



Titania-supported silver nanoparticles: An efficient and reusable catalyst for reduction of 4-nitrophenol



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ABSTRACT

Supported silver nanoparticles were synthesized via *in situ* sol–gel followed by reduction method with dextrose as reductant and sodium dodecyl sulfate as stabilizer. The synthesized nanoparticles were characterized by X-ray diffraction, transmission electron microscopy, Fourier transform Infra-Red spectroscopy and UV–visible measurements. The XRD peaks confirm the metallic face-centered cubic silver particles. The formation of silver nanoparticles was confirmed from the appearance of surface plasmon absorption maxima at 412 nm; which shifted to the longer wavelengths after supported on titania host lattice. TEM showed the spherical nanoparticles with size in the range of 18–23 nm. An efficient and simple method was reported for the reduction of 4-nitrophenol using titania-supported silver nanoparticles at room temperature. The reaction was first order with respect to the concentration of 4-nitrophenol with higher efficiency. Titania supported silver nanoparticles are reusable and stable heterogeneous catalyst.

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1. Introduction

Supported silver based catalysts attract significant attention due to their remarkable efficiency for reduction of aromatic compounds [1–4]. It has been understood that silver nanoparticles are catalytically active only when they are dispersed on an oxide support. In particular, solid-supported metal NPs are also efficient bi-functional catalysts [5–10]. The specific metal–metal oxide interactions plays important role for exhibiting new physical properties as well as enhanced catalytic activities. In such cases, the function of oxide matrix strongly deviates from its conventional task as a simple support [11–13]. Coupling of noble metals with semiconductor oxides show increased photocatalytic responses in various conversions [14–16]. Thus, the preparations of dispersed nano sized silver-based catalysts are being widely investigated [1,5,17]. The usefulness of solid-supported metal nanoparticles for their catalytic properties is related to their higher surface to volume ratio as well as to their size and shape dependent optical properties. Besides, the dispersed Ag nanoparticles act as an efficient substrate for surface-enhanced Raman scattering and metal-enhanced fluorescence and thus they are promising materials for chemical and biological sensor [18–21]. Further the

lower cost of silver compared to other noble metals is an additional benefit for industrial application for reduction of nitro compounds to amino compounds [1–5]. These nanoparticles have been used for reduction of nitro compounds [1,2], alkylations of arenes [22], and sensor [23]. Pal et al. reported the reduction of 4-nitrophenol (4-NP) using silver nanoshells stabilized with cationic polystyrene beads [24] as well as silver deposited on silica gel [2]. Pradhan et al. studied the catalytic reduction of aromatic nitro compounds using *in situ* microelectrode silver nanoparticles [4]. Sakthivel et al. have reported the kinetics of 4-NP to 4-aminophenol (4-AP) using silver-nanocrystals prepared by fungus *Cylindrocodium floridanum* [25]. Silver and gold nanoparticles grown on calcium alginate gel beads are reported to catalyze nitro-phenol reduction [26]. However, the overall catalytic efficiency for conversion of nitro compounds reported in these studied are lower.

In order to increase the catalytic efficiency newer procedures for preparation of metal nanoparticles is a challenge in research. Thus, several approaches using the colloidal chemistry principles are being explored for preparation of Ag nanoparticles. Silver NPs have been prepared in solution by radiolytic [27], chemical [28], photochemical [29] or photocatalytic reduction of silver salts [30] in the presence of a variety of organic stabilizers or inside micelles [3,31]. However some major limitations, like complexity, stability of suspensions and cost effective procedures highlight the urgency of improved preparative routes. Hence, supported silver particles can play a dominant role for improving the catalytic properties

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through ease separation, stability as well as reusability of catalysts with desired chemical properties. Among various supportive materials, TiO_2 is the most studied semiconductor for environmental cleanup applications, due to its unique physico-chemical properties, chemical inertness and non-toxicity [16].

Thus, the composites of silver NPs with titania bear a lot attention for synergetic improvement of their functional properties. In the present communication we report the details of preparation of titania supported Ag nanoparticles and catalytic efficiency for reduction of 4-NP to 4-AP in presence of NaBH_4 .

2. Experimental details

2.1. Synthesis of silver nanoparticles

All chemicals used in this study were of AR grade. The silver NPs were obtained by using a reactive bath containing 5 mL (1×10^{-3} M) silver nitrate solution, 10 mL (9×10^{-3} M) sodium dodecyl sulfate solution, 10 mL (1×10^{-2} M) dextrose solution. The whole content was stirred constantly and heated at temperature 60°C for 1 h. The pale-yellow color of silver suspensions was observed indicating the formation of silver NPs in the medium.

