

Ag₇ AND Ag₈ QUANTUM CLUSTERS SUPPORTED ON ALUMINA: NEW CATALYSTS FOR ORGANIC REACTIONS

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Silver quantum clusters (QCs) stabilized by mercaptosuccinic acid (MSA) have been synthesized at room temperature from Ag nanoparticles through an interfacial etching process. The as-synthesized red emitting QCs were coated on alumina and the supported clusters have been characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX) and fluorescence spectroscopy. Catalytic activity of Ag QCs supported on alumina have been exploited for the reduction of 4-nitrophenol in presence of sodium borohydride. The reaction followed pseudo-first order kinetics. The catalyst separated from the product remains active and can be recycled several times. Other nitroaromatic compounds have also been tested. Synthesis of the solid phase catalyst, applications and detailed kinetic studies of the reduction of 4-nitrophenol are reported.

Keywords: Quantum clusters; nanoparticles; nanocatalysis; enhanced catalytic activity; fluorescence.

1. Introduction

Quantum clusters (QCs) of noble metals are a class of molecules with sub-nanometer cores and appropriate ligands protecting them. They exhibit unique properties due to the confinement of electrons in discrete energy levels. A number of such clusters are now known such as Au₂₅, Au₂₃, Au₂₂, Au₁₅, Au₈, etc., which are, apart from having many molecular properties, highly luminescent.¹ Nanocluster reactivity is sensitive to its size, it is reported that Au clusters greater than 2 nm, supported on TiO₂, yield propylene oxide from propylene but Au with less than 1.5 nm on the same support, ends up as propane.² Au₂₅ exhibited high catalytic activity for

epoxidation of styrene adsorbed on hydroxyapatite compared with large clusters.³ Reactivity of the catalyst depends on supported material also. For example, Ag particles of 0.8 nm supported on alumina showed high selectivity for C–C cross coupling of 1-phenylethanol with benzyl alcohol.⁴ Several methods have been reported for the reduction of nitrophenol using nanoparticles and supported nanomaterials.^{5–7} There are also reports of the conversion of nitro groups to amino groups in H₂ atmosphere.^{8,9} In this work, we explore the catalytic activity of Ag₇ and Ag₈ QCs for the reduction of nitrophenol with NaBH₄. The rate constant obtained in the present case is the highest amongst those reported.^{5–7,10,11} Reusability of the

material has been demonstrated. Products were confirmed with UV-visible spectroscopy and electrospray ionization mass spectrometry (ESI-MS).

2. Experimental Details

All the following chemicals were from commercial sources and were used without further purification. Silver nitrate (AgNO_3 , 99%), mercaptosuccinic acid (MSA, 97%), methanol (GR grade), toluene (GR grade) and neutral alumina were purchased from SRL Chemical Co. Ltd., India. Sodium borohydride (NaBH_4 , 98%) was purchased from Sigma Aldrich. 4-Nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$, 97%) and 4-aminophenol ($\text{C}_6\text{H}_7\text{NO}$, 98%) were purchased from Lobo.

2.1. Synthesis of nanoparticles

Ag@MSA were synthesized by using the reported method.¹² To 100 ml of methanol, MSA (1795 mg) and aqueous AgNO_3 (340 mg, dissolved in 6.792 mL of water) were added. The mixture was allowed to stir for half an hour in ice bath. To that mixture, freshly prepared ice cold sodium borohydride (756.6 mg in 100 mL of water) was added drop-wise under vigorous stirring to reduce the aggregation of the particles. Final mixture was allowed to stir for an hour. The precipitated particles were separated, washed with methanol and dried to yield brownish Ag@MSA .

2.2. Synthesis of supported clusters

A mixture of red emitting QCs of Ag_7 and Ag_8 was synthesized by using the interfacial method as per our earlier report.^{13,14} In this process, about 300 mg of MSA were added to 100 mL of toluene and stirred for 10 min and to this mixture, a solution of as-prepared silver nanoparticles (100 mg in 100 mL of water) was added. The mixture was allowed to stir for 48 h during which the color of the solution changed from orange to brown. UV-Visible spectra were recorded. The solutions were freeze dried to obtain a powder which was repeatedly washed with methanol and the material was dried using rotavapor. The sample prepared this way is known to be a 80:20 mixture of Ag_8 : Ag_7 . No separation of isolated clusters was done in the present case, unlike in the case of pure clusters.¹⁴

Alumina powder was added to the quantum cluster solutions, followed by stirring for 5 min. The

color of the quantum cluster solution changed gradually to colorless, indicating their absence in the supernatant. The amount of QCs in the solution was controlled to get various weight ratios of loading. The quantum cluster loaded materials were washed with water and dried in ambient air. Maximum loading achieved was 0.1/1 g. This material is referred to below as $\text{Al}_2\text{O}_3\text{@Ag}_{7,8}$, implying that $\text{Ag}_{7,8}$ clusters are stabilized over Al_2O_3 .

