

A Novel Synthesis of Tellurium Nanoparticles using Iron (II) as a Reductant

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Abstract

A clean and wet chemical method, employing sodium tellurite (Na_2TeO_3) as a source of tellurium and iron (II) as a reducing agent, has been developed for the generation of tellurium nanoparticles. The method can produce tellurium nanoparticles in the size ranging from 25-80 nm at room temperature. The procedure is simple, convenient, rapid and involves the use of inexpensive and highly pure reagents and the products of which can easily be washed away from the nanoparticles of tellurium in aqueous environment. The method consists in dissolving the above tellurium salt in about 9 - 10M phosphoric acid, 1M hydrochloric acid medium and slowly adding two fold excess of iron (II) solution [that required for the reduction of tellurium (IV)] to the above acid mixture. The reaction process involves the reduction of tellurium (IV) present in the salt (Na_2TeO_3) by iron (II) to elemental tellurium. The phosphoric acid present in the reaction medium enhances the reducing ability of iron (II) while the chloride ion acts as a catalyst. The as synthesized nanoparticles of tellurium have been separated from the liquid phase and dried at 40°C and characterized by X-Ray Diffraction (XRD) , Energy Dispersive X-Ray (EDS) , Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) techniques. These studies indicated the formation of hexagonal structure of trigonal tellurium and the possible growth mechanism of the particles has been elucidated. In the liquid phase, however, the size of the particles has been assessed by Dynamic Light Scattering Particle Size Analyzer (DLS) .

Keywords: Tellurium Nanoparticles; Iron (II) as Reductant; Phosphoric acid-Hydrochloric acid Medium, Synthesis and Characterisation

Introduction:

Tellurium is known to be one of the most interesting semiconductors with a band gap of 0.35 eV^{1, 2}. It exhibits a unique combination of useful and interesting properties³⁻⁶ such as photoconductivity, catalytic activity towards hydration and oxidation reactions³⁻⁶, high piezoelectric, thermoelectronic, and non-linear optical responses and All these properties of tellurium promote the element to find numerous applications such as in thermoelectronics, photoconductors and highly resistive and piezoelectronic devices⁷⁻¹⁵. In addition solid tellurium reacts with other elements to generate wealth of functional materials such as Bi₂Te₃, ZnTe, CdTe¹⁶⁻¹⁸, etc.

However, the availability of tellurium nanostructures with low dimensionalities would no doubt bring new types of applications or enhance the performance of currently existing devices relation to the above mentioned properties³⁻⁷. Thus, the synthesis and characterization of tellurium nanoparticle fabrications caused profound interest to researchers.

A review of literature, however, reveals that till recently, tellurium nanoparticles or nanofabricates have been mainly synthesized through solution phase procedures. In these methods, tellurium (IV) or tellurium (VI) present in its corresponding salt is reduced its elemental or zero oxidation state employing variety of reducing agents such as hydrazine^{8, 19, 20}, hydrazine hydrate²¹⁻²⁵, ethylene glycol^{8, 26-28}, sodium sulphite^{5, 29}, sodium borohydride^{30, 31}, ethylenediamine³² hydrogen³³, polyvinyl pyrrolodine³⁴, formamide³⁵, starch³⁶ etc. In addition, methods such as hydrothermal disproportion of tellurium in aqueous ammonia have also been developed⁹.

However, all these methods suffer from the common disadvantage that the redox reaction involving the precursor (tellurium salt) and a reductant must be refluxed at elevated temperatures for a long time. In some instances where hydrazine hydrate²¹⁻²⁵, formaldehyde³⁵ and starch³⁶ are used as reductants, the redox process was carried out at about 100-180⁰C for 15-24 hours. In some other methods, the use of expensive stabilizers^{21, 34} or capping agents²³ (e.g. polyvinyl pyrrolodine^{21, 34} and surfactants²⁹ (e.g. sodium dodecyl benzene sulfonate, sodium dodecyl sulfonate²⁹, etc.) is imperative. In a few other cases²⁵, annelation of nanoparticles at high temperature is a pre requisite.

