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Preparation of nano selenium particles by water solution phase method from industrial dust

ABSTRACT

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In this study, selenium was recovered from an industrial dust. After the purification process, the researchers were able to prepare selenium micro powder. The objective of this study was to prepare selenium nano particles by water solution phase method from the micro powders. The results showed that selenium micronized powder and nano particles had high purity. The obtained nanoparticles were tube shaped with 20 nm size.

Keywords: *Industrial dust, Selenium recovery, Nano selenium particles, Water solution phase*

INTRODUCTION

Metal production industrial dust and cupellation contain selenium compounds and selenium act as pollutants and may cause environmental contamination. Therefore, its recovery will be economically valuable. Recently, lots of efforts have been made to prepare selenium nano particles as one-dimensional structure (ie. nano wire, nano tubes, and nano rods), due to the variety of application as active objects or intermediate material in production of electrical, electro-optical, electro-chemical, and electro-mechanical devices [1]. Also, selenium is one of the most important elements among semi-conductors because of its various applications [2,3]. Selenium is a semi-conductor with indirect band gaps of 1.85 eV and its melting point is relatively low (~490 K) [4]. It has high catalytic activity towards oxidation reaction and organic-hydration; in addition, it has refractive indices, intrinsic chirality, and birefringence [4, 5]. It has interesting spectrum properties which include photovoltaic [4] and photoelectrical effects [6], high photoconductivity [4,5,7-9] and piezoelectricity, thermoelectricity and non-linear optical responses [4,5].

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These characteristics make it suitable for such photo cell production [8], rectifiers [9-14,2], catalyst [10], xerography [2,9-13,15,16], photovoltaic [13,15,16], solar cells[2,8-12] and medical diagnostics [9,7]. Selenium also exhibits glass forming tendencies [2,17]. Because of anti-oxidant [6,7,18] and per oxidant effects [6,7], selenium prevents cells and tissues from injury with the help of free radicals [12]. Thus it is an essential element for maintaining the man's health [4, 12-14, 19], mammalian animals [20,7] and the vegetation [20] as well. It has a very narrow margin between its lowest acceptable level of intake and its toxicity[7].

Selenium has several allotropic forms [13]. The stable form at ordinary temperature, i.e., the gray or hexagonal selenium is the densest and is semimetallic in appearance [8,13]. The electrical conductivity, which makes gray selenium useful in photoelectrical and photochemical applications, is low in the dark but increases several hundredfold once exposed to the light. Electrolytic copper refinery slimes are the principal sources of selenium. The primary purpose of slimes treatment is the recovery of the precious metals and recovery of selenium is the secondary concern. Some methods for precious metals and selenium recovery have been developed in all over the world because of complication and variety of sludge compounds, which include alkaline autoclaving, sulphation roasting, soda ash roasting, etc. [13]. There are also methods for selenium nanoparticles preparation which involve refluxing method, sonochemical method, physical evaporation [5], laser ablation, and the chemical reduction which is the most important method in preparing (OD) nanoparticles [7]. Zhu et al [10] used γ radiation method to prepare the trigonal selenium nanocrystals. Gates et al [10] reported their findings on preparing selenium nanowires by aging amorphous in the dark. The chemical methods based on solution-phase procedures seem to provide an excellent route to fabricate selenium nanoparticles, although only a small number of routine techniques are capable of synthesizing selenium nanoparticles [21]. However, there is no report or any work to (i) recover selenium and (ii) prepare nanoparticles from this type of industrial dust.

In this study, selenium powder is first extracted from industrial waste and then the obtained selenium is transferred to nano-tubes. In this procedure, first selenium powder is soluted in definite solvent by heating, then, it is crystallized to nano particle form as soon as the heat is removed. The definite solvent is capable to solve the more solute and those solutes could be crystallized again once the conditions are changed. The form and size of the final product are carefully checked under the period reaction and different values of used alkaline.

MATERIALS AND METHODS

The materials used in these experiments are sodium hydroxide, sodium Meta bi-sulphide, sulphuric acid, ethanol from Merk Co., and the dust from the filter bag of cupellation furnace. The chemical analysis of the dust is shown in [Table 1](#).