2.3. Catalytic test and reaction conditions

For the reduction reaction, 1 mL of freshly prepared ice cold aqueous solution of NaBH_4 (160 mM) was introduced to 1 mL of aqueous 4-np solution (7 mM), taken in a sample bottle. Next, $\text{Al}_2\text{O}_3\text{@Ag}_{7,8}$ (10% loading, 50 mg) were added to the above solution mixture and time dependent absorption spectra were measured. From changes in the absorption of 4-nitrophenolate ion at 400 nm as a function of time, the rate constants were calculated. The product was identified by comparison with the spectrum of an authentic sample of 4-aminophenol (4-ap). The experiment was carried out at 15, 25 and 35°C.

3. Instrumentation

UV-Visible optical absorption spectra were recorded with a 25 Perkin-Elmer instrument. Fluorescence spectroscopy measurements were carried out by a HORIBA JOBIN VYON Nano Log instrument. X-ray photoelectron spectroscopy (XPS) measurements were made using an Omicron ESCA Probe spectrometer with unmonochromatized $\text{Mg K}\alpha$ X-rays ($h\nu = 1253.6$ eV). The samples were spotted as drop cast films on a sample stub. High resolution transmission electron microscopy (HRTEM) was carried out with a JEOL 3010 instrument. The samples were casted on carbon coated grids, followed by drying at ambient conditions. SEM and EDAX measurements were done with HITACHI S-4800 FESEM and the samples were spotted on ITO (indium tin oxide) glass plates, followed by drying at ambient conditions. ESI-MS measurements were done with a MDX Sciex 3200 Q-TRAP LC/MS/MS (Applied Biosystems) in which the spray and extraction are orthogonal to each other. Product formed was made to 10 ppm (1:1 ratio of water and methanol) and sprayed at 5 kV.

4. Results and Discussion

Figure 1(a) shows the characteristic metallic nature of Ag nanoparticles showing surface plasmon resonance at 390 nm. After etching for 48 h, the peak got vanished with the appearance of a feature around 550 nm due to the HOMO–LUMO (4d valence to 5sp conduction band) transitions of the QCs. This is due to the decrease in the number of atoms giving rise to intra-band transitions.^{15,16} Absence of nanoparticles in the solution is proven by transmission electron microscopy of the material after etching. This was done to ensure that the peak at 550 nm is not due to aggregated nanoparticles. Inset photographs depict the color of the freeze-dried powder before (a) and after (b) the etching process; the color of the powder changed to orange after etching.

Photoluminescence spectra (Fig. 1(b)) of Ag QCs coated on alumina showed a maximum excitation at 550 nm and emission at 650 nm. This confirms that the clusters present on alumina are largely Ag₈. Inset picture depicts QCs on alumina under a UV lamp. The cluster-loaded materials showed intense emission.

SEM and EDAX images of supported QCs were measured. It was clear that the clusters are uniformly coated on the substrate. The EDAX spectrum indicates the composition of the material made. Nearly 1:1 ratio of Ag:S is observed in the sample. The corresponding EDAX images taken for various elements reflect the atomic composition of the materials. MSA protection of the clusters was evident from the data.

TEM image of supported QCs (shown in Fig. 2) clearly indicates that the clusters are uniformly coated on the surface of alumina. As typical of QCs and their strong electron sensitive nature, they began aggregating upon electron beam exposure. As the exposure time increases, the particles fuse to become large nanoparticles showing the lattice spacing of Ag (111).

XPS investigation shows all the expected elements. Survey spectrum and the expanded regions are shown in Fig. 3. Ag 3d shows peak at 368.3 and 374.3 eV due to Ag_{5/2} and Ag_{3/2} of Ag (0), respectively. This is slightly shifted from the metallic peak positions. Spectral charging was corrected with respect to C 1s at 285.0 eV. Al 2p shows a peak at 74.7 eV and O 1s appears at 530.8 eV. The O 1s position indicates hydroxyl groups at the surface, as expected. The C 1s region shows two peaks at 285.0 and 288.3 eV, corresponding to the CH and CH₂ groups and the COO[−] group.