In the present paper, we have described a solution phase redox procedure for the generation of tellurium nanoparticles at room temperature. The method consists in dissolving sodium tellurite (Na₂TeO₃) in 9-10M phosphoric acid and about 1M hydrochloric acid medium and then slowly adding two fold excess of iron (II) solution [that required for the reduction of tellurium (IV) present in the salt] to the above acid mixture at room temperature. The phosphoric acid present in the reaction medium enhances the reducing ability of iron (II) causing the smooth reduction of tellurium (IV) present in the salt to elemental tellurium (or tellurium zero) , while chloride ion acts as a catalyst. The method is simple, rapid and inexpensive and does not suffer from any of the disadvantages of the earlier methods mentioned above. The procedure enables us to produce nanoparticles of tellurium in the useful range, which can find wider technical applications without the aid of any stabilizer or surfactant. The reaction medium (phosphoric acid and hydrochloric acid) and the reducing agent [iron (II) or Mohr's salt] are common and inexpensive laboratory reagents. These reagents

are available in a high state of purity and all the reagents present in the reaction medium can be easily washed away from the tellurium nanoparticles by rising with distilled water. Further, a very common analytical reagent, iron (II) , has been proposed for the first time to generate tellurium nanoparticles.

Materials and Methods

Required volume of 0.75M solution of iron (II) was prepared in 1M sulphuric acid medium from an AR grade ammonium iron (II) sulphate hexahydrate. AR grade orthophosphoric and hydrochloric acids were made use of in the investigation.

XRD patterns were obtained on a Philips X'pert MPD X-ray diffractometer using Cu Ka (1.054059 Å) radiation with the X-ray generator operating at 45 KV and 40 mA. SEM images were obtained on JEOL 2010 microscopes. The particle image measurements were conducted on a Hitachi H-700H transmission electron microscope (TEM) operated at 150 kV accelerating voltage. TEM samples containing nano-tellurium particles were prepared by dip coating of the dispersed colloidal solutions on formvar/carbon film Cu grids (200 mesh; 3 mm, Agar Scientific Ltd.) . Energy dispersive X-ray (EDS) analyses have also been conducted on the sample particles to verify their composition and purity. The resulting dispersions of tellurium nanoparticles at various growth stages were subjected to the measurements for their structural images. It reflects the variation of particle mean diameters over a period of time due to agglomeration.

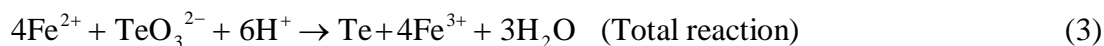
Procedure

To about 0.5 g (about 2.2 milli moles) of sodium tellurite (Na_2TeO_3) taken into a 250 ml Pyrex beaker, enough orthophosphoric acid and concentrated hydrochloric are added such that their concentrations are about 9-10M and 1.0M respectively after final dilution to 100ml. The solution is now diluted to about 100ml with distilled water and it is stirred on a magnetic stirrer until the tellurium salt is completely dissolved to get a clear solution, which is achieved in about 10 minutes. Then about 25.0ml of about 0.75M iron (II) solution [approximately two fold excess of iron (II) required for total reduction of tellurium (IV) taken] is slowly added to the acid mixture keeping it under stirring. After the addition, stirring of the solution is continued for about 30 minutes to ensure complete reduction of tellurium (IV) . The solution is kept undisturbed for about two hours to allow it to settle most the nanoparticles of tellurium. The solution is now centrifuged and the elemental tellurium separated from the centrifugate. The tellurium particles are washed carefully thrice with distilled water followed by absolute alcohol and acetone. The substance is then dried at about 40⁰C for two hours and made use of in the analysis process.

Results and Discussion:

The reduction of tellurium (IV) present in sodium tellurite (Na_2TeO_3) to zero charged or elemental tellurium in phosphoric –hydrochloric acid medium may be represented

by the following chemical redox reactions.



