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# Synthesis of Se nanoparticles by using TSA ion and its photocatalytic application for decolorization of cango red under UV irradiation

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## Abstract

In this study, we describe a size-controlled synthesis of selenium nanoparticles based on the reduction of selenious acid ( $H_2SeO_3$ ) by UV-irradiated tungstosilicate acid ( $H_4SiW_{12}O_{40}$ , TSA) solution which serves both as reducing reagent and stabilizer. The nanoparticles are characterized by ultraviolet-visible spectroscopy (UV–vis), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), the Raman spectra, transmission electron microscopy (TEM) and Zetasizer, respectively. The characteristic catalytic behavior of the Se nanoparticles is established by studying the decolorization of cango red in the presence of UV light. It is obvious that selenium catalyzes the reaction efficiently. The results show that the rate of dye decolorization varies linearly with the nanoparticle concentration and the rate of dye decolorization decreases with the size of the Se nanoparticles increasing.

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# 1. Introduction

Semiconductor nanocrystals have attracted considerable attention since they offer many applications in a wide range of areas [1–3]. Among all the semiconductors, selenium is one of the most important ones in view of its various applications. It has a number of attractive features desired for various applications in photonics and electronics [4]. It is an excellent photoconductor whose conductivity can be enhanced by several orders of magnitude when it is exposed to visible light. For this reason, it has found widespread use in applications that include the fabrication of photocopy machines, photodetectors sensors and electrical rectifiers [5]. Selenium also possesses a range of unique physical and chemical properties that will be beneficial to the fabrication of photonic crystals [6]. First of all, selenium has a relatively high refractive index ( $\geq$ 2.5) and is transparent at wavelengths longer than 650 nm [7]. Second, selenium exhibits a relatively low melting point ( $\sim$ 217 °C) and high solubility in various solvents (CS<sub>2</sub> and N<sub>2</sub>H<sub>4</sub>), and it is fairly easy to remove when used as the template for fabricating inverse opals. Third, selenium exhibits a glass-transition temperature around 31 °C, which allows for precipitation from a solution phase solely as an amorphous solid at room

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temperature [6]. The elimination of crystallization should greatly facilitate the formation of spherical particles having uniform diameters and smooth surfaces. Fourth, selenium is reactive with a variety of chemical reagents that can be potentially explored to transform selenium into many other functional materials [5,6]. Fifth, the surfaces of selenium nanostructures could be readily coated with other materials such as Pt and CdSe (due to the reduction and disproportionation capabilities of elemental Se) to produce core/shell or core/sheath nanostructures [8]. All of above altogether make this an important field of study. Recently, Xia and co-workers have exploited sonochemical irradiation, and selfseeding solution-phase processes for the preparation of trigonal selenium nanowires [9,10]. Zhang and co-workers prepared  $\alpha$ -monoclinic selenium nanowires via the decomposition of selenodiglutathiones [11]. Abdelouas et al. have also attempted to employ a reduction reaction route using cytochrome c<sub>3</sub> for the synthesis of monoclinic Se nanowires [12]. More recently, Xie and co-workers reported a laser ablation method for the preparation of trigonal selenium nanorods at different temperatures [13].