Having characterized the supported QCs, we proceeded to investigate the catalysis of the materials. The absorption maxima of 4-nitrophenol got shifted from 317 to 400 nm, after treating with freshly prepared ice-cold NaBH₄. This was due to the formation of the phenolate ion.^{17,18} However, the peak at 400 nm got reduced within 10 min, after the addition of supported QCs. A new peak appeared at 290 nm, corresponding to 4-aminophenol as shown in Fig. 4(a). This transformation was confirmed by checking the absorption spectrum of an authentic sample. Color of the solution changed to brown from yellow. Without the addition of Al₂O₃@Ag_{7,8}, the phenolate peak remained even for several days, with

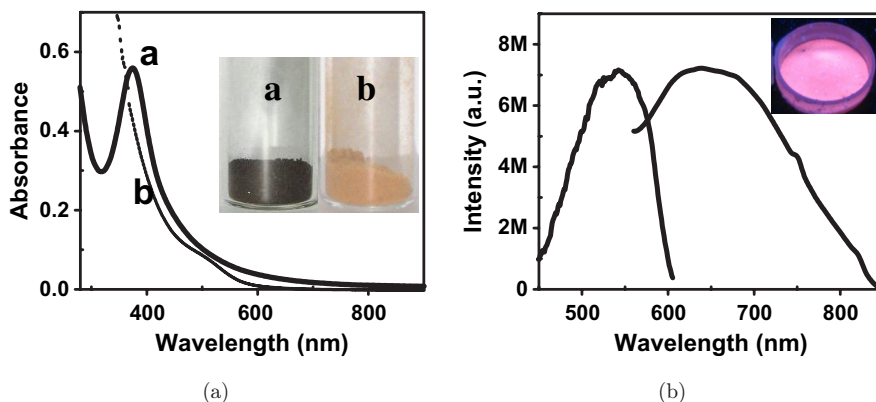


Fig. 1. (a) UV-Visible spectra of Ag@MSA nanoparticles (a) and QCs after etching (b). (b) Excitation and emission spectra of Ag@MSA QCs supported on alumina. The sample corresponds to a loading of 0.1/1 g on Al₂O₃. Inset of (a) shows photographs of the freeze-dried samples of the nanoparticles and QCs in white light. Inset of (b) is a photograph of Ag@MSA QCs on alumina under UV lamp.

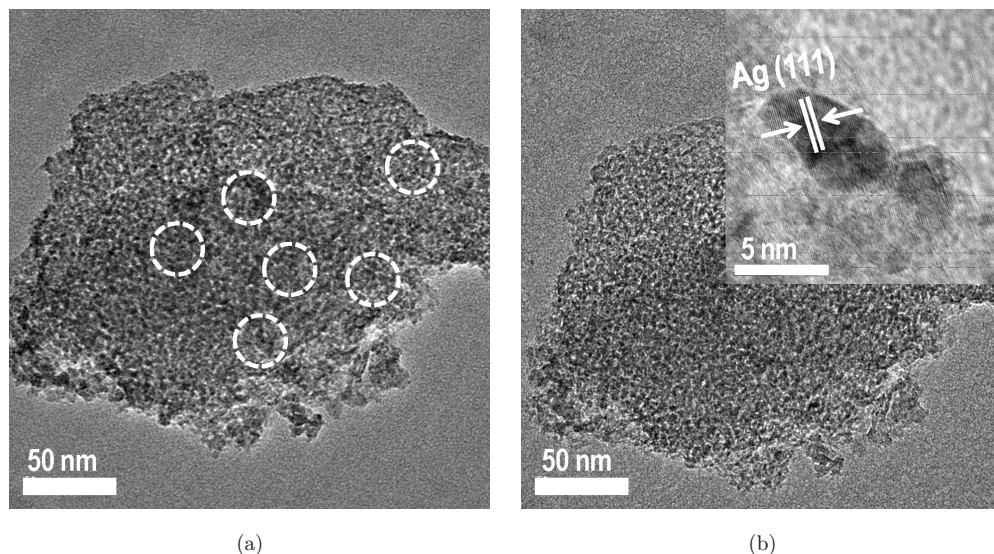


Fig. 2. TEM images of $\text{Al}_2\text{O}_3@\text{Ag}_{7.8}$ initially (a) and after 10 min of electron beam exposure (b). Black dots in a correspond to the QCs which are marked. The (111) plane of Ag is marked in inset of (b).

no noticeable reduction. The plot of $\ln[A]$ of phenolate versus time (Fig. 4(b)), confirmed that reaction was pseudo-first order in nitrophenol. The rate constant was found to be $8.23 \times 10^{-3} \text{ s}^{-1}$ at 298 K. It was found to be high because the catalyst facilitates electron transfer from the reductant BH_4^- to the phenolate ion.⁷ After the reduction, the QCs on alumina were separated, washed reused for

reduction reaction several times. Activation energy was found to be 55.6 kJ mol^{-1} at 298 K and turn over frequency was $0.001874 \text{ mol g}^{-1} \text{ s}^{-1}$, which is comparatively better than the reported catalytic conversion reactions using silver nanoparticles.⁵ Formation of 4-aminophenol was confirmed with a peak at m/z 109 in the ESI MS while the precursor nitrophenol peak at m/z 139 disappeared.