It is a known fact that most of the wet chemical reactions using iron (II) as a reducing agent proceed smoothly in dilute sulphuric acid medium. However, it is known from a long time that, particularly in phosphoric acid medium, the reducing ability of iron (II) is considerably enhanced³⁷. In phosphoric acid medium, iron (III) [the oxidized product of iron (II) obtained in the redox process] is bound in the form of a complex by phosphoric acid (probably by H_2PO_4^- ion) causing considerable decrease in the redox potential of iron (III) /iron (II) couple, thus enhancing the reducing ability of iron (II) . In fact, several metal ions³⁸ and organic compounds^{39, 40} which do not normally react with iron (II) under normal conditions have been found to undergo rapid reduction with iron (II) in phosphoric acid medium.

Gopal Rao and co-workers³⁷ reported that the formal redox potential of iron (III) / iron (II) couple decreases from 0.680V to about 0.380V as the concentration of phosphoric acid increases from 0.0M to 11.0M. According to these authors the formal redox potential of iron (III) /iron (II) couple in about 9-10 M phosphoric acid medium is about 0.400V³⁷ while that of tellurium (IV) /tellurium (0) couple as available in literature is about 0.600V⁴¹. Thus there is a potential difference of about 0.200V to allow the reduction of tellurium (IV) by iron (II) . Since it is a four electron change reduction, [Te (IV) to Te (0)], the difference in potential is sufficient to bring the reduction of tellurium (IV) by iron (II) . However, the authors observed that the reduction of tellurium (IV) by iron (II) is slow even in 9-10M phosphoric acid medium and the reaction is found to be catalysed by chloride ion. We further found that for rapid generation of tellurium nanoparticles in this redox process with iron (II) , the reaction medium must contain at least 9.0M phosphoric acid and 1.0M hydrochloric acid. We speculate that chloride ion acts as a catalyst in the reaction, because catalysis by chloride in the redox analytical methods involving iron (II) as a reductant in phosphoric acid medium [in the determination of antimony (V)⁴² and arsenic (V)]⁴³ has already been reported from our laboratories^{42, 43}. Further, very recently, we developed a similar method for the generation of selenium nanoparticles using iron (II) as a reducing agent in H_3PO_4 - HCl medium in which the catalysis by chloride ion has been envisaged⁴⁴.

Characterisation:

The X-ray diffraction pattern shown in Figure-1 confirms the realization of tellurium nanoparticles generated by the present redox wet chemical method. The spectrum of the sample was in accordance with the values in the standard card of hexagonal tellurium [JCPDS No. 36-1452] with the major reflections being at 100, 101, 102, 110 and 111 etc. These peaks can be indexed to perfect hexagonal structure of trigonal tellurium with cell constant of $a=4.4579\text{\AA}$. Strong tellurium peaks undoubtedly confirm

that the hexagonal tellurium really existed in the product. No other peak can be found indicating that the grains of elemental tellurium with high crystalline purity were obtained. The abnormal intensity of 101 peak indicates that these tellurium particles had been preferentially grown. The hexagonal structure consists of a spiral chain of atoms with three atoms per turn and the corresponding atoms in each chain form into a hexagonal network as shown in Figure-2 and elucidated by the earlier authors^{35, 45}. The bonds between atoms of the same chain are covalent, whereas between chains they are thought to be combined interactions of electronic and Vander Waals^{35, 45}.