In this study, we have described the selenium nanoparticles synthesized by reaction of  $H_2SeO_3$  solution with the UVirradiated tungstosilicate acid ( $H_4SiW_{12}O_{40}$ , TSA) solution. Utilizing TSA ion to synthesize selenium nanoparticles is the first time. TSA ions form a subset of polyoxometalates of keggin structure. Polyoxometalates of keggin structure have the general formula ( $XM_{12}O_{40}$ )<sup>(8-n)-</sup>, where 'M' stands for element W or Mo and 'X' stands for heteroatoms such as P, Si, Ge with *n* being the valency of X [14]. The TSA ions, accompanying cations and other components such as water are arranged in a well-defined secondary three-dimensional structure, the stability of which depends on the nature of counterions, amount of water, etc. [15]. It is well known that Keggin ions undergo stepwise multielectron redox processes without a structural change [16]. They may be reduced electrolytically, photochemically and chemically (with suitable reducing agents). Their redox chemistry is characterized by their ability to accept and release a certain number of electrons, in distinct steps, without decomposition [17]. Recently, Papaconstantinou and co-workers have shown that photochemically reduced polyoxometalates of the Keggin structure phosphotungstic acid  $[(PW_{12}O_{40})^{3-}]$  [18], lead to the formation of the corresponding metal nanoparticles. Sastry and co-workers have used  $(PW_{12}O_{40})^{3-}$  for making phasepure core-shell nanoparticles [19]. They have also used  $(PW_{12}O_{40})^{3-}$  as a template for the in situ growth of metal nanoparticles [20,21], star-shaped calcium carbonate crystals [22]and CdS nanoparticles [23].

 $PW_{12}O_{40}^{3^{-1}}$  is stable at pH ca. 1, whereas TSA is stable up to pH ca. 5 [18]. It is noted that these two Keggin ions have similar photochemical behavior except that reaction rates with  $PW_{12}O_{40}^{3^{-1}}$  appear to be about 2–3-fold faster than with TSA [24]. Faster reaction rate leads to the difficulty to control morphologies of particles. So TSA is preferable. In this paper, we propose a general synthetic method that produces selenium nanoparticles in water. The methods offer the advantages of being easily scalable and able to produce essentially naked particles still exhibiting long-term stability; Sizes of synthesized particles are from 40 to 80 nm simply by varying reaction temperature. We have also addressed the catalytic behavior of selenium nanoparticles without any other chemicals for the reaction. There are several published reports [25–28] of dye decolorization by different reagents. However, this is one of the first fruitful attempts where the selenium nanoparticles have been exploited as a catalyst for such type of dye degradation in a clean photochemical pathway.

# 2. Experimental

#### 2.1. Chemicals

Tungstosilicate acid ( $H_4SiW_{12}O_{40}$ , TSA), selenious acid ( $H_2SeO_3$ ), cango red and isopropanol ( $CH_3CH(OH)CH_3$ ) were all A.R. grade and obtained from Shanghai reagent Co. All the reagents in the experiment were used as received. Double distilled water was used throughout the experiment to prepare the solutions.

### 2.2. Preparation of Se nanoparticles

In a typical experiment, 30 mL of a 1 mM aqueous deaerated solution of tungstosilicate acid was taken in a test tube along with 30 mL of a 1 mM aqueous deaerated solution of  $H_2SeO_3$  and 2 mL of propan-2-ol. This mixture was irradiated by UV light (Pyrex filter, >280 nm, 450 W Hanovia medium pressure lamp) for 5 h. UV-irradiation leads to the in situ reduction of  $H_2SeO_3$  by the electron-rich  $(SiW_{12}O_{40})^{5-}$  ions (which are formed by the photochemical reduction of  $(SiW_{12}O_{40})^{4-}$  ions) and is clearly seen by the appearance of a redish yellow color in the solution. Two milliliter of 10% NH<sub>3</sub> (aq) was added to the UV-irradiated solution of Se-TSA to dissolve the TSA ion.

# 2.3. Decolorization of cango red under UV irradiation

Then the dye decolorization was studied employing preformed selenium nanoparticles (100  $\mu$ L, 3.1 × 10<sup>-4</sup> M) with aqueous solution of the dye (10<sup>-4</sup> M, 3 mL), and the solution was irradiated with UV inside the photoreactor. The successive decrease in absorbance of the reaction mixture was monitored at regular time intervals by the UV–vis spectrophotometer.

