Se-doped TiO_2 nanoparticles with photocatalytic activity under visible light irradiation

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Abstract
Se-doped TiO_2 nanoparticles were prepared by a simple solid-state method. The photocatalytic activity of the resulting Se-doped TiO_2 particles was evaluated by photo degradation of methyl orange under visible light irradiation. Se-doped TiO_2 nanoparticle's structures were characterized by scanning electron microscope (SEM), energy dispersive X-ray accessory (EDX) and UV–Vis diffuse reflectance spectrum (UV–Vis DRS). All the Se-doped TiO_2 samples showed photocatalytic activity higher than pure TiO_2. The results showed that if the doping content of Se (which is used in the staring reaction medium) is more than 3%, the photocatalytic activity of the prepared Se-doped TiO_2 will not be affected noticeably. In addition, it could be seen that the material's shape is not changed after doping. The EDX results of the doped samples show the presence of Se in the synthesized TiO_2 nanoparticles. Se-doped TiO_2 prepared by the molten salt method might have the potential to be applied in wastewater treatment due to its ease of preparation.

Keywords: Se-doped TiO_2, Photocatalytic activity, Molten salt method.

Introduction
In recent years, photocatalysts has gained an enormous interest for effective treatment of organic pollutant. TiO_2 is an excellent choice among various semi-conductorphotocatalysts, because of its various advantages, such as high photocatalytic activities, inexpensiveness and non-toxicity [1]. However, the disadvantage of this material is that the wide band gap of TiO_2 (3.2 eV) in lightabsorption can only absorb in the ultravioletrange, so its photocatalytic activity is not suitable for commercial applications [2]. So many efforts of doping TiO_2 have been paid by the adding some metallic and non-metallic ions [3]. It has been reported that doped metal ions exhibit an isomorphic replacement of Ti^{4+} ions in TiO_2 and induce visible light absorption by either introducing localized electronic states within the band gap or conducting electrons to the valence band. Furthermore, metal ion dopants influence the photo-reactivity of TiO_2 by altering charge carrier recombination rates [4].
Particularly, the Se-doped TiO_2 is proved to be an effective and widely used method. The positive effect of Se on titania catalytic efficiency is associated to the change in the anatase

electronic structure which decreases the band gap and the introduction of specific Se related surface sites. The studies on Se-modified titania show that it can improve the charge-hole separation, increase photo excited electron–hole life time within a single particle and alter the electronic structure of the metal oxide photocatalysts [5]. For example, Lübke *et al* (2015) synthesized on pure anatase TiO_2 nanoparticles and Se-doped TiO_2 nanoparticles using hydrothermal method as an excellent high power performance anode for a Li-ion battery [6]. Nemadeand Waghuley (2014) fabricated Se-doped titanium dioxide nanoparticles by microwave-assisted and solid-state diffusion path as Gas based for carbon dioxide sensing [12]. Sui *et al*. (2010) reported the synthesis of Se-doped TiO_2 by sol–gel method with high aspect ratios [8]. Xiufeng *et a*l. (2011) produced the Se-doped TiO_2 nanoparticles as a visible-light photocatalyst synthesized by vapor transport method [9].
Among various synthesis techniques of TiO_2 nanoparticles, molten salt method has significant advantages in preparation of nanoparticles e.g. most of the traditional steps in catalyst preparation, such as saturation and reduction can be avoided, the produced materials are pure (no chemical agents were used) and this synthetic procedure is rapid and simple [2,10-13]. Additionally, this method results in the production of less than 100 nm of pure TiO_2 nanoparticles [10]. Previously, some researcher have synthesized Se doped TiO_2 by various method such as solvothermal and incipient wet impregnation method [4,6,14]. So far, there is no study reported in the literature on molten salt synthesized Se-doped TiO_2. Therefore, in this study synthesis and characterization of Se-doped TiO_2 nanoparticles as an active and visible-light driven photo catalyst is performed by this method.

Experimental

Materials

TiO_2, selenium and methyl orange were purchased from Merck. All reagents had analytical grade and were used as received without any further refinement.

Preparation Se doped TiO_2

Se doped TiO_2 powders were made by a modified synthetic procedure of Lotfian and Ghorbanpour [10]. Appropriate amounts of Selenium powder (Merck) and TiO_2 (Merck), i. e. , 0.1, 0.5, 1 and 3 % (weight of Se to the weight of TiO_2)were completely mixed and placed in a furnace at 700 °C for 60 minutes. Then, the prepared nanoparticles were washed adequately with distilled water. After dissolution, the nanoparticles were dried in an oven at 25 °C.