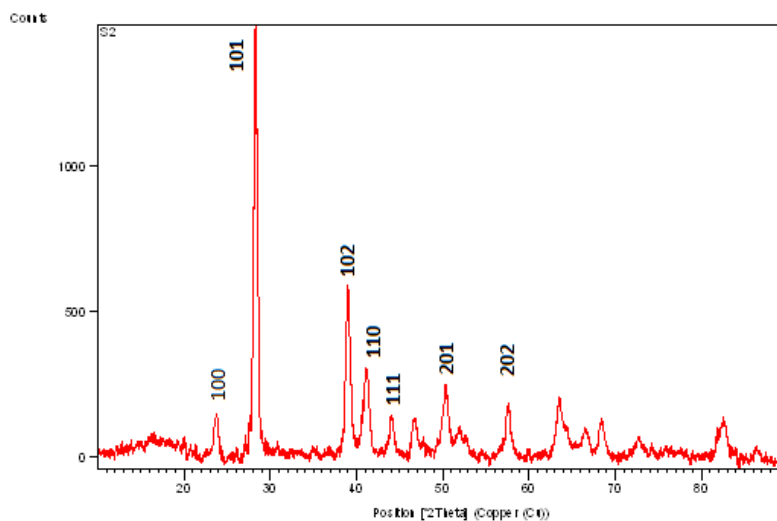


Figure 1: XRD Pattern of Tellurium Nanoparticles.

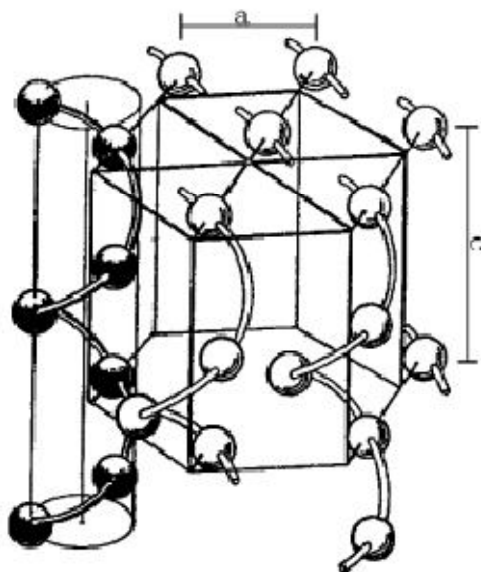


Figure 2: Crystal structure of trigonal tellurium

The average crystallite size of pure selenium nanoparticles was calculated using Debye Scherrer formula⁴⁶⁻⁴⁸ $L = 0.89 \lambda / (\beta \cos \theta)$ Where L is the crystallite size, λ , the X-ray wavelength, θ , the Bragg diffraction angle and β , the full width at halfmaximum (FWHM) and found to be about 35nm.

The EDX spectra of pure tellurium nanoparticles is shown in Figure-3 and it shows the peaks of pure tellurium.

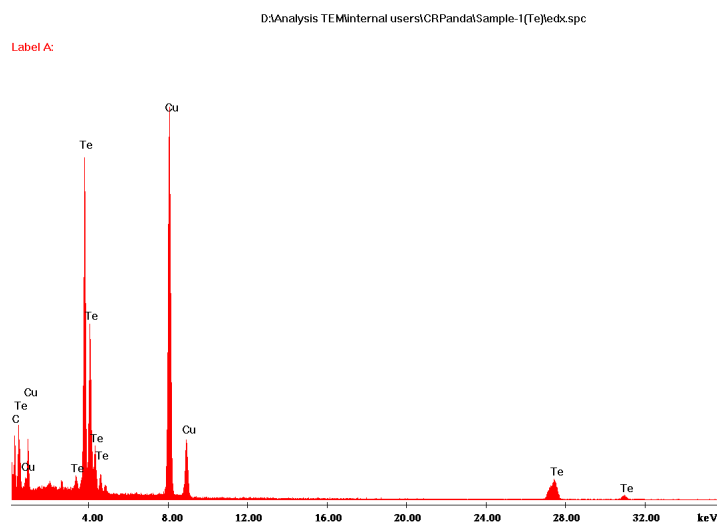


Figure 3: EDX Image of Tellurium Nanoparticles.

Form of the Produced Nanoparticles - SEM and TEM Studies

The formation of tellurium nanoparticles was verified by the corresponding SEM images presented in Figure-4. The tellurium particles were found to be coarse and irregular but well separated.