### 2.4. Analysis

UV-vis spectroscopy measurements of the samples were carried out on a TU-1901 model UV-vis double beam spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China) operated at a resolution of 2 nm. Samples for FTIR spectroscopy were prepared by drop-coating films on Si(1 1 1) wafers. FTIR spectroscopy measurements were carried out on a Nexus 870 FTIR spectrophotometer with a resolution of  $4 \text{ cm}^{-1}$  (America Nicolet Co.). The dynamic process of the H<sub>2</sub>SeO<sub>3</sub> reduced by irradiated TSA solution was investigated by monitoring the conductivity of Se-TSA solution. The conductivity of this solution as a function of reaction time was measured using a DDSJ-308A model conductivity meter (Shanghai Precision & Scientific Instrument Co., Ltd.). The Raman spectra were recorded on a Jobin Yvon HR800 (Horiba group), using 514.5 nm as the excitation line. XPS measurements of Se nanoparticles were carried out on a VG ESCALAB MKII instrument at a pressure less than  $10^{-6}$  Pa. The general scan and Se corelevel spectra were recorded with un-monochromatized Mg K $\alpha$  radiation (photon energy = 1253.6 eV). The core level binding energies (BEs) were aligned with respect to the  $C_{1s}$  binding energy (BE) of 285 eV. Samples for TEM analysis were prepared by drop-coating films of the Se solution on carbon-coated copper TEM grids, allowing the grid to stand for 2 min following which the extra solution was removed using a blotting paper. Samples for TEM analysis of above were carried out on a JEM model 100SX electron microscope instrument (Japan Electron Co.) operated at an accelerating voltage at 80 kV. The size distributions of nanoparticles were measured by PCS on the Zetasizer 3000HS<sub>A</sub> (Malvern Instrumments Limited). In the case of dye decolorization the experimental solution was taken in a quartz cuvette of 1 cm path length and photoirradiated in a photoreactor fitted with ordinary germicidal lamps (Philips, India) of wavelength  $\sim$ 365 nm.

# 3. Results and discussion

A representative Keggin-structure  $[SiW_{12}O_{40}]^{4-}$  was chosen to study the reaction between the one-equivalent of the photochemically reduced tungstosilicate,  $[SiW_{12}O_{40}]^{5-}$  and  $HSeO_3^{-}$  ions. The  $[SiW_{12}O_{40}]^{5-}$  ion was obtained by photolysis of a deaerated propan-2-ol/ $[SiW_{12}O_{40}]^{4-}$  aqueous solution with  $\lambda > 280$  nm light, in the presence of, for instance, propan-2-ol as a sacrificial reagent [29] [Eq. (1)].

$$2[SiW_{12}O_{40}]^{4-} + (CH_3)_2CHOH \rightarrow 2[SiW_{12}O_{40}]^{5-} + (CH_3)_2C = O + 2H^+$$
(1)

After UV-irradiation, the above solution color turned from colorless to redish yellow (Se) gradually [Eq. (2)]. This should be due to two reasons: one is the ability of the reduced  $[SiW_{12}O_{40}]^{5-}$  to transfer the electrons efficiently to  $HSeO_3^-$  ions [30]; the other is the lower potential of the one-equivalent-reduced tungstate couple  $[SiW_{12}O_{40}]^{4-/}$   $[SiW_{12}O_{40}]^{5-}$  (0.057 V versus NHE;) relative to  $Se^{4+}/Se^0$  (0.74 V versus NHE).

$$[SiW_{12}O_{40}]^{5-} + HSeO_3^{-} + 3H^+ \rightarrow [SiW_{12}O_{40}]^{4-} + Se + 2H_2O$$
<sup>(2)</sup>

Fig. 1 shows the UV–vis spectra of aqueous mixtures of 1 mM TSA and 1 mM  $H_2SeO_3$  solutions at different stages of treatment. Prior to UV-irradiation, it is observed that there is little absorption in the visible region of the electromagnetic spectrum. The UV–vis absorption spectrum recorded after UV-irradiation of the 1 mM TSA/1 mM  $H_2SeO_3$  aqueous solution for 5 h is shown as curve 2 in Fig. 1. It is seen clearly that there is an absorption band starting from ca. 620 nm. The UV–vis spectrum of the Se nanoparticles in solution after alkali treatment is shown as curve 3 in Fig. 1. Removing the TSA ions leave behind reasonably Se nanoparticles. So we can get a considerable increase in the intensity of the band attributed to the Se particle. From curve 3, a slight broadening of the absorption band is observed. The broadening of the surface plasmon absorption band indicates some degree of aggregation of the Se nanoparticles



