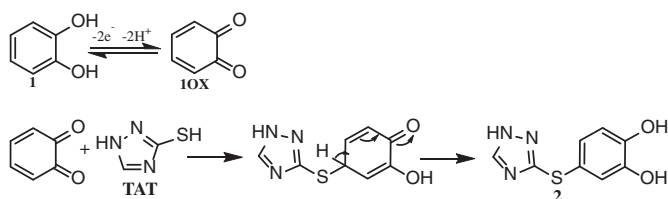


Fig. 1. Cyclic voltammograms of 1.0 mM catechol at a glassy carbon electrode, in aqueous phosphate buffer solution (0.2 M, pH = 7.0); Part I: (a) in the absence and (b) in the presence of 1.0 mM 1,2,4-triazole-3-thiol (TAT) by scan rate of  $100 \text{ mV s}^{-1}$  and part II: in the presence of 1.0 mM 1,2,4-triazole-3-thiol (TAT) in various potential scan rates. Scan rates from a to f are 10, 25, 50, 100, 250 and  $500 \text{ mV s}^{-1}$ , respectively. Inset:  $I_p^{Cl}/I_p^{A1}$  vs. scan rate.



Scheme 1. EC mechanism for the electrochemical oxidation of catechol in the presence of TAT.

## 2. Experimental

### 2.1. Reagents and apparatus

Catechol, 1,2,4-triazole-3-thiol and  $\text{AgNO}_3$  were obtained from Sigma-Aldrich. All other chemicals used in this investigation were of analytical grade. Cyclic voltammetry, controlled-potential coulometry and preparative electrolysis were performed using an Autolab model PGSTAT 302 N potentiostat/galvanostat. The working electrode used in the voltammetry experiment was a glassy carbon disc (1.8 mm diameter) and a platinum wire was used as counter electrode. The working

electrode used in controlled potential coulometry was an assembly of four carbon rods (6 mm diameter and 4 cm length) and a large platinum gauze served as the counter electrode. The working electrode potentials were measured versus Ag/AgCl electrode (saturated KCl) (all electrodes from AZAR electrode). The glassy carbon electrode was polished using alumina slurry ( $0.05 \mu\text{m}$ , from Iran Alumina Co.).

### 2.2. Synthesis of AgNPs

AgNPs protected with 1,2,4-triazole-3-thiol were prepared as reported in the reference [21]. Aqueous  $\text{AgNO}_3$  was combined with an ethanolic solution of 1,2,4-triazole-3-thiol in excess to form the insoluble Ag(I)-TAT precursor. To solubilize the precursor, the pH was then adjusted to 9.0 with CsOH and to stabilize the final cluster product was further adjusted to 12.0. After dropwise addition of aqueous  $\text{NaBH}_4$  with stirring, the mixture was allowed to incubate for an hour. The clusters were precipitated with DMF and separated from the reaction mixture. Then acetic acid was added until the cluster was completely dissolved in DMF, yielding the final products of 1,2,4-triazole-3-thiol-protected silver nanoparticles, which was then isolated by precipitation.

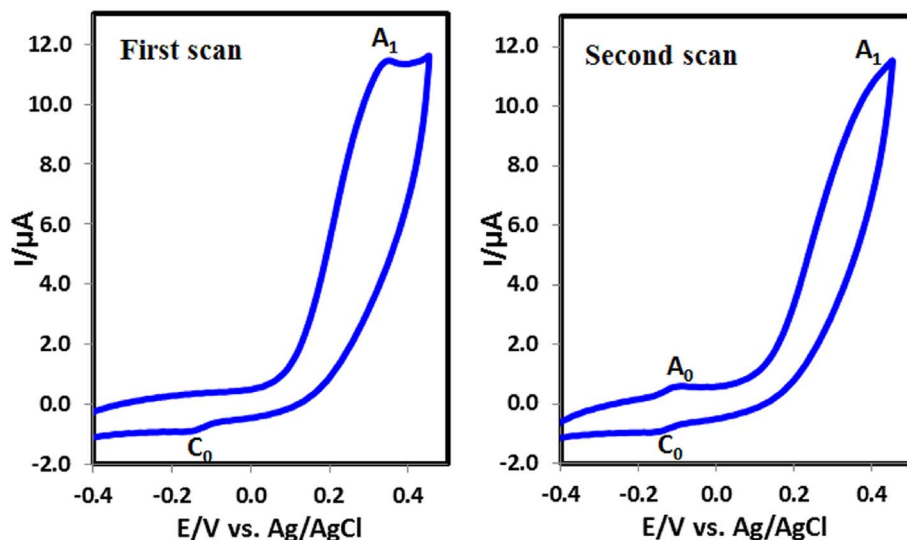


Fig. 2. First and second scan of cyclic voltammogram of TATAgNPs/GCE immersed in aqueous phosphate buffer solution (0.2 M, pH = 7.0), containing 1.0 mM catechol. Scan rate:  $100 \text{ mV s}^{-1}$ .

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