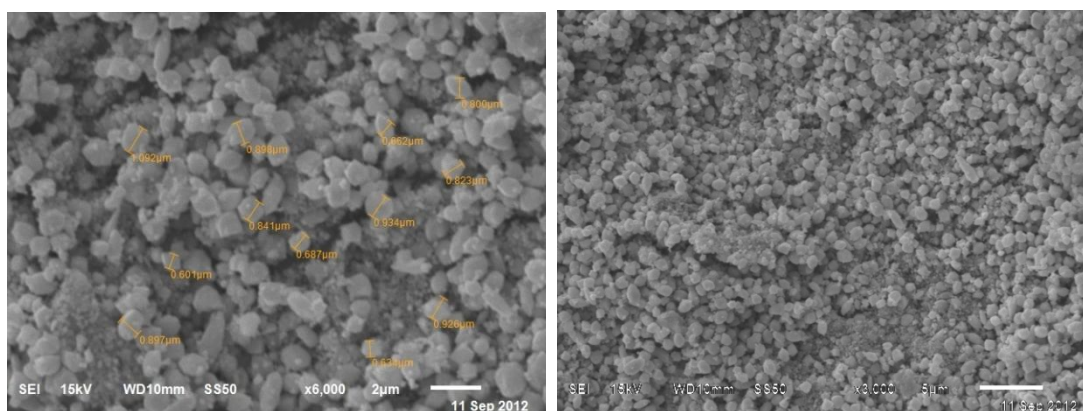


Figure 4: SEM Images of Tellurium Nanoparticles

The formation of hexagonal tellurium nanostructures can be rationalized by a mechanism of nucleation- dissolution – crystallization process. When the reaction was processed by adding iron (II) to sodium tellurite present in phosphoric acid-hydrochloric acid medium, the formation of elemental tellurium, as per chemical equation shown above, is rapid even at room temperature. The initial products most likely are the spherical colloids of amorphous tellurium and nano crystallites of trigonal tellurium. Thereafter, slowly, the spherical colloids of amorphous tellurium would dissolve into solution phase due to high free energy of amorphous tellurium compared to that of trigonal tellurium. The dissolved particles of the latter could be subsequently deposited on the surfaces of trigonal tellurium nanocrystal (seeds) which crystallize and grown into hexagonal structure of trigonal tellurium. The SAED pattern (Figure-5) reveals several diffraction rings which can be indexed to hexagonal tellurium in agreement with the XRD result.

