

Wet-chemical synthesis of spherical arsenic nanoparticles by a simple reduction method and its characterization

Anjali Pal*, Sandip Saha, Sanjoy Kumar Maji, Mainak Kundu, Arpan Kundu

Department of Civil Engineering, Indian Institute of Technology, Kharagpur 721302, India

*Corresponding author. Tel: (+91) 3222-281920; Fax: (+91) 3222-282254; E-mail: anjaliipal@civil.iitkgp.ernet.in

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ABSTRACT

This paper has demonstrated, for the first time, the synthesis of yellowish-brown colored stable As(0) sol by borohydride-reduction of aqueous sodium arsenite maintained at pH 7-9 under ambient condition. Scanning electron microscopic (SEM) images reveal the formation of spherical As(0) nanoparticles having size in the range 67 ± 2 nm. The transmission electron microscopic (TEM) studies show the particle size lie within the range 60 ± 3 nm. The X-ray photoelectron spectroscopy (XPS) indicates the zero oxidation state of arsenic. The dynamic light scattering (DLS) studies show that the average particle size is around 45 nm. The absorbance of yellowish-brown As(0) sol at 300 nm shows excellent correlation with arsenic concentration in the range $15.6 - 45.4 \times 10^{-5}$ M. The method is simple and reproducible. Also by measuring the turbidity, the quantification of arsenic is possible in the range mentioned. The effects of various ions and temperature on the formation of arsenic nanosol have been reported. The as-prepared As(0) nanoparticles may have potential applications in medicine and sensors. Copyright © 2012 VBRI Press.

Keywords: Borohydride reduction of arsenite; spherical nanoparticles of As(0); characterization.



Anjali Pal obtained her Ph.D. degree in Chemistry from Calcutta University. She is appointed as a faculty in the Department of Civil Engineering, IIT, Kharagpur. She worked as a visiting scientist at ORNL, USA with Prof. Tuan Vo-Dinh. She received several national and international awards including R & D-100 Award (USA), International Hall of Fame Award (USA), Convention Award (Indian Chemical Society). Dr. Pal is a reviewer of many journals, and an editorial board member of

'Recent Patents on Nanotechnology' and 'Research Journal of Chemistry and Environment'. Her research interest includes 'Synthesis and Application of Nanomaterials' and 'Environmental Engineering'.



Sanjoy Kumar Maji is working as a post doctoral research associate in the Department of Bioenvironmental Systems Engineering, National Taiwan University, Taiwan. He obtained Ph.D. from the Department of Chemistry, Indian Institute of Technology Kharagpur under the supervision of Prof. T. Pal and Dr. A. Pal in 2008. He completed his M.Sc. from BNMU, Madhepura and B. Sc. from University of Calcutta. He has worked as research assistant in the Department of Biochemistry

and Molecular Biology, University of Parma, Italy in 2006-07. He has published more than 13 papers in the reputed International Journals.



Sandip Saha is a Senior Research Fellow (UGC) in the Department of Chemistry of Indian Institute of Technology Kharagpur. He is pursuing his Ph.D. under joint supervision of Prof. T. Pal, Chemistry and Dr. Anjali Pal, Civil Engineering. He has received B.Sc. and M.Sc. from Vidyasagar University and Indian Institute of Technology Madras respectively. His field of research is green synthesis of various mono and bimetallic metal nanoparticles for spectroscopic and catalytic applications.

Presently he is working on synthesis of various metal oxide nanoparticles for the environmental application through photocatalytic and advanced oxidation process.