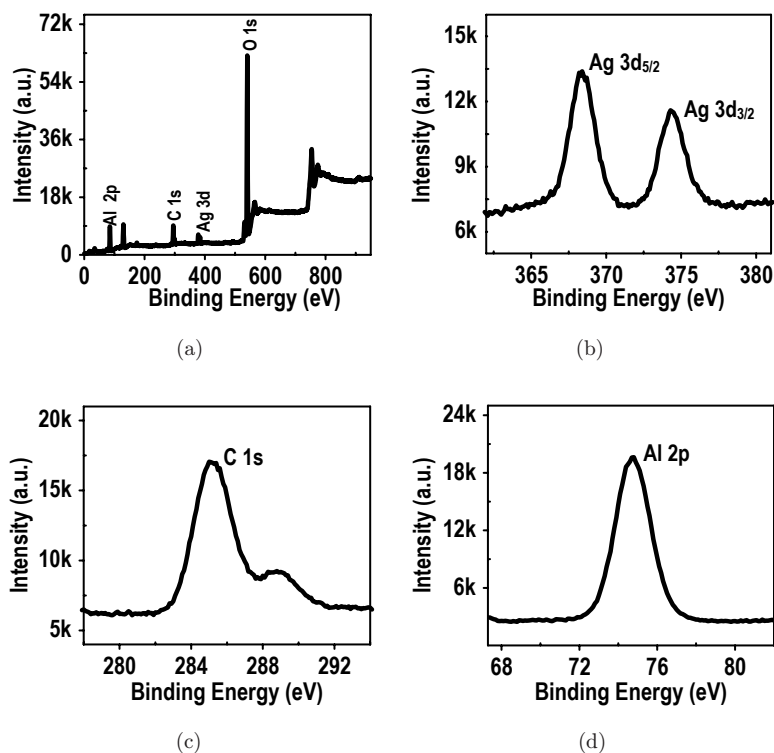
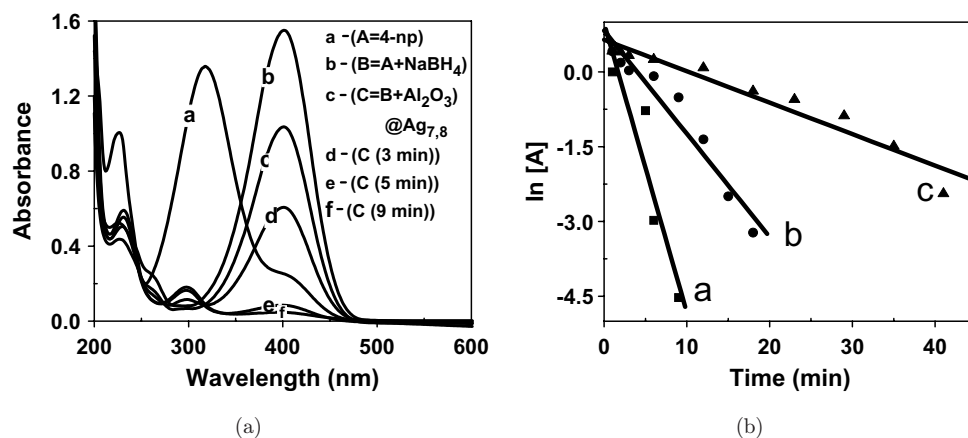


Fig. 3. X-ray survey scan (a) and the expanded spectra in the Ag 3d (b), c 1s (c) and Al 2p (d) regions of $\text{Al}_2\text{O}_3@\text{Ag}_{7.8}$.



It was found that other nitro compounds such as 3-nitrophenol, 4-nitroaniline, 3-nitroaniline were also reduced using supported QCs in presence of NaBH₄.

5. Conclusion

In conclusion, we have prepared Ag_{7.8} QCs and supported them on Al₂O₃. The catalytic activity of the QCs was tested, taking the reduction of aromatic nitro compounds as the typical reaction. The pseudo-first order rate constant was found to be twice larger than the earlier report.⁵ The activation energy was calculated to be 55.6 kJ mol⁻¹ at 298 K. The results suggest the cluster system to be a better catalyst for the reaction investigated.

Acknowledgment

We thank the Department of Science and Technology (DST), Government of India for constantly supporting our research program on nanomaterials.

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