

Synthesis of Monodisperse Selenium Nanospheres and Self-assembled Monolayers Using Poly(vinyl pyrrolidone) as Dual Reductant/colloid Stabilizer

Ungki Lee, Jangwoo Choi,[†] Noseung Myung,^{*} Il-Ho Kim,[‡] C. Raman Nair Chenthamarakshan,[§] Norma R. de Tacconi,[§] and Krishnan Rajeshwar^{§,*}

Department of Applied Chemistry, Konkuk University, Chungju, Chungbuk 380-701, Korea. *E-mail: myung@kku.ac.kr

[†]Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea

[‡]Department of Materials Science and Engineering/ReSEM, Chungju National University, Chungju, Chungbuk 380-702, Korea

[§]Center for Renewable Energy Science & Technology (CREST), The University of Texas at Arlington, Arlington, TX 76109-0065, USA

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Elemental selenium (Se) is a narrow band gap (~1.7 eV) semiconductor which has been extensively used in solar cells, xerography and rectifiers. It is also a photoconductor with a relatively low melting point (~217 °C), high refractive index and high reactivity leading to a wealth of functional materials such as Ag₂Se,¹⁻³ CdSe,^{1,2,4,5} ZnSe⁴ and PbSe.⁴ Monodispersed colloidal spheres of Se are also relevant to the fabrication of photonic crystals by self assembly.⁶ In previous studies, such materials have been prepared by the chemical reduction of selenious acid by sodium borohydride,⁷ ascorbic acid,³ hydrazine,^{6,8} or glucose.⁹

However, two studies more pertinent to the present one, report the large-scale synthesis and growth mechanism of single crystal Se nanobelts⁹ and the crystallization and shape evolution of single crystal Se nanorods at a liquid-liquid interface.⁸ In both studies, PVP was used in addition to a chemical reductant. There is literature precedence for the use of PVP as a macroligand for stabilizing metals such as Pt,¹⁰ as a shape-controlling reagent in the so-called polyol process for producing nanostructures with different shapes¹⁰⁻¹² and as a flexible membrane around metal colloids influencing the selectivity of catalytic reactions.¹²

The potential role of PVP as a reducing or nucleation agent dates back to 1997 and studies since then.¹³⁻¹⁸ Thus PVP has been used in this capacity for the kinetically controlled synthesis of triangular nanoplates of Ag.¹⁹ In this paper, we show that PVP functions as a dual reductant/nanoparticle stabilizer during the synthesis of monodisperse selenium nanospheres. Finally, the results presented in this Note build upon our long-standing interest in Se and on the template driven deposition of oxide and chalcogenide semiconductors.²⁰⁻²⁴

Experimental

Selenium dioxide (SeO₂) and PVP (MW = 10,000, 40,000, 55,000) were from Sigma-Aldrich and used as received. All solutions were prepared with double-distilled water (Corning Megapure) and purged with ultrapure N₂ to expel dioxygen as needed. In each synthesis, a specific amount of

PVP was added to a 50 mL flask and fully dissolved with copious amount of water. Then, specific amounts of SeO₂ were added into the flask and diluted to the mark after making the solution clear with repeated shaking. 10 mL of this reaction mixture were transferred into a vial and kept in a convection oven at 70 °C with a tight cap. Reaction time was varied from 1 h to several days. At different stages of the reaction, samples were taken from the reaction mixture, centrifuged with a commercial centrifuge (Hanil Science Industrial Model Mega21R) at 16,000 rpm for 15 min, and washed with water twice to remove excess PVP. The Se-PVP precipitate was dissolved in 0.3 mL of water and 30 μL of sample was spin coated onto cleaned glass slides using a commercial spin coater (Midas-Spin1200D). For cleaning, the glass slides were previously treated with aqua regia (HCl:HNO₃ = 3:1) and rinsed with distilled water several times.¹⁶

Film morphology and composition were obtained on a field emission scanning electron microscope (JEOL Model 6700F) equipped with an energy dispersive X-ray analysis (EDX) probe operated at an accelerating voltage of 10 kV. Reaction efficiency was measured on time-elapsed aliquots from the reaction mixture on an ICP-OES (Perkin-Elmer Optima 5300DV) spectrometer and calculated based on the Se concentration in the starting solution and in the final solution after complete reaction. The X-ray diffraction pattern (XRD) was recorded using a Rigaku RINT2000 diffractometer with a Cu K_α radiation source.