Introduction

Arsenic and its compounds have manifold applications. Arsenic trioxide is a very highly efficacious agent for acute promyelocytic leukemia [1], and very recently arsenic trioxide-liposome conjugate nanoparticle has found success for breast cancer treatment [2]. Arsenic is well-known as both Homoeopathic (e.g. as antisyphilitic agent) and Ayurvedic medicine in Indian scenario. From ancient times arsenic compounds are used as pest-controlling agent and pigments. Crystalline gallium arsenide (GaAs) has long been known as a direct semiconductor with wide electronic and optoelectronic applications [3]. Very recently a simple colorimetric and dynamic light scattering assay for arsenic has been demonstrated which is based on As(III) mediated aggregation of glutathione-, dithiothreitol-, and cysteine-modified gold nanoparticles [4]. The age old Marsh's test was used for the detection of arsenic involving the decomposition of AsH_3 on a heated glass surface forming a metallic arsenic mirror. Synthesis and application of As(0) nanoparticles for many such purposes, however, still remained unexplored.

Here we report, for the first time, the synthesis of stable yellowish-brown colored spherical As(0) nanoparticles. The wet-chemical synthesis method developed is simple and reproducible. The characterization of the As(0) nanoparticles was done by SEM, TEM, XPS, DLS, and UV-visible spectroscopic analysis.

Experimental

Reagents

NaAsO_2 (Loba Chemicals, GR) was used for the preparation of 1×10^{-2} M As(III) stock solution. Further dilutions of As(III) solution were made from the stock solution as and when required. $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ was from Nice Chemicals. NaBH_4 used was from BDH. Other chemicals NaCl , Na_2SO_4 , CaCl_2 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaNO_3 , K_2HPO_4 , Na_2SiO_3 , Na_2SO_3 and Na_2EDTA were of AR grade and purchased from BDH. The water used was double distilled.

Synthesis of As(0)

Aqueous freshly prepared solution of NaBH_4 stored at $\sim 5^\circ\text{C}$ was used for reducing As(III) to As(0). The reduction was carried out on aqueous sodium arsenite solution already maintained at pH 7-9, and under ambient condition. To make the calibration curves (both spectrophotometric and turbidimetric), an appropriate volume of As(III) solution (1×10^{-2} M) was mixed with 3.0 ml of distilled water to maintain the concentration of arsenic in the range $15.6 - 45.4 \times 10^{-5}$ M, and to this was added 150 μl of 1×10^{-1} M ice-cold NaBH_4 solution. On addition of NaBH_4 solution the pH of the medium increases slightly. The mixtures were allowed to stand at room temperature for 2 h when yellowish-brown colored As(0) sol appeared. The solution was then heated to $\sim 60^\circ\text{C}$ for 15 min, and cooled to room temperature. A blank solution following the same procedure but containing no arsenic is also prepared.

Instrumentation

A digital pH meter (Orion, London), a high precision electrical balance (Sartorius GMBH), a Spectrascan UV 2600 spectrophotometer (Chemito) equipped with a 1-cm quartz cell, Gilson micropipette with disposable tips, a digital Nepheloturbidimeter equipped with a glass cell of 30-ml volume were used. High resolution SEM images were accumulated by placing the samples on a carbon tape in a Carl Zeiss Supra-40 scanning electron microscope. The samples were prepared by drop casting 10 μl of As(0) sol on glass slides, and dried overnight under ambient condition. TEM images were obtained in a FEI TECHNAI G^2 20S TWIN instrument operating at 200 kV. The sample for TEM analysis was prepared mounting a drop of As(0) sol on a carbon coated Cu grid and allowing it to dry in desiccators. X-ray photoelectron spectra were collected using an electron spectrometer (JEOL, JPS-9010MC) equipped with a chamber at a base pressure of $\sim 2 \times 10^{-8}$ Torr. X-rays from the Mg-K α line at 1253.6 eV were used for excitation. The as-prepared yellowish-brown colored As(0) sol was centrifuged for an hour to precipitate out the suspended particles. Concentrated As(0) was dried on a glass slide placed over a hot plate. Slow evaporation left a solid brown mass on glass slide which was re-dispersed in water and centrifuged. Precipitate was collected and dried in air and analyzed for XPS. The dynamic light scattering (DLS) experiment was carried out with the As(0) sol in a Malvern Nano ZS instrument equipped with 4mW He-Ne LASER ($\lambda = 632.8$ nm).