Fig. 1. UV–vis spectra recorded from: 1 mM tungstosilicate acid before UV irradiation (curve 1); the mixing of 1 mM tungstosilicate acid and 1 mM  $H_2SeO_3$  after UV irradiation for 5 h (curve 2); solution shown as curve 2 after addition of 10% NH<sub>3</sub> (aq) solution (curve 3).

consequent to removal of the TSA scaffold, we did observe some long-term instability in the solution. In an alkaline medium, it is known that tungstosilicate ions which are not stabilizers dissociate into other ions [31], so broadening absorption band is observed. This absorption band is characteristic of Se nanoparticles. This agrees with the literature [32].

Fig. 2 represents the FTIR spectra in the region 700–1200 cm<sup>-1</sup> for the pure TSA (curve 1) and the mixing of H<sub>2</sub>SeO<sub>3</sub> with TSA solutions before UV-irradiation (curve 2), after UV-irradiation (curve 3), and after dissolving the Keggin ion by alkali treatment (curve 4). Curve 1 shows the W–O asymmetric stretching vibration frequency at 981 cm<sup>-1</sup> and the Si–O asymmetric stretching vibration at 1079 cm<sup>-1</sup> for pure tungstosilicate acid, and curves 2 and 3 show a shifted W–O bond stretching vibration at 985 cm<sup>-1</sup>, respectively. Comparing curve 3 with 1 and 2, it is seen that the position of the W–O asymmetric stretching and the W–O–W bending vibration bands occur at almost the same wavenumbers as those observed for pure TSA (curve 1). This indicates the underlying keggin structure is retained after UV irradiation. Curve 4 in Fig. 2 shows the FTIR spectrum recorded from the Se solution after alkali treatment. In this



Fig. 2. FTIR spectra recorded from the drop coated film on Si(1 1 1) wafer of pure tungstosilicate acid solution (curve 1); the mixing of 1 mM tungstosilicate acid and 1 mM H<sub>2</sub>SeO<sub>3</sub> before UV irradiation (curve 2); the mixing of 1 mM tungstosilicate acid and 1 mM H<sub>2</sub>SeO<sub>3</sub> after UV irradiation for 5 h (curve 3); the solution shown as curve 3 after addition of 10% NH<sub>3</sub> (aq) solution (curve 4).

spectrum, it is observed that the W–O and Si–O stretching vibration bands are absent, suggesting that the TSA has completely decomposed upon alkali treatment. In the other word, without alkali treatment, UV-irradiation is not make TSA structural change. The UV–vis absorption spectra before and after a UV-irradiation are shown as curves 1 and 2, respectively, in Fig. 1. Two prominent and sharp absorption peaks at 201 and 256 nm are characteristics of the TSA [18], indicating Keggin ions of TSA undergo stepwise redox processes without undergoing a structural change, just as mentioned briefly in Section 1.

Fig. 3 shows the conductance of the H<sub>2</sub>SeO<sub>3</sub>–TSA reaction mixture measured as a function of the time of reaction. The conductance value of 1 mM aqueous TSA is 1.060 mS while that for 1 mM H<sub>2</sub>SeO<sub>3</sub> is 923.50  $\mu$ S. pK<sub>a1</sub> of H<sub>2</sub>SeO<sub>3</sub> is 2.57, through calculating, there are 99% H<sub>2</sub>SeO<sub>3</sub> molecules ionize to HSeO<sub>3</sub><sup>-</sup> ions in solution. After UV-irradiation, it is expected that the solution conductivity decreases steadily. From Fig. 3, it is seen that the conductivity decrease rapidly. It implies the concentration of HSeO<sub>3</sub><sup>-</sup> ions in solution reduced swiftly because of the HSeO<sub>3</sub><sup>-</sup> ions in solution reduced by the (SiW<sub>12</sub>O<sub>40</sub>)<sup>5-</sup> ions. With the development of the reaction, HSeO<sub>3</sub><sup>-</sup> ions in the solution decreases steadily and saturates after ca. 5 h of reaction and thus is an estimate of the optimum time of reaction for formation of Se colloidal nanoparticles. At the same time, the appearance of a redish yellow color in the solution is observed, which farther testified that the HSeO<sub>3</sub><sup>-</sup> ions are reduced to Se nanoparticles by the (SiW<sub>12</sub>O<sub>40</sub>)<sup>5-</sup> ions, too.