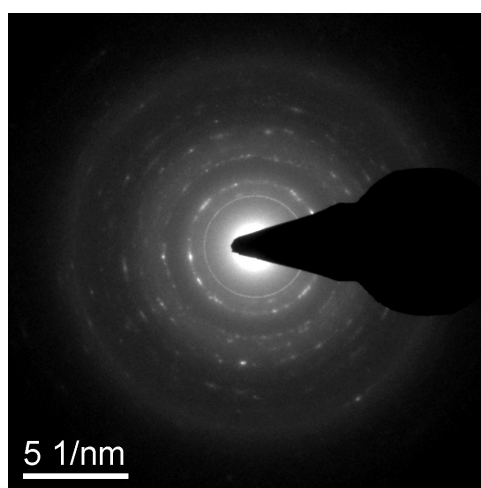


Figure 5: SAED image

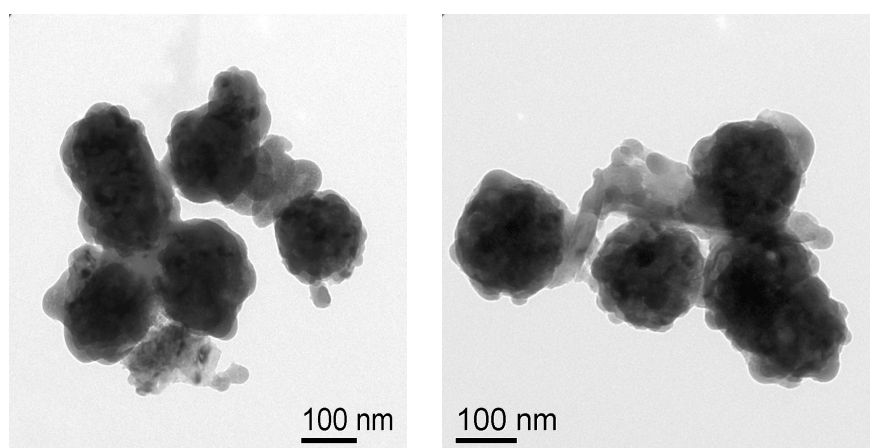


Figure 6: TEM Images

The TEM images shown in Figure-6 reveals the agglomeration of the particles in the solid phase. This is attributed to the fact that no stabilizer or surfactant which prevents the agglomeration of nanoparticles is employed in the reaction medium during the production of tellurium nanoparticles. These substances are supposed to adsorb on the surface of nanoparticles and prevent the formation of large agglomeration in the solid phase.

Liquid Phase Particle Size Analysis:

In the liquid phase, however, there is well separation of tellurium nanoparticles. The size of the particle has been assessed by Dynamic Light Scattering Particle Size Analyser (DLS) in the liquid phase. Table -1 gives the diameter (in nm) , the % frequency (in nm) and the % undersize of the tellurium nanoparticles in the liquid phase obtained by DLS measurements. Figure 7 gives the histogram diagram of these particles. From the Table as well as from the Figure, it may be seen that nearly 95% of the tellurium particles were found to be below 57nm in size and the average size of the particle was found to be around 36.8 nm.

Table :- 1. Particle Diameter and the % Frequency of the Particles.

Diameter (nm)	Frequency (%/nm)	Undersize (%)
24.29	3.454	3.454
27.45	15.209	18.663
31.01	19.821	38.484
35.03	18.404	56.888
39.58	14.532	71.420
44.72	10.438	81.858
50.53	7.040	88.898
57.09	4.535	93.433
64.50	2.815	96.248
72.87	1.691	97.938
82.33	0.984	98.922
93.02	0.553	99.476
105.10	0.299	99.775
118.74	0.153	99.928

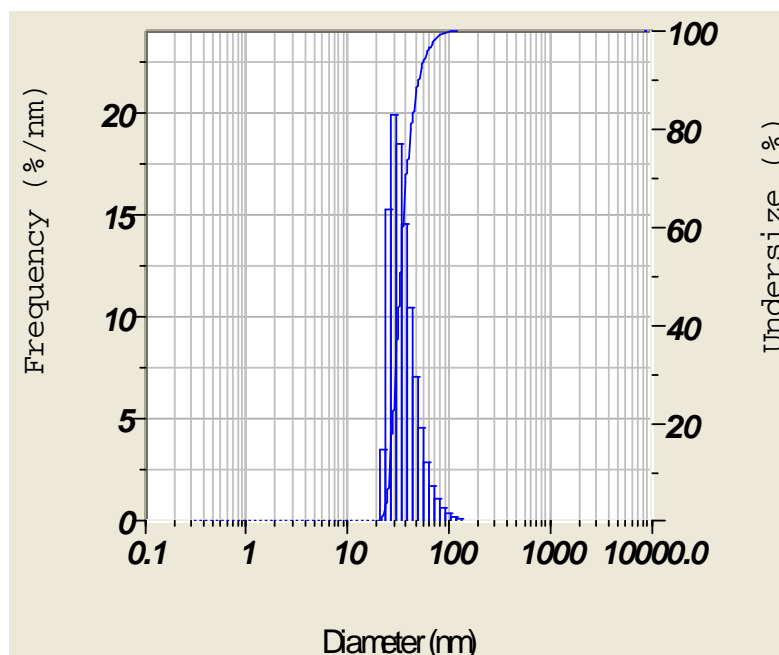


Figure:-7. Particle Size Distribution of Tellurium Nanoparticles

Conclusions

In summary, we have developed a wet chemical approach for the generation of tellurium nanoparticles of technologically useful range (25-80 nm) by employing sodium tellurite as a precursor and iron (II) as a reducing agent in 9-10M H_3PO_4 - 1M HCl medium without using any surfactant / stabiliser or heating at elevated temperatures. The method is simple, convenient, inexpensive and does not suffer from any of the disadvantages of the earlier reported methods.

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