Results and discussion

Synthesis of As(0)

Using NaBH_4 as reducing agent, the reduction of As(III) to As(0) is possible in aqueous medium already maintained at pH 7-9. However, the same reducing agent can reduce As(III) to AsH_3 (where arsenic is in -3 oxidation state) if the pH is low (< 4). The latter procedure is extensively used for quantification of arsenic [5]. In our studies, however, the reduction of As(III) to As(0) is achieved and further reduction to AsH_3 stage has been restricted. This is possible because the standard reduction potential of $\text{AsO}_2^-/\text{As(0)}$ is -0.7 V and that of $\text{As(0)}/\text{AsH}_3$ is -1.4 V in basic medium. The standard reduction potential of $\text{BH}_4^-/\text{BO}_2^-$ is -1.33 V. Thus BH_4^- under the experimental pH condition can reduce AsO_2^- to As(0) easily and this is indicated by the formation of yellowish-brown colored sol (**Fig. 1**) upon addition of NaBH_4 to NaAsO_2 solution. The As(0) sol did not show any distinct peak but absorbed in the range of 250-350 nm, and the intensity is proportional to arsenic concentration. The calibration drawn at $\lambda = 300$ nm in the range of arsenic concentration $0 - 45.4 \times 10^{-5}$ M shows excellent linearity ($R = 0.988$) as shown in the inset of **Fig. 1**. The equation of the straight line was Absorbance = $0.0402 \times \text{Conc.}$ (1×10^{-5} M) - 0.136. The method was reproducible and the relative standard deviation was $< 8\%$. The time dependent studies for As(0) formation (Conc. 23.8×10^{-5} M) showed that 2 h time is optimum to grow particles fully under the experimental conditions (**Fig. 1**). However, under increased temperature the reduction of As(III) to As(0) is much

faster. It is observed that at $\sim 5^{\circ}\text{C}$ the rate of As(0) formation is very slow and takes ~ 24 h to complete.

The method of As(0) synthesis is reproducible and by measuring the turbidity the quantification of arsenic is possible in the range $0 - 45.4 \times 10^{-5}$ M. The equation of the straight line was: Turbidity (NTU) = $0.5889 \times C (1 \times 10^{-5} \text{ M}) + 0.744$. The correlation coefficient was found to be 0.990. The relative standard deviation (RSD) was $< 5\%$.

The formation of As(0) is also possible from arsenate in a two stage process: first, reduction of arsenate to arsenite by SO_2 gas (generated in a separate chamber on reaction of Na_2SO_3 with concentrated HCl); and second, reduction of arsenite to As(0) by NaBH_4 . However, before adding NaBH_4 , the excess SO_2 gas has to be removed by boiling the solution.

The reduction of arsenite to As(0) is not interfered by the presence of Cl^- (up to 1000 mg/l), NO_3^- (up to 100 mg/l), SO_4^{2-} (up to 500 mg/l), HPO_4^{2-} (up to 100 mg/l), SiO_3^{2-} (up to 100 mg/l), and Fe^{2+} (up to 3 mg/l). Although the presence of Ca^{2+} has a strong interference, but Ca^{2+} can be tolerated up to 70 mg/l after masking with Na_2EDTA .

The As(0) sol is soluble in alkali and acid. Also it shows a strong reducing property under normal condition.