Results and Discussion

Time is an important variable in the reaction between selenious acid and PVP to form Se nanospheres. As SEM results in Figure 1 shows, size and regularity of Se nanospheres can be tuned by controlling the reaction time. First, particle size increased from ~100 nm to ~380 nm by increasing reaction time from 1 h to 8 h at 70 °C. However, reaction at room temperature resulted in no particle formation, which can be indicated from color change of reaction solution and SEM pictures. The Se nanosphere colloids were transferred

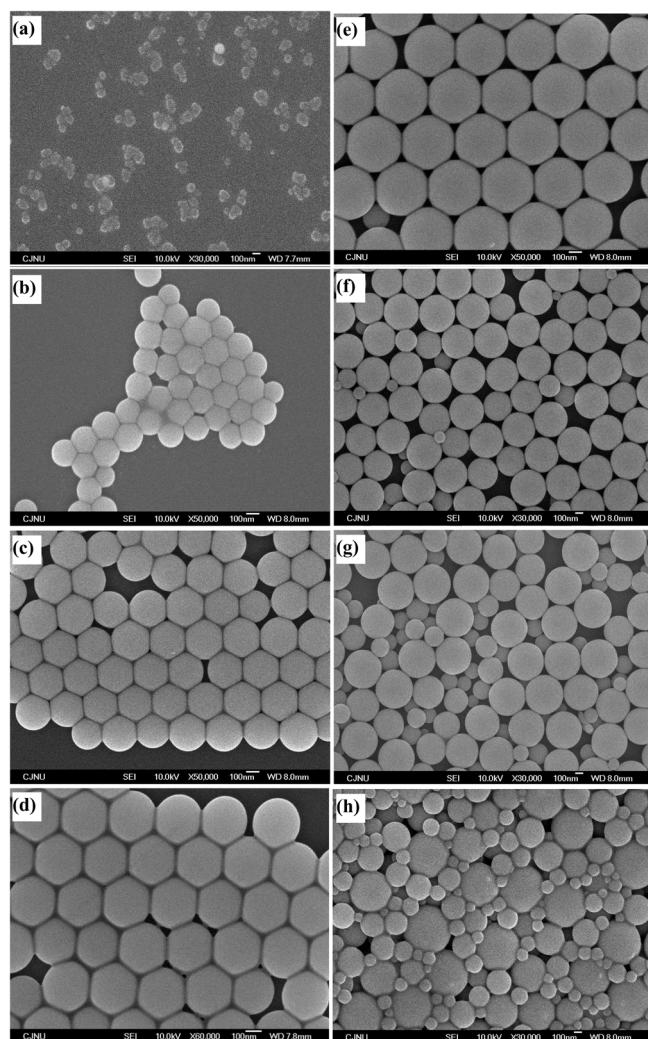


Figure 1. Representative SEM data monitoring the evolution of Se nanoparticle morphology at reaction times of: (a) 1 h, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, (f) 10 h, (g) 12 h, (h) 24 h. The reaction mixture: 5% PVP, MW = 10,000, 0.1 M Se(IV). The Se nanospheres were transferred onto glass slides after the reaction times shown for SEM examination.

onto glass slides *via* self assembly prior to SEM examination (see Experimental section). The nanospheres self assemble in hexagonal close packed sphere geometry (see, for example, Figure 1d) – a trend reminiscent of the packing of silica or polystyrene nanospheres on a substrate.²² While the size distribution is monodisperse up to ~8 h reaction time, longer times lead to the nucleation of smaller size nanospheres. This is exemplified by the SEM data in Figures 1g and h. Also, monodispersity and hexagonal geometry were not obtained when reaction time is not enough. Of particular interest are the mechanical characteristics of these packed nanoparticles. These materials are quite soft as seen by the progression in shape from spherical when the particles are not in contact to hexagonal when they are in mechanical contact as in the self-assembled films.

