



# Dendritic macromolecules supported Ag nanoparticles as efficient catalyst for the reduction of 4-nitrophenol



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## ABSTRACT

Polymer supported Ag nanoparticles, generated in situ by silver nitrate ( $\text{AgNO}_3$ ) reduction under reaction conditions, catalyzed the hydrogenation of 4-nitrophenol with high efficiency in water at room temperature in the presence of an excess amount of  $\text{NaBH}_4$ . Amphiphilic linear-dendritic copolymers containing a poly(ethylene glycol) (PEG) core and poly(2-ethyl-2-oxazoline)-poly( $\epsilon$ -caprolactone) arms were able to load the Ag nanoparticles. The Ag nanoparticles with a diameter of 8–10 nm were found to show a comparable catalytic activity towards formation of the aromatic amine as single product with short reaction time.

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## 1. Introduction

Aromatic amines are valuable chemical compounds widely used in the manufacture of pharmaceuticals, fibers, pesticides, explosives, polymers, dyes and cosmetics [1]. Recently, numerous protocols have been reported in the literature for the reduction of nitroarenes. They include: i) hydrogenation under  $\text{H}_2$  at various pressures promoted by various catalysts [2–5]; ii) catalytic reduction process in the presence of CO and  $\text{H}_2\text{O}$  [6], iii) photocatalytic hydrogenation [7]; iv) catalytic transfer hydrogenation promoted, for example, by Cu [8], Au [9], Pd [10], Ru [11], Ag [12] and  $\text{Fe}_3\text{O}_4$ -Ni [13a,b] nanoparticles with reducing agents other than molecular hydrogen [13a,b], including silanes [14], hydrazine [15], and sodium borohydride [1].

Each of the above protocols has its own merits, while some of the methods are plagued by limitations of poor yields, acidic condition, formation of harmful byproducts, excessive amounts of catalysts and generation of large amounts of toxic wastes in scaling up for industrial applications leading to environmental issues. However, this major problems remains unsolved and the development of more efficient, less toxic, and handle convenient

catalysts for this chemical process is still highly desirable [1]. With the aim to develop innovative catalytic processes that enable chemical transformations to be performed under mild and sustainable conditions with high efficiency, we decided to evaluate the catalytic activity of a dendritic polymer supported Ag nanocatalyst for the hydrogenation of aromatic nitro compounds in water.

Ag nanoparticles have been a subject of much intensive research because of their unique chemical and physical characteristics that are different from their bulk counterparts, leading to a wide range of application in various fields of industry biomedicine, antibacterial activity, imaging and nanophotonics, surface-enhanced Raman scattering (SERS) detection [16] and catalytic processes [17–19].

Stability of the nanoparticles is an important issue and supported metal nanoparticles as catalytic systems have potential to show greater efficiency and prevent aggregation during the reaction to be catalyzed so that catalytic nanoparticles are usually immobilized on solid supports, such as carbon, metal oxides, polymer and zeolites [20]. Alternative synthetic strategies based on using polymers as support for the generation of stable metal have been developed. The resulting nanoparticle-polymer nanocomposites have been shown to be useful in catalytic systems. The major advantage of using a polymeric matrix as a stabilizing agent is that it can be used to tailor the nanocomposite properties and also to provide long term stability of the particles by preventing nanoparticle agglomeration [21]. Although many polymers and

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dendrimers have been used as the stabilizing agents to synthesize Ag nanoparticles in the literatures, reports of the preparation of polymer–nanosilver nanocomposites are occasional. In the literatures, many kinds of polymers such as azopolymer [22], polyethylene naphthalate [23], poly(4-vinylpyridine) [24], polypropylene glycol [25], poly(amidoamine) dendrimer [26] poly(propyleneimine) dendrimer [27], and polyaminocyclodextrin [28], were used to prepare the Ag nanoparticles. Linear–dendritic copolymers are hybrid large macromolecules containing dendrimers and linear polymers. Interesting properties of this type of dendritic polymers have stimulated investigation in this area [19,29]. Synthesis of poly(ethylene glycol)–poly(2-ethyl-2-oxazoline)–poly( $\epsilon$ -caprolactone) (PEG–POX–PCL) linear–dendritic copolymers and their ability to encapsulate inorganic and organic molecules was reported previously [19,29]. These biocompatible dendritic copolymers with encapsulated inorganic compounds, the stability of hybrid systems in the presence of water and solubility in organic solvents and water, can be applied as a nanoreactor for the chemical catalytic process.

In this work, we reported the new preparation of Ag nanoparticles stabilized by the PEG–POX–PCL linear–dendritic copolymer in water by adding reducing agent NaBH<sub>4</sub>. The amphiphilic copolymer, containing a poly(ethylene glycol) (PEG) core and poly(2-ethyl-2-oxazoline)–poly( $\epsilon$ -caprolactone) arms, used for the Ag nanoparticles fabrication. Ag nanoparticles were found to be a highly efficient catalyst for the reduction of 4-nitrophenol under ambient condition (Scheme 1).

## 2. Experimental section

### 2.1. Materials and methods

Chemical reagents in high purity were purchased from Merck and Sigma. All materials were of commercial reagent grade. UV/Vis spectra from various Ag nanoparticles solutions for the measurement of the surface plasmon band of the silver nanoparticles were recorded by UV GBC Centra 6 UV–visible spectrophotometer at room temperature. The particle size and morphology were investigated by a JEOL JEM-2010 transmission electron microscope (TEM) on an accelerating voltage of 200 kV.