2.2. Synthesis of titania-supported silver nanoparticles

Titania-supported silver NPs were synthesized by a combination of sol-gel method followed by reduction. Dextrose was used as a reducing agent. Titanium(IV) isopropoxide with glacial acetic acid were taken in a 250 mL round-bottom flask and stirred for 15 min at room temperature. The aqueous solution of sodium dodecyl sulfate (SDS) was added into it. The content was stirred at room temperature for 2 h. The pH of the resulting solution was adjusted to 10 by adding ammonia solution. The solution was stirred at 60°C for 3 h and then cooled to room temperature [32]. Thereafter, mixture of 5 mL (1×10^{-3} M) silver nitrate solution and 10 mL (1×10^{-2} M) dextrose solution was added into the titanium precursor solution. The theoretical silver loading was 1.0 mol% to that of Ti^{4+} ion in titania host lattice. The resulting solution was stirred for 3 h at 60°C . The resulting solution was then centrifuged for 2 h, and the obtained precipitate was washed with deionized water and ethanol. Further they were dried at 110°C and calcinated at 300°C for 5 h.

2.3. Characterization techniques

X-ray diffraction (XRD) studies were carried out by using a Bruker D8-Advance diffractometer. The diffraction patterns were recorded in the two theta range of $10\text{--}90^\circ$ by using $\text{Cu K}\alpha$ (1.5418 \AA) radiation. Transmission electron microscope (TEM) images of the samples were recorded on a Tecnai F30 field emission transmission electron microscope operating at 300 kV. Energy dispersive X-ray spectroscopy (EDAX) was recorded by using FEI Quanta 200 Environmental SEM. Fourier transform Infra-Red (FTIR) spectra of the NPs were recorded in transmission mode by using Bruker Alpha FT-Infra-Red spectrometer. UV-visible spectra of the samples were recorded in the range of $250\text{--}800 \text{ nm}$ by using Perkin-Elmer Lambda 750 model UV-VIS spectrophotometer. Thermal analysis was performed on Shimadzu TGA-DTA 60H from room temperature to 500°C . Zeta potential measurement was carried out using a PSS/NICOMP 380 ZLS particle sizing system (Santa Barbara, CA, USA).

2.4. Catalytic activity

For the reduction of 4-NP experiment, $50 \mu\text{L}$ (4.3×10^{-3} M) 4-NP solution, NaBH_4 solution and supported silver powders were

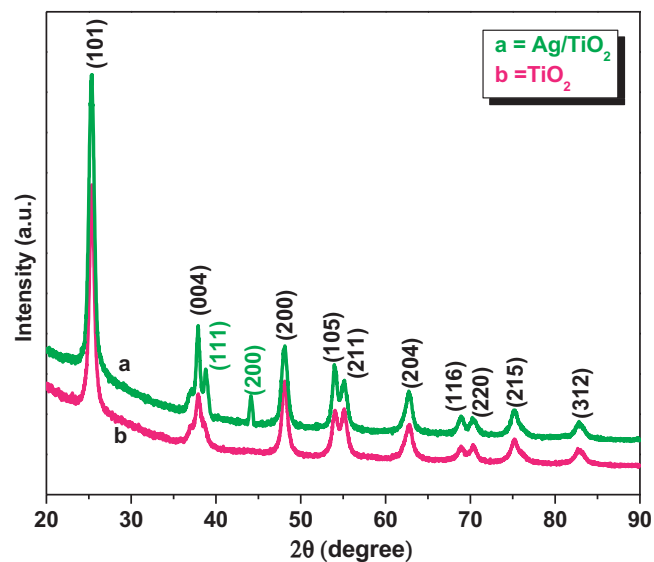


Fig. 1. XRD patterns of pure titania and titania-supported silver NPs.

placed in a 4 mL quartz cuvette. The cuvette was then placed in a UV-visible spectrophotometer to monitor the time-dependent absorption in the wavelength of $200\text{--}800 \text{ nm}$ at room temperature. The conversion (%) and product yield (%) of reduction of 4-NP were derived at different concentration of NaBH_4 as well as silver powders.

3. Results and discussions

3.1. X-ray diffraction studies

XRD patterns of pure titania and titania-supported silver NPs are shown in Fig. 1. All the peaks were indexed with silver [JCPDS#03-0931] and pure anatase titania [JCPDS#22-1272]. The diffraction peaks at 38.78° , 44.12° are consistent with (1 1 1), (2 0 0) reflections of the metallic silver particles. These silver particles have face-centered cubic crystal structure. No peaks corresponding to oxides of silver are observed with titania samples. The remaining diffraction peaks showing for tetragonal titania in anatase phase only. No signatures of rutile or brookite phases are observed in XRD patterns. The presence of distinct reflections of silver suggests that silver particles are not incorporated in TiO_2 lattice, but deposited on the surface of the matrix.

The increase in peak intensities of titania reflections is observed in the XRD patterns of titania-supported silver NPs compared unsupported ones. This can be attributed to the increase in the crystallinity of titania as observed from the decrease in width of (1 0 1) reflection. This present investigation is contradictory to the results of reported by Li et al. which shown decrease in crystallinity of TiO_2 with silver content [33].

The crystallite size of NPs is calculated by using Scherrer's equation [30]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where D is the average crystallite size, λ is the wavelength of X-ray ($\text{Cu K}\alpha = 1.5418 \text{ \AA}$) radiation, β is the FWHM of the diffraction peak, and θ is the Bragg angle. The average crystallite size of silver NPs was calculated using (1 1 1) reflection at 38.78° , while average crystallite size of titania was calculated using (1 0 1) reflection at 25.34° . All the crystallographic parameters of supported silver NPs and pure titania are given in Table 1.

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