Figure 2a maps how the Se nanosphere diameter scales with the reaction time. As an indicator of the degree of size monodispersity, the associated standard deviations are also

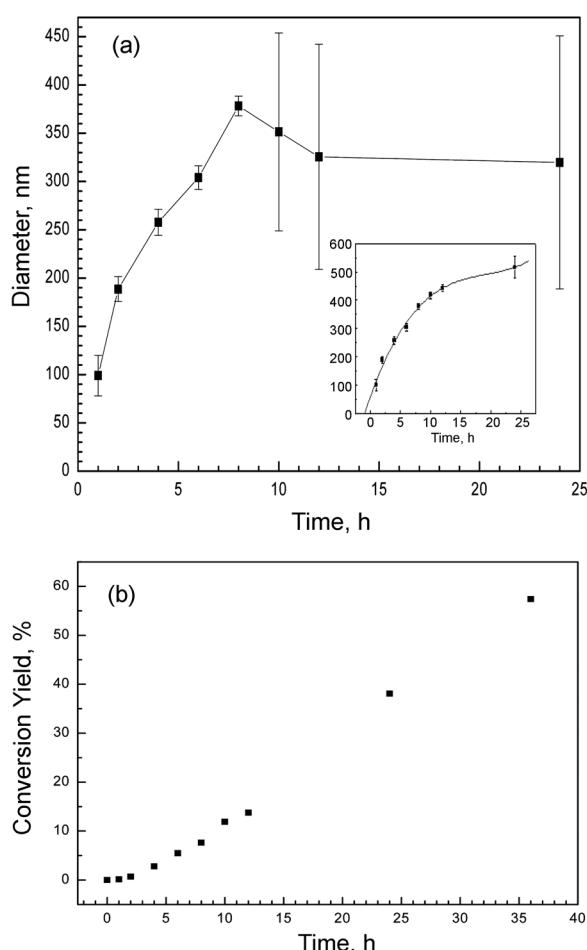


Figure 2. (a) Evolution of the selenium nanosphere diameter (as measured by SEM) as a function of reaction time. The insert is based on considering only the large and regular Se nanoparticles. The lines were simply drawn through the data points. The error bars denote one standard deviation. (b) Reaction yield (*i.e.*, percent selenium converted to the elemental state, see Experimental) as a function of reaction times spanning 1 h to 36 h. Reaction mixture specifications as in Figure 1.

shown in each case. The monodispersity is clearly lost after a reaction time longer than ~8 h. The insert in Figure 2a shows that the trend is much smoother if only the large and regular nanospheres are considered. The reaction yield (*i.e.*, % of selenium converted from the dissolved +4 oxidation state to the reduced elemental state) scales linearly with the reaction time, after an initial ~2 h induction period, as shown in Figure 2b.

The cross-sectional SEM data in Figure 3a illustrates again the order and regularity associated with the Se self-assembled monolayers on glass substrate. This figure clearly shows the high degree of size monodispersity and mechanical characteristics. The above data were obtained from 5% PVP (MW = 10,000) as the dual reductant/colloid size capping agent. However, higher molecular weights lead to the loss of size monodispersity and the nucleation of a large number of Se nanospheres as the SEM data in Figures 3b and c illustrate. The effects of molecular weight on the particle formation will be further investigated in the lab.

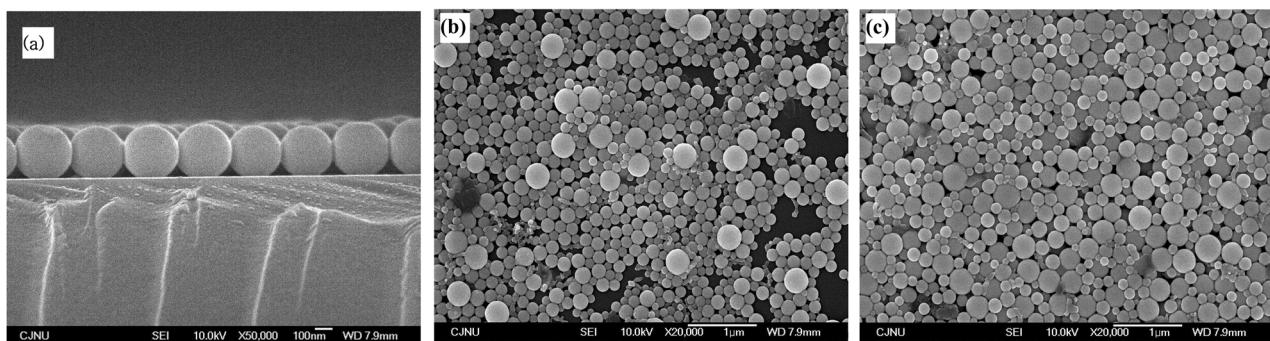


Figure 3. (a) Cross-sectional SEM view of a representative Se self-assembled monolayer on glass substrate. This monolayer was assembled from a reaction mixture (as in Figure 1) after 8 h. As in Figure 1 but showing the influence of PVP molecular weight: (a) 10,000; (b) 40,000; (c) 55,000. Figure 3a is reproduced from Figure 1e and the reaction mixture specifications otherwise are as in Figure 1. These SEM data pertain to 8 h reaction time.