### 2.2. Synthesis of linear–dendritic amphiphilic copolymers

Detailed procedure for preparing the linear–dendritic polymers is described elsewhere [19]. In brief, PEG was functionalized using cyanuric chloride and obtained PEG–Cl<sub>4</sub>. Then, 0.2 g (0.15 mmol) of PEG–Cl<sub>4</sub> was dissolved in 10 mL of dried acetonitrile. 0.63 mL (6.2 mmol) of 2-ethyl-2-oxazoline was added to this solution, and was stirred at 110 °C for 48 h. Diethanolamine (excess) was added to the solution and stirred for 2 h, after the temperature of reaction was reduced to 60 °C. The solution was filtered, and solvent was evaporated under reduced pressure. Residue viscose was dissolved in methanol, and star copolymer (PEG–POX–OH) was precipitated in diethyl ether as a yellow viscose product in 80% yield. For synthesis of amphiphilic copolymer, 0.2 g of PEG–POX–OH was added to a polymerization ampule equipped with a magnetic stirrer and

vacuum inlet. 1 mL of Sn(Oct)<sub>2</sub> in toluene ( $1 \times 10^{-3}$  M) was added to this polymerization ampule, and solvent was evaporated under vacuum at 60 °C for 30 min. Then 1 mL of  $\epsilon$ -caprolactone was added to the polymerization ampule, and it was left under vacuum for 1 h at 60 °C. The polymerization ampule was sealed under vacuum, and it was stirred at 120 °C for 6 h. Then it was cooled and the ampule contents were dissolved in chloroform. The solution was filtrated, and the PEG–POX–PCL copolymer was precipitated in diethyl ether. The yield of the reaction was 80% (Scheme 2).

### 2.3. Formation of silver nanoparticles via using (PEG–POX–PCL) copolymers

A 100 mL round bottom flask with 50 mg of PEG–POX–PCL copolymers were dispersed with 10 mL of de-ionized water, and then 10 mL of 0.01 M of AgNO<sub>3</sub> solution was added drop wise to the mixture and was stirred for 1 h. Finally Ag<sup>+</sup> reduced with 0.01 M NaBH<sub>4</sub> (10 mL). The water was evaporated under reduced pressure and the product was dissolved in chloroform and it was filtrated, and the product was precipitated in diethyl ether and was dried overnight under vacuum.

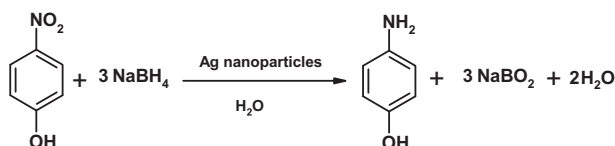
### 2.4. Catalytic reduction of *p*-nitrophenol

To evaluate the catalytic performance of the synthesized silver nanoparticles loaded PEG–POX–PCL copolymer catalyst, the catalytic reduction process was carried out in a standard quartz cell with a 1 cm path length and about 4 mL volume. 0.3 mL of NaBH<sub>4</sub> (0.1 M) was mixed with a given amount of silver nanoparticles and a portion of ultrapure water, keeping the final concentration of NaBH<sub>4</sub> at 10 mM. After the addition of 30  $\mu$ L of 4-nitrophenol (0.01 M), the UV/Vis absorption spectra were recorded by a UV/Vis spectrometer at certain time interval in a scanning range of 250–500 nm at 20 °C at time interval of 1 min.

## 3. Results and discussions

The synthesis and characterization of PEG–POX–PCL copolymers were performed following a literature procedure [19]. Based on our research on PEG–POX–PCL copolymers according to reported procedure in the literature, these linear–dendritic polymers are promising materials to load the inorganic molecules [19,29]. The amphiphilic linear–dendritic copolymers firstly self-assembled into micelles in aqueous solution [19]. Polymeric micelles derived from amphiphilic copolymers of poly(ethylene glycol)–poly(2-ethyl-2-oxazoline) (PEG–POX) and poly( $\epsilon$ -caprolactone) (PCL) were prepared in an aqueous phase. Then a certain amount of AgNO<sub>3</sub> was added into this aqueous solution. The solution turned from colorless to golden yellow color. The reduction of Ag<sup>+</sup> to Ag nanoparticles was achieved via coordination reduction by NaBH<sub>4</sub>. For TEM experiments, a fresh aqueous solution of PEG–POX–PCL and copolymers containing Ag nanoparticles were dropped on to the surface of a graphitic sampler and the solvent was evaporated at room temperature, then TEM micrographs were recorded. TEM images of PEG–POX–PCL copolymers and Ag nanoparticles shown in Fig. 1 (a) and (b), respectively. A comparison of the figures, follow that Ag nanoparticles stabilized on the PEG–POX–PCL. As can be seen in Fig. 1(c), the mean size of Ag nanoparticles, formed by this process, was estimated to be 14 nm, which was graphically analyzed by Digimizer software.

In order to evaluate the catalytic efficiency of the Ag nanoparticles, the catalytic reduction reaction of 4-nitrophenol was monitored by UV/Vis spectroscopy at room temperature using an excess of NaBH<sub>4</sub> as the reducing agent in aqueous medium. As can be seen in Fig. 2, upon the addition of Ag nanoparticles as



Scheme 1. Catalytic by Ag nanoparticles.

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