Photocatalytic activity test

The photocatalytic activities of the pure TiO_2 and Se doped TiO_2 photocatalyst were tested in the degradation reaction of methyl orange (100 ml, 25 ppm) aqueous solution, under irradiation of a 250 W visible lamp (Osram, Germani). For a typical photocatalytic experiment, a total of 0.1 g catalyst powder was added into 100mL of the above mentioned methyl orange solution in quartz tube. Prior to irradiation, the suspensionswere magnetically stirred in the dark for 15 min to ensure the establishment of an adsorption/desorption equilibrium. At given time intervals, about 2mL aliquots were sampled and centrifuged to remove the particles. The filtrates were analyzed by measuring maximum absorbance of methyl orange at 664nm using the UV–Vis spectrophotometer.

Characterization Se doped TiO_2

The morphology of samples was observed with a scanning electron microscope (LEO 1430VP, Germany). UV-Vis diffuse reflectance spectroscopy (DR UV-Vis) was taken within the wavelength range of 200–800 nm using a spectrophotometer (Scinco S4100, S. Korea). Powder X-ray diffraction analysis was done with a PW 1050 diffractometer (Philips, The Netherlands) with a Ni filter and Cu Kα (λ=1. 54 Å) radiation. The particle size was calculated by means of Scherrer equation. The average crystallite sizes of the molecules were counted based on the width of the peak due to 101 planes by the Scherer's equation (1):

$$D = \frac{k\lambda}{\beta \cos\theta} (1)$$

Where k is a constant (k = 0. 9), λ is denoted the wavelength of X-ray used, β indicates the full-width at the half-maximum (FWHM) and θ represents the Bragg diffraction angle.

Results and discussion

Photocatalytic activity of Se-doped TiO_2

Figure 1 shows the degradation of methyl orange data when different TiO_2 photocatalysts were used. It can be seen that the parent TiO_2 has weak photocatalytic activity. However, when Se is introduced, there is a significant increase in the degradation rate of methyl orange. This can be mainly attributed to the Se dopants in the TiO_2 structure. Furthermore, the results showed that the doping content more than 3 % of Se used in the starting reaction medium could not affect the photocatalytic activity of the prepared Se-doped TiO_2. Thus, sample doped with 3 % Se exhibited the same photocatalytic activity as orther doped TiO_2 samples.

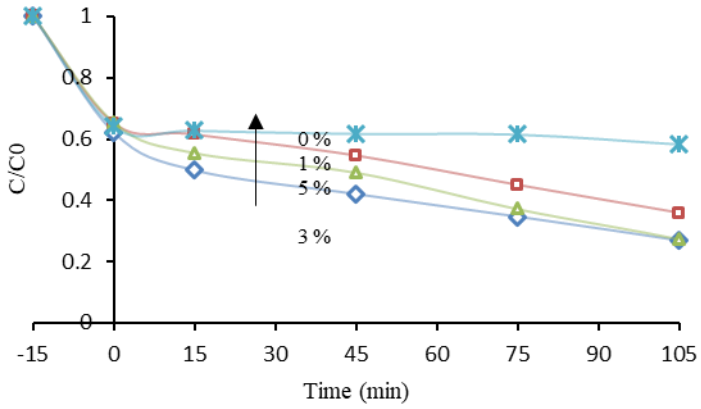
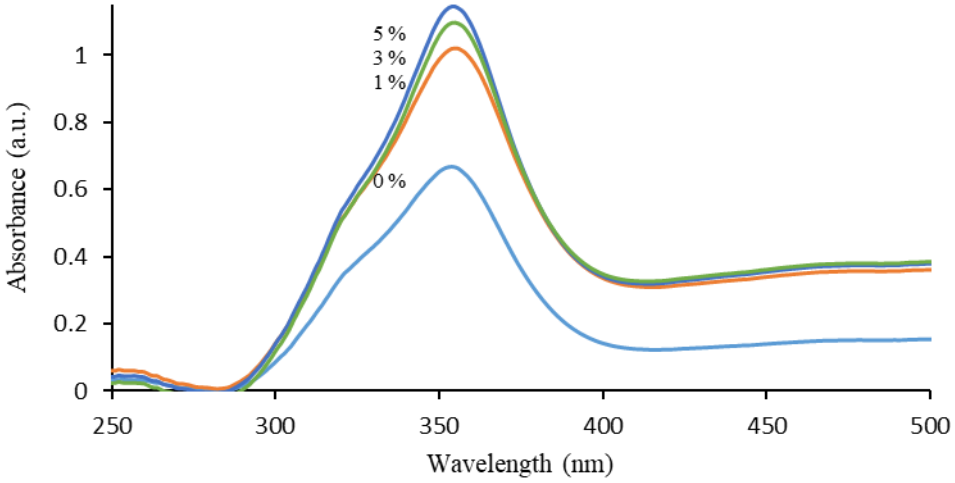


Figure 1. Photo degradation of methyl orange by Se doped TiO_2 with different Se contents and undoped TiO_2