In the first stage, 10 g of the primary dust sample was poured in 20 cc sulphuric acid (20%) at the temperature of 80 °C and it was left for 30 minutes. The mixture then was stirred continuously by a magnetic stirrer. After filtration, selenium powder was formed by addition of 50 g sodium Meta bi-sulphite to the liquid phase then it was filtered, washed with hot water, purified, and separated. In the next step, previous selenium powder was changed to nano powder by the dissolution and precipitation. It can be explained as follows: Selenium micro powder (0.10 g) was refluxed at 120-140 °C with 40 ml water. During reflux, sodium hydroxide (1.20-3.0 g) was added. Then, the mixture was left to reach the room temperature. Finally, the gray precipitant was filtered, washed by water and ethanol respectively.

The effect of sodium hydroxide concentration, reaction time as parameters on morphology and size of the final product were considered. Scanning electronic microscope (Philips XL30) was used to see the morphology and EDAX analysis. Also, for XRD analysis, the Seifert 3003 TT Cu $K\alpha$ radiation, $\lambda=1.54 \text{ \AA}$ and for TEM analysis Philips 120 kv were used.

Table 1. Chemical analysis of raw dust and recovered selenium powder (conc. w/w%)

Element	Of Raw dust % conc.	conc.% selenium micro powder
Se	6.2	> 99
Fe	0.2	0.031
Pb	51	0.06
S	5.6	0.7

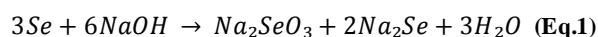
RESULTS AND DISCUSSION

Result of primary recovered selenium powder

SEM and XRD pictures for the primary recovered selenium powder are shown in Figures 1, 2 and Table 1. As Table 1 shows it is clear that the primary recovered selenium powder has the highest purity and the least impurities. The XRD analysis shows that selenium with hexagonal structure is dominant.

The effect of the reaction time on size and form of the produced particles

The SEM images and EDX analysis of synthesized selenium powder refluxed with 2.40 g NaOH at 120-140°C in different times are shown in Figure 3. As Figure 3a shows, in 1hr the morphology of selenium particles are spherical agglomerated, when the reflux time increased to 5hr, the morphology changed to nano tube that is clearer by TEM results (Figure 4). It is believed that the formation mechanism of particles is similar to what Zhou & Zhu [22] have described. In this mechanism, as the first step, Selenium is dissolved in hot alkaline solution (Equation 1).



In the second step, selenium solution has done a reversible reaction during cooling period (Equation 2).

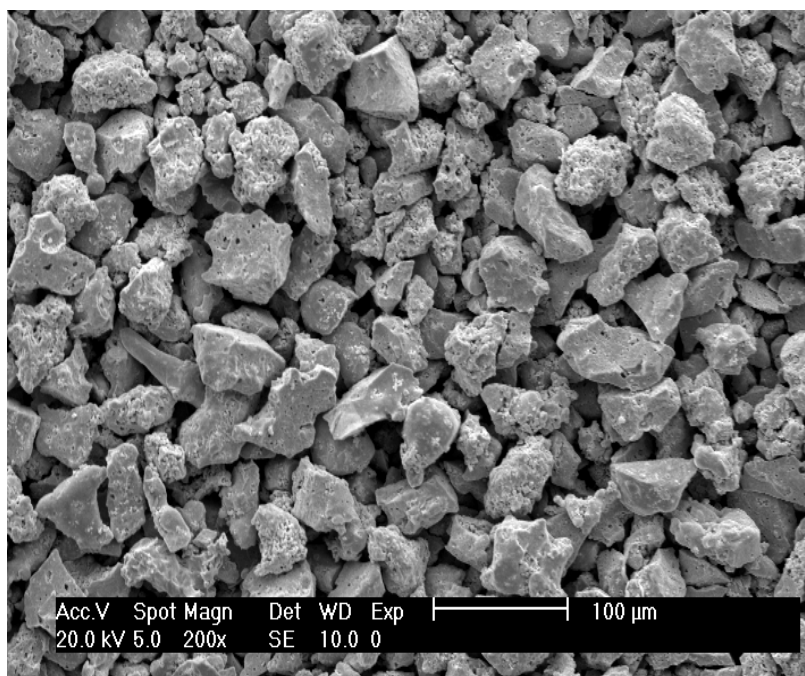
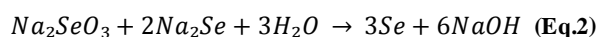