Fig. 4A presents the Raman spectrum of the sample before addition of the ammonia solution. The resonance peak at 233 cm<sup>-1</sup> is a characteristic signature of trigonal selenium, which can be assigned to the vibration of the Se helical chain [9]. In comparison, the characteristic Raman peaks for monoclinic selenium and  $\alpha$ -Se are at 256 and 264 cm<sup>-1</sup>, respectively [33]. The XRD pattern recorded from a drop-coated film of the UV-irradiated sample before addition of the ammonia solution on a glass substrate is shown in Fig. 4B. All of the strong and sharp reflection peaks can readily be indexed to a single phase of trigonal-structured selenium (t-Se, space group  $P_{3,21}$  (152) with infinite, helical chains of selenium atoms packed parallel to each other along the *c*-axis), with cell parameters *a* = 0.4367 nm and *c* = 0.4959 nm. These values are in agreement with the values reported in the literature (JCPDS Cards No. 86-2246). The background is most likely caused by Brownian motion of the particles during the scan, solvent scattering or the short-range order of the solvation cage around the particles. Fig. 4C shows the XPS of the as-synthesized product before addition of the ammonia solution. The binding energy at 54.32 eV, corresponding to Se<sub>3d</sub>, is the characteristic peak for elemental selenium [34,35], implying that the valence of selenium in the film is zero. These results, obtained from Raman spectroscopy, XRD and XPS, indicate that the product is well crystalline and high pure.

Fig. 5A representative TEM images recorded from a drop-coated film of the Se-nanoparticles solution synthesized by reaction of  $H_2SeO_3$  solution with the UV-irradiated TSA solution on a carbon-coated copper TEM grid. From the TEM image (Fig. 5A), it is clearly seen that the nanoparticles are monodisperse with sizes in diameter ~40 nm and

![](_page_4_Figure_6.jpeg)

Fig. 3. Conductivity measured as a function of time of mixing equal-volume aqueous solutions of 1 mM tungstosilicate acid and 1 mM  $H_2SeO_3$  during UV irradiation for 5 h.

![](_page_5_Figure_0.jpeg)

Fig. 4. (A) Raman spectrum recorded from drop-coated films on glass substrates of 1 mM tungstosilicate acid and 1 mM H<sub>2</sub>SeO<sub>3</sub> during UV irradiation for 5 h before addition of the ammonia solution; (B) XRD patterns of the sample as used in A; (C) XPS spectrum of the same sample as used in A.

![](_page_6_Figure_2.jpeg)

Fig. 5. Respresentative TEM images of Se nanoparticles reduced by UV-irradiated TSA solution before (A) and after the second recycle of the reaction with cango red (B).

have spherical colloids of t-Se forms. Such colloids were quite uniform and could be obtained in copious quantities. The image implies these spheres are smooth. To the best of our knowledge, this is the first time on studying the spheres of t-Se nanoparticles.