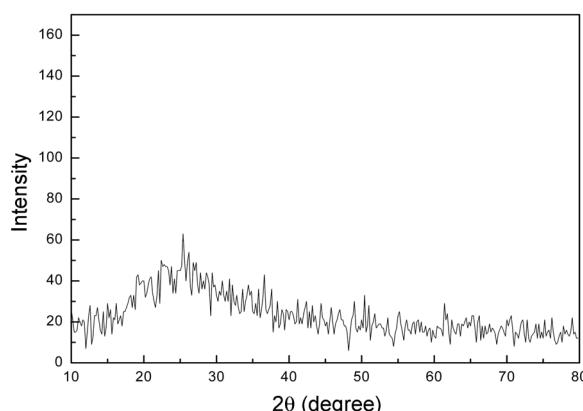


Figure 4. X-ray diffraction of as synthesized Se nanoparticles. The Se nanospheres were drop coated onto glass slides to form thick films after reaction times of 8 h. Reaction mixture specifications as in Figure 1.

Figures 1 and 3 indicate that experimental conditions including reaction time and molecular weight of PVP should be optimized to obtain monodisperse Se nanoparticles.

X-ray diffraction in Figure 4 shows that Se nanoparticles produced from the reaction of PVP with selenious acid are amorphous and this result is in well agreement with the previous result.⁸ Figure 5 contains a parallel set of SEM data mapping the evolution of the Se colloidal morphology at an initial Se(IV) concentration of 0.01 M instead. Note that the size monodispersity is preserved to much longer reaction times (~31 h) in this case contrasting with the trend observed

earlier for the 0.1 M Se(IV) case (Figs. 1 and 2). Interestingly, Se nanowire formation is observed at reaction times 36 h or longer (c.f., Figs. 5d and e) when using a low Se(IV) concentration. A similar trend has been observed in a previous study on Se using a somewhat different synthetic approach.⁹

In summary, selenium nanospheres and nanowires were prepared by the reaction of selenious acid with PVP and thus synthesized nanoparticles were stable at room temperature for more than several months. Unlike in the previous studies, no chemical reductant was deployed other than PVP and nanowires could be prepared without a liquid-liquid interface (c.f., Ref. 8) by simply using a low Se(IV) concentration in the reaction mixture. Standard electrode potentials (E^0 , vs. standard hydrogen electrode) for Ag^+/Ag^0 , $\text{Pt}^{2+}/\text{Pt}^0$ and $\text{Se}^{4+}/\text{Se}^0$ are 0.799 V, 0.758 V and 0.739 V, respectively and those ions can be reduced by PVP at elevated temperature.^{17,26} However, we found that PVP can not reduce Te^{4+} to Te^0 ($E^0 = 0.551$ V), which implied the strength of PVP as a reducing agent at the same temperature.²⁷ Further studies on the use of these Se colloids and self-assembled monolayers are in progress in the two laboratories.

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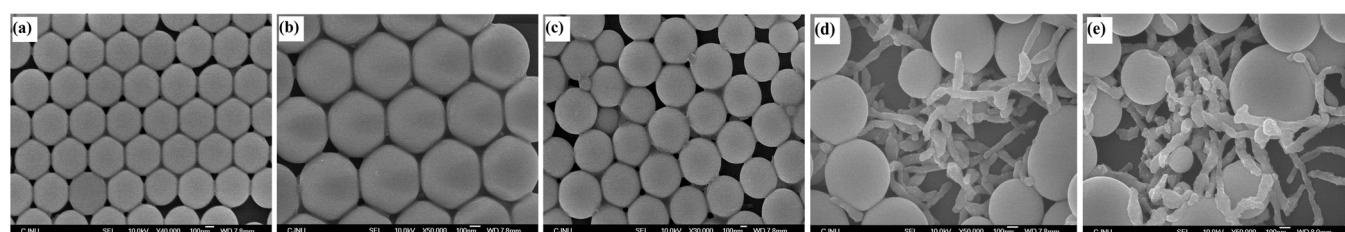


Figure 5. As in Figure 1, but showing the influence of Se(IV) concentration in the initial reaction mixture which was 0.01 M (instead of 0.1 M). Reaction times: (a) 12 h; (b) 18 h; (c) 31 h; (d) 36 h; (e) 48 h. PVP specifications and concentration as in Figure 1.

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