Fig.1. SEM picture of recovered selenium micronized powder

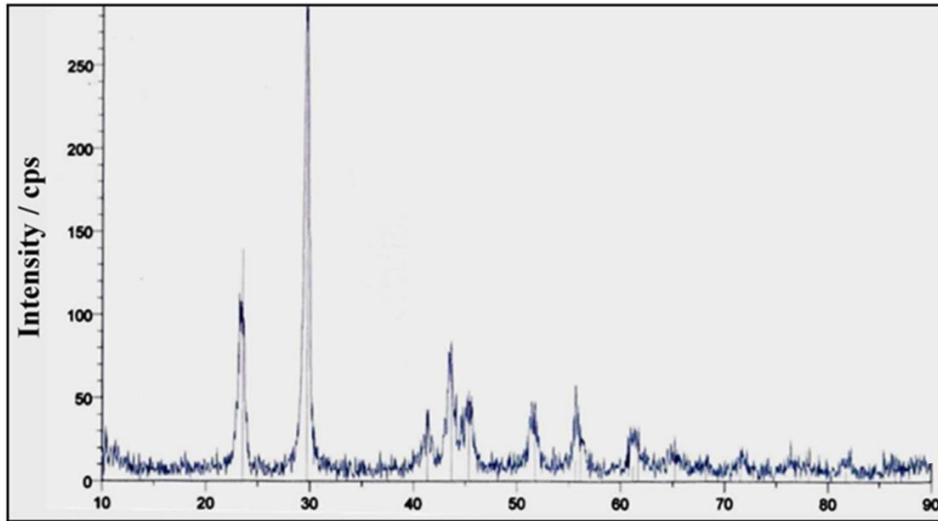


Fig.2. XRD pattern for recovered selenium micronized powder

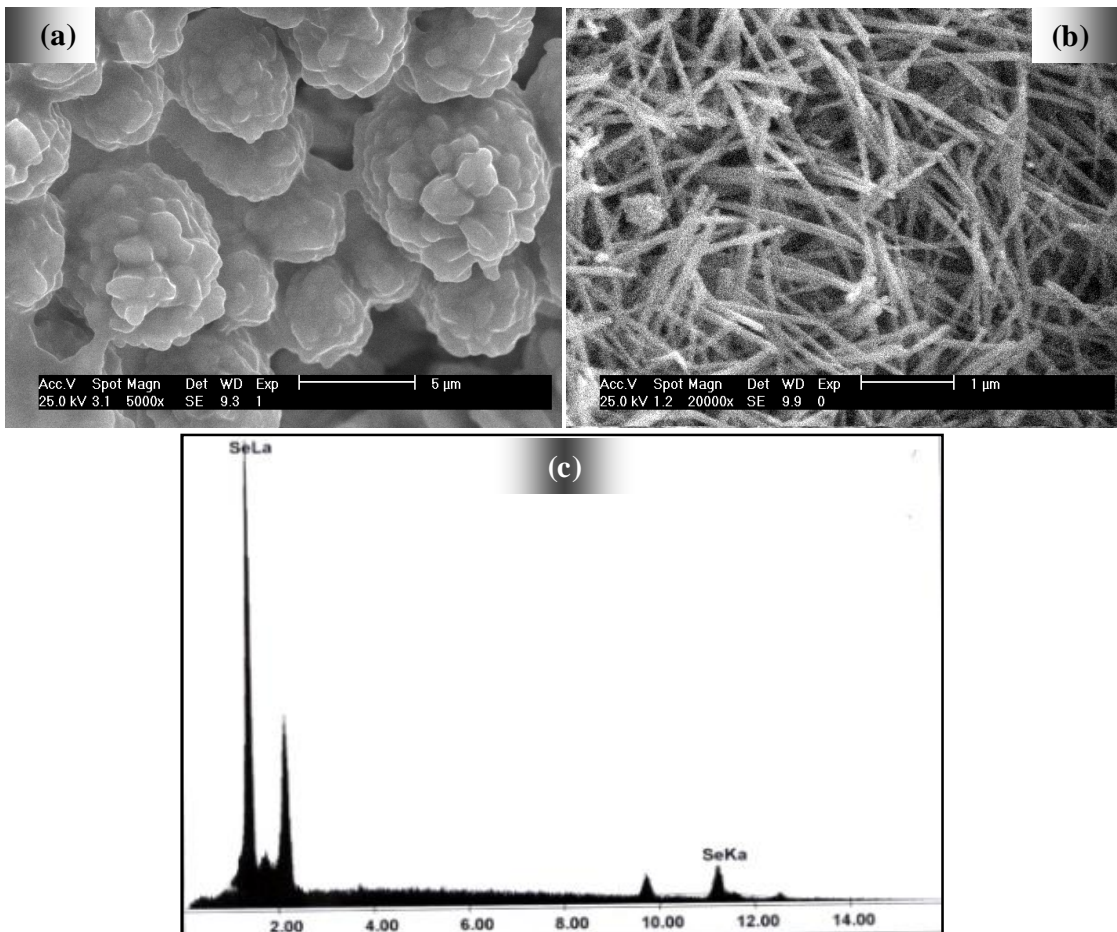


Fig.3. SEM picture of refluxing 0.10 g recovered selenium powder with 2.40 g NaOH and 40 ml water at (a) 1hr (b) 5hr and (c) EDX related to part b

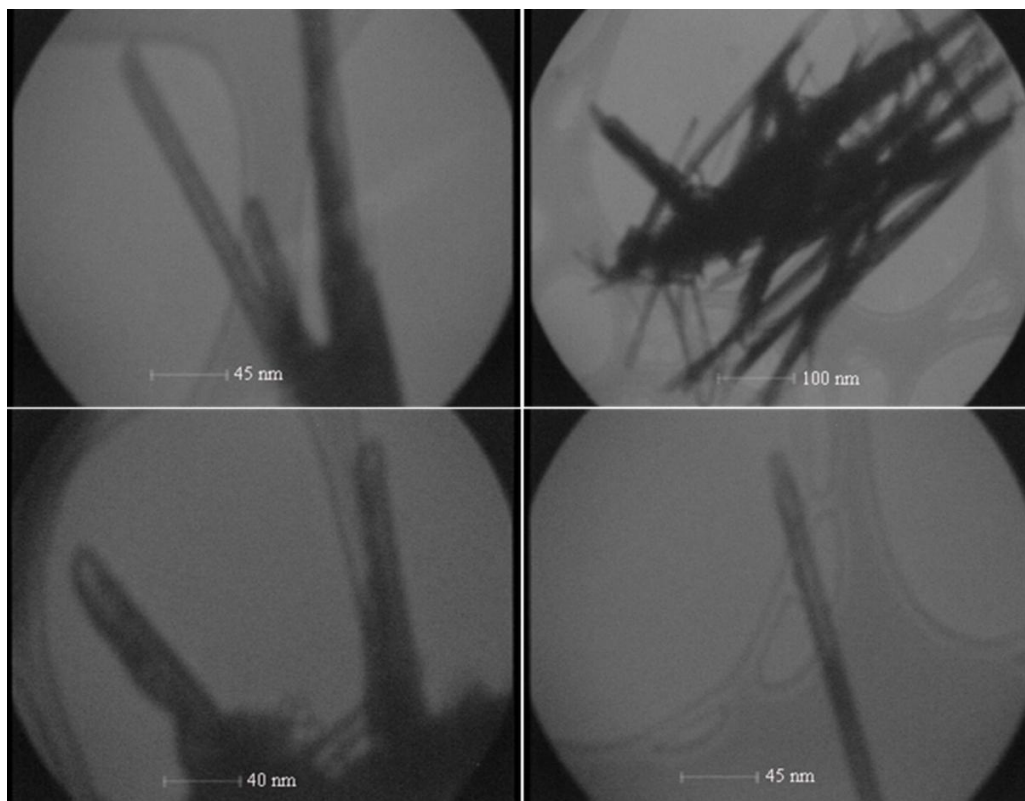


Fig.4. TEM images of refluxing 0.10 g selenium with 2.40 g NaOH and 40 ml water at 5hr

The results of the NaOH on the size effect and shape of selenium particles

The effects of NaOH variation amounts of (1.20, 2.40 and 3.00g) of sodium hydroxide, in the same condition reflux are considered. The SEM images of selenium particles in 5hr reflux with 1.20 and 3.00 g of sodium hydroxide are shown in **Figures 6a** and **6b** respectively.