Fig. 6A–D is the corresponding size distributions of Se nanoparticles solution on the different temperature. Fig. 6E shows the dependence of the particle diameter on the temperature based on Fig. 6A-D. Fig. 6A-D show images of four typical samples of Se nanoparticles with mean diameters of 44.7, 66.5, 74.5 and 83.3 nm. As demonstrated in Fig. 6E, the size of these t-Se colloids can be conveniently controlled by simply varying the reaction temperature, which changes from 20 to 80 °C, the diameter monotonically increases from ~44.7 to ~83.3 nm. At the same time, we find that if the temperature is increased to values near  $\sim 80$  °C, the resultant particles tended to agglomerate into irregular structures in the course of the reaction, and the final product exhibited a poor distribution in size (see Fig. 6D). The colors of varying the temperature reflect their sizes. We find that the well-known belief that nano-Se is "red" [36] is somewhat misleading. By examining the evolution of the change color, the suspension of the 45 nm diameter Se nanoparticles has, in fact, a yellowish orange appearance, at about 30 °C. We observe that a red color represents a mean colloidal size of ca. 60–75 nm from 40 to 60 °C. At about 80 °C, we notice that color of the solution turns dense and black. These color changes may relate directly to the absorption features of the particles in the visible region of the spectra. Since t-Se colloids can be synthesized in copious quantities with diameters ranging from 40 to 80 nm, it is believed that the procedure described here should provide an effective route to spheres of t-Se with controllable size. We also find that the diameter of Se do not depend on neither the different molar ratio of H<sub>2</sub>SeO<sub>3</sub> to TSA, or different pH at room temperature.

To the best of our knowledge, there are no reports on the catalytic activity of Se-TSA solutions in the dye of cango red, so cango red was chosen as a model compound.

To study the photodegradation process, aqueous solutions of cango red were employed along with Se-TSA solutions for UV irradiation. The progress of the dye decolorization was monitored by the decrease in absorbance of the peak due to cango red at 488 nm. In Fig. 7 the absorption spectra of successive decolorization of the cango red is shown. It has been found that the reaction follows an overall first-order kinetics. The UV light leads to the degradation of the dye structure, which is again catalyzed to a great extent in the presence of selenium nanoparticles. In the absence of Se under the same experimental condition, a very slow rate of degradation was observed in the experimental time scale. It is, therefore, obvious that selenium catalyzes the reaction efficiently. It is interesting to note that the reaction is catalyzed to a negligible extent with Se particles without TSA. A comparison of reaction parameter is shown in Fig. 8 where the catalytic activity of Se-TSA solutions is found to play an extremely important role. It appears that TSA is very important in the reaction. This is attributed to the stabilizing role of TSA which prevents aggregation of the Se particles without TSA, but very fast degradation to Se-TSA. It has also been shown that the decolorization of the dye

![](_page_7_Figure_1.jpeg)

Fig. 6. (A–D) Size distributions of Se nanoparticles synthesized by reaction of  $H_2SeO_3$  solution with the UV-irradiated TSA solution. (E) Dependence of the particle diameter on temperature based on (A–D). (Conditions: [TSA] = 1 mM, [H\_2SeO\_3] = 1 mM, reaction time = 5 h, pH ca. 2.5).

depends linearly with the concentration of the catalyst particles used. The linear variation in rate (the rate has been calculated, considering the first-order kinetics of the degradation process) with the change in concentration of nanoparticles in the reaction mixture is shown in Fig. 9. Interestingly, the rate of decolorization has been found to have a bearing on the size of the Se. So the detail study has been carried out for the dye decolorization with variable size of the Se keeping all other parameters unaltered. From Fig. 10, it can be clearly seen that the rate reveals a continuous decrease with the increasing size of Se from about 40–80 nm. However, the decrease rate diminishes gradually from 40 to 60 nm, and when the size value is between 60 and 80 nm, there is a great decrease for the rate of decolorization. That

![](_page_8_Figure_1.jpeg)

Fig. 7. UV-vis spectra for the photodecolorization of cango red in water. The time interval between successive measurements is 5 min. Conditions:  $[CR] = 10^{-4} M$ ,  $[Se-TSA] = 10^{-5} M$ , flux of UV light = 340 lx.

is, the rate of decolorization decreases with the increasing size of Se. In nanometer scale, the Se nanoparticles of high surface-area-to-volume ratio, which are easily accessible to reactant molecules, thus enhance catalytic activity of the Se and make them highly attractive for catalysis.