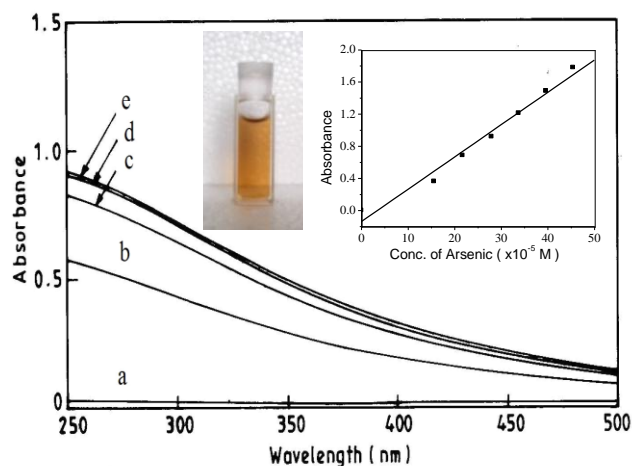


Fig. 1. Time-dependent UV-vis absorption spectroscopic study on As(0) formation (Conc. 23.8×10^{-5} M): (curve a) 0 min, (curve b) 30 min, (curve c) 60 min, (curve d) 90 min, and (curve e) 120 min. Inset: Calibration of As(0) at 300 nm.

Characterization of As(0) nanoparticles

The SEM images of the arsenic sol indicates the presence of spherical As(0) nanoparticles in the size range of 67 ± 2 nm (**Fig. 2a**). The XPS analysis of the as-prepared As(0) shows the band corresponding to As3d at 40.3eV (**Fig. 2b**), which is close to the value 40.7eV reported earlier for As(0) [6]. The TEM analysis of the As(0) nanoparticles have been shown in **Fig. 2c**. This indicates that the particles are spherical with average size 60 ± 3 nm. A high resolution image of selected particles is shown in the inset of **Fig. 2c**. The DLS studies indicate that the average size is 45 nm for As(0) particles (**Fig. 2d**). DLS studies carried out on three individually prepared As(0) sols showed excellent reproducibility. It is important to mention that in the described procedure no stabilizer is used. The particles, however, are stable for at least 7 days at $\sim 5^{\circ}\text{C}$.

To the best of our knowledge this is the first report of As(0) nanoparticle synthesis, and its characterization. The synthetic method applied here is facile and reproducible. In recent years many programme have been initiated by both Government and industries to accelerate the growth of nanotechnology, and to better understand and treat diseases [7]. It is believed that the As(0) nanoparticles has the potential for many such applications.

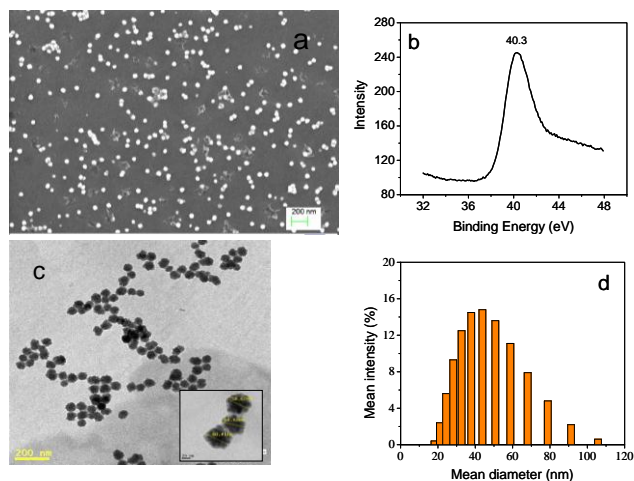


Fig. 2. Characterization of As(0) nanoparticles: (a) SEM image; (b) XPS spectrum showing As 3d band; (c) TEM image (Inset: High resolution TEM image of selected nanoparticles); (d) DLS analysis.

Conclusion

Yellowish-brown As(0) sol is produced from aqueous arsenite solution maintained at pH 7-9 upon its reduction with NaBH_4 . SEM and TEM images show the presence of spherical As(0) nanoparticles in the size range 67 ± 2 nm and 60 ± 2 nm, respectively. DLS studies indicate that the particles have the average size of 45 nm. This is the first report of stable As(0) nanoparticles synthesis. The wet-chemical synthetic method applied in the present work is simple and reproducible. The absorbance at 300 nm and turbidity show excellent linear correlation with arsenic concentration. The XPS analysis confirms the zero oxidation state of arsenic.

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