The SEM results indicated that nano tubes with agglomerated particles are obtained in 1.02g that compare in more amount of sodium hydroxide concentration. The value of selenium micro powder concentration was considered to be constant. In **Figures 3b** the SEM of nano selenium particles with 2.40 g sodium hydroxide concentration are shown. The results indicated optimum conditions for improving of nano tube particles with time and NaOH concentration. The

dosage of NaOH can be decided from the form and size of selenium nano tubes particles. Nano tubes formation under 2.40 g of NaOH concentration as optimum conditions were determined by SEM, EDX and XRD results (**Figures 3-5**). According to alkaline selenium salvation in water, the particle size is decreased with the increasing of NaOH concentration. In lower alkaline concentration, some selenium particles remained insoluble. In 2.40 g NaOH as alkaline media, nucleation occurred because salvation completed. Thus in more concentration, the selenium micro powder be solved and homogenous phase was disturbed.

(**Figure 6b**). The XRD analysis shows that selenium with hexagonal structure is dominant (**Figure 5**) and EDX shows that particles are entirely pure (**Figure 3c**).

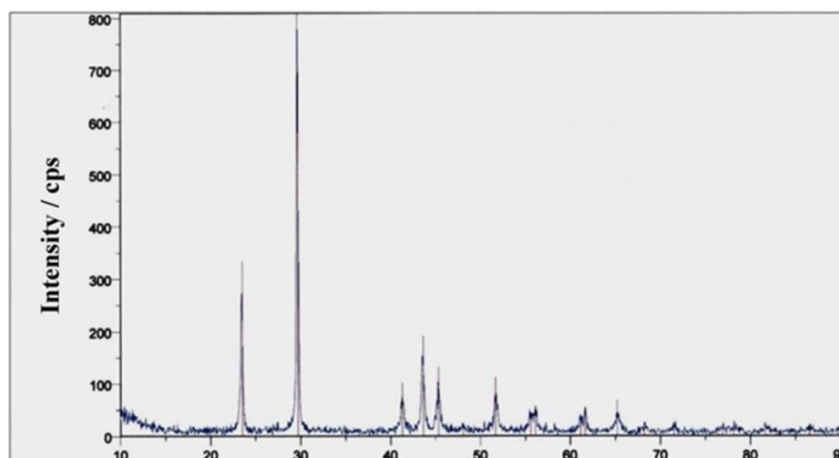


Fig.5. XRD pattern for selenium nano tube particles

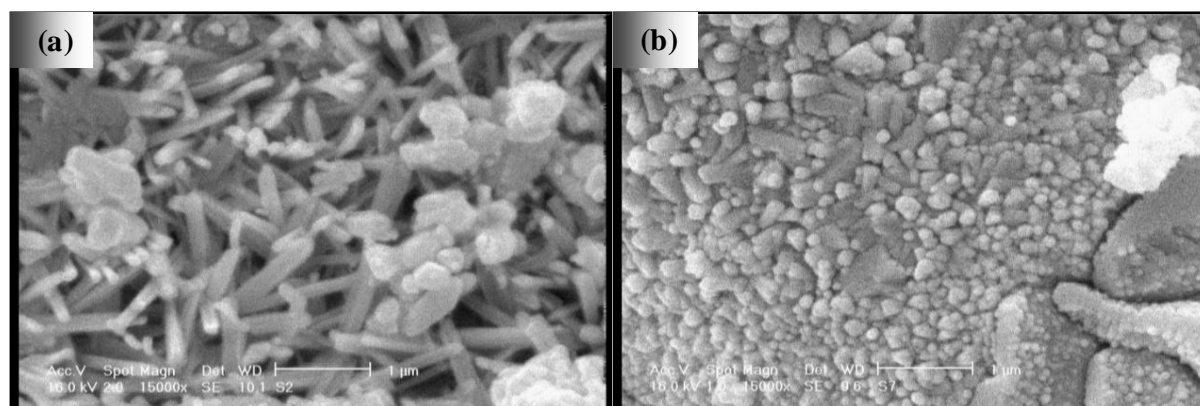


Fig.6. SEM picture of refluxing 0.10 g selenium with 40ml water at 5hr in different quantity of NaOH: (a) 1.20 g, (b) 3.00 g

CONCLUSION

The possibility of selenium powder recovery from industrial dust was proved. The effect of time enlargement on shape and size of the particles showed that the increasing time increased solubility and homogenous nucleation to nano tubes formation. The effect of the NaOH value on shape and size of particles showed by increasing of concentration solubility decreased particle size.

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