It is to be mentioned that the TSA not only imparts reducing reagents to synthesis of Se nanoparticles but also stability to the nanoparticles [18]. Control experiments showed no obvious bleaching of cango red upon UV irradiation in the presence of Se without TSA (see Fig. 8). This result clearly shows the important role played by the TSA in the observed degradation of cango red.

We are also curious to check the recycle ability of the Se-TSA nanoparticles catalyst for decolorization of cango red under UV irradiation. The catalyst Se-TSA nanoparticles are efficiently recycled for the decolorization reaction, that is to say, the nanostructure and dispersivity of the Se nanoparticles have not changed after the recycle reactions. This is supported by the TEM images of the catalyst from the reaction mixture before and after the recycle (Fig. 5). In both cases, it is observed that the Se nanoparticles are irregularly shaped, and there is a small change in the average size of the nanoparticles. However, there are some drawbacks such as purity of the product, recovery and regeneration of the catalyst. In this study as well, we could not separate our catalyst from the reaction products.

![](_page_8_Figure_6.jpeg)

Fig. 8. Absorbance as a function of time in the presence of ( $\blacksquare$ ) only TSA, ( $\bullet$ ) t-Se without TSA and ( $\blacktriangle$ ) Se-TSA nanoparticles solution. Conditions: [CR] = 10<sup>-4</sup> M, [Se-TSA] = 10<sup>-5</sup> M, flux of UV light = 340 lx.

![](_page_9_Figure_1.jpeg)

Fig. 9. The variation of rate with different concentrations of selenium nanoparticles in aqueous medium. Conditions:  $[CR] = 10^{-4}$  M, flux of UV light = 340 lx.

![](_page_9_Figure_3.jpeg)

Fig. 10. The variation of rate with different diameter of selenium nanoparticles in aqueous medium. Conditions:  $[CR] = 10^{-4} \text{ M}$ ,  $[Se] = 10^{-5} \text{ M}$ , flux of UV light = 340 lx.

#### 4. Conclusions

In summary, a novel and facile method has been proposed to synthesize size-controlled Se nanoparticles by using UV-irradiate TSA solution which acts as reducing reagent and stabilizer. The size of the Se nanoparticles can be controlled by varying the reaction temperature. The characteristic catalytic behavior of the Se nanoparticles is established by studying the decolorization of cango red in the presence of UV light. It has been authenticated from the study that the nanoparticles afforded a complete mineralization process and the rate of dye decolorization varies linearly with the Se nanoparticles concentration. The size of the Se nanoparticles affects the rate of dye decolorization also, that is, the rate of decolorization decreases with the increasing size of Se.

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### References

- [1] M. Modreanu, M. Gartner, E. Aperathitis, N. Tomozeiu, M. Androulidaki, D. Cristea, P. Hurley, L. Maltings, Phys. E 16 (2003) 461.
- [2] D.J. Milliron, A. PAlivisatos, C. Edder, M.J. Jean, Adv. Mater. 15 (2003) 58.
- [3] D. Wang, A.L. Rogach, F. Caruso, Nano Lett. 2 (2002) 857.
- [4] L.I. Berger, Semiconductor Materials, CRC Press, Boca Raton, FL, 1997.
- [5] D.M. Chizhikov, V.P. Shchastlivyi, Selenium and Silenides, Collet's, London, 1968.
- [6] R.A. Zingaro, W.C. Cooper (Eds.), Selenium, Van Nostrand Reinhold, New York, 1974.
- [7] T. Innami, T. Miyazaki, A. Adachi, J. Appl. Phys. 86 (1999) 1382.
- [8] B. Mayers, X. Jiang, D. Sunderland, B. Cattke, Y. Xia, J. Am. Chem. Soc. 125 (2003) 13364;
   X. Jiang, B. Mayers, T. Herricks, Y. Xia, Adv. Mater. 15 (2003) 1740.
- [9] B. Gates, Y. Yin, Y. Xia, J. Am. Chem. Soc. 122 (2000) 12582.
- [10] B. Gates, B. Mayers, A. Grossman, Y. Xia, Adv. Mater. 14 (2002) 1749.
- [11] X. Gao, T. Gao, L. Zhang, J. Mater. Chem. 13 (2003) 6.
- [12] A. Abdelouas, W. Gong, W. Lutze, J.A. Shelnutt, R. Franco, I. Moura, Chem. Mater. 12 (2000) 1510.
- [13] Z. Jiang, Z. Xie, X. Zhang, R. Huang, L. Zheng, Chem. Phys. Lett. 368 (2003) 425.
- [14] J.A. Huheey, Inorganic Chemistry, third ed., Harper and Row, New York, 1983, pp. 698.
- [15] M. Misono, Mater. Chem. Phys. 17 (1987) 103.
- [16] M.T. Pope, A. Muller, Angew. Chem. Int. Ed. Engl. 30 (1991) 34;
   V. Kogan, Z. Izenshtat, R. Neumann, Angew. Chem. Int. Ed. 38 (1999) 3331.
- [17] M.T. Pope, Inorganic Chemistry Concepts, vol. 8, Springer Verlag, West Berlin, 1983, pp. 101.
- [18] A. Troupis, A. Hiskia, E. Papaconstantinou, Angew. Chem. Int. Ed. 41 (2002) 1911.
- [19] S. Mandal, P.R. Selvakannan, R. Pasricha, M. Sastry, J. Am. Chem. Soc. 125 (2003) 8440.
- [20] S. Mandal, D. Rautaray, M. Sastry, J. Mater. Chem. 13 (2003) 3002.
- [21] A. Sanyal, S. Mandal, M. Sastry, Adv. Funct. Mater. 15 (2005) 273.
- [22] D. Rautaray, S.R. Sainkar, M. Sastry, Langmuir 19 (2003) 10095.
- [23] S. Mandal, D. Rautaray, A. Sanyal, M. Sastry, J. Phys. Chem. B 108 (2004) 7126.
- [24] A. Hiskia, A. Troupis, A. Hiskia, E. Papaconstantinou, Environ. Sci. Technol. 35 (2001) 2358.
- [25] E. Stathatos, T. Petrova, P. Lianos, Langmuir 17 (2001) 5025.
- [26] A.J. Hallock, R.N. Zare, J. Am. Chem. Soc. 125 (2003) 1158.
- [27] W. Chu, C.W. Ma, Chemosphore 37 (1998) 961.
- [28] S. Nath, S.K. Ghosh, T. Pal, Langmuir 20 (2004) 7880.
- [29] E. Papaconstantinou, Chem. Soc. Rev. 16 (1989) 1;
  A. Hiskia, A. Mylonas, E. Papaconstantinou, Chem. Soc. Rev. 30 (2001) 62;
  A. Mylonas, A. Hiskia, D. Androulaki, E. Dimotikali, Papaconstantinou, Phys. Chem. Chem. Phys. 1 (1999) 427.
- [30] I.A. Weinstock, Chem. Rev. 98 (1998) 113.
- [31] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fifth ed., John Wiley and Sons, New York, 1988, pp. 817.
- [32] Z.H. Lin, C.R. Chris Wang, Mater. Chem. Phys. 92 (2005) 591.
- [33] B. Gates, B. Mayers, B. Cattle, Y. Xia, Adv. Funct. Mater. 12 (2002) 219.
- [34] X. Gao, J. Zhang, L. Zhang, Adv. Mater. 14 (2002) 290.
- [35] Ch.H. An, K.B. Tang, X.M. Liu, Y.T. Qian, Eur. J. Inorg. Chem. (2003) 3250.
- [36] S. Zhang, H.L. Wang, Y.P. Bao, L.D. Zhang, Life Sci. 75 (2004) 237.