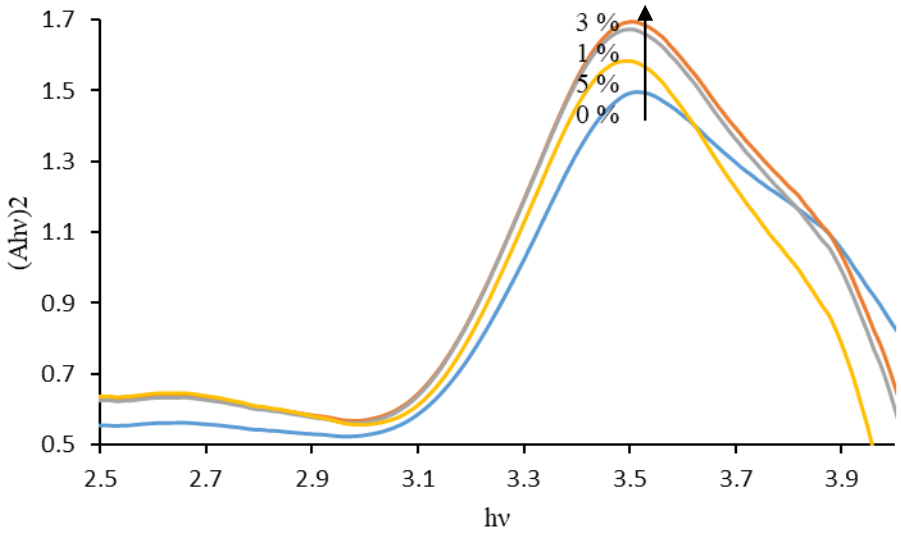
Characterization Se doped TiO_2

The optical absorbance spectra of the pure TiO_2 and Se-doped TiO_2 nanoparticles photocatalysts measured in the UV–Vis region are shown in Figure 2. It is observed that pure TiO_2 sample mostly absorbs UV light with a limited amount of visible light, while the prepared Se-doped TiO_2 absorbs more visible light. Accordingly, this absorption feature suggests that the photocatalytic activities of Se doped TiO_2 can possibly be activated by visible light [1].

Furthermore, it can also be observed that the Se-doped TiO_2 slightly red-shifted to the visible-light region. Figure 2b presents this change clearly in which the band gap tends to less energies. This reduction for doped samples with 3% selenium was higher than other samples. The red shift can be attributed to the charge-transfer transitions between doped Se^{4+} electrons and the TiO_2 conduction band. It is believed that the photocatalys is process of semiconductors is the direct absorption of a photon by the material's band gap and generates electron-hole pairs in the semiconductor particles [15].



(a)



(b)

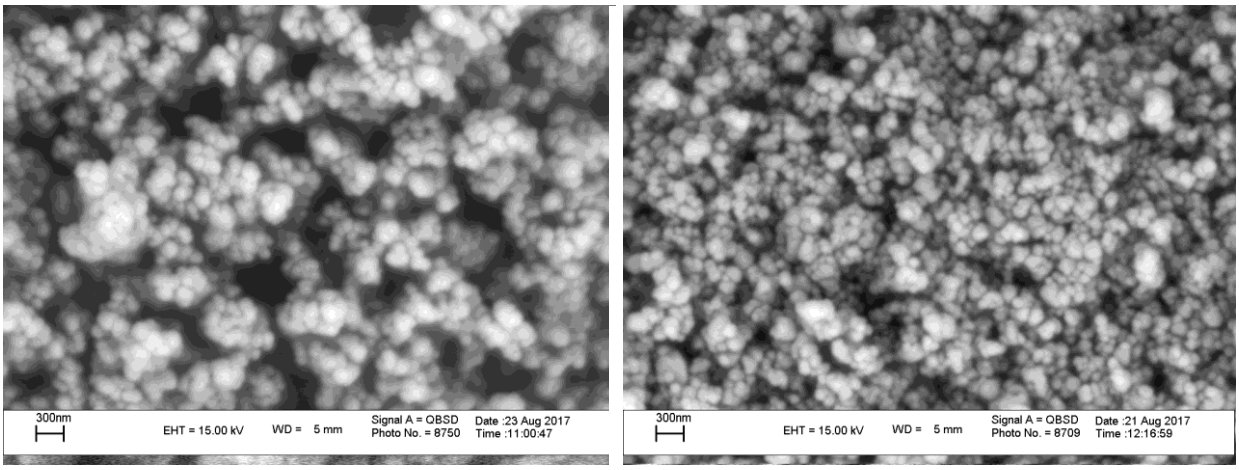
Figure 2. UV/Vis reflectance spectra (a) and band gap (b) of pure TiO_2 and TiO_2 doped with selenium

The dopant ion concentration and the morphology of the doped catalyst particles were investigated by scanning electron microscopy with attached energy dispersive X-ray accessory (SEM-EDX). The EDX results (table 1) of the doped samples show the presence of Se in the synthesized TiO_2 nanoparticles. This analysis did not show any Se in the synthesized TiO_2 nanoparticles doped with 1 % Se due to detection limits of instrument. As seen in this table, Se concentration did not change in TiO_2 with more than 3 % increase indopant concentration in the starting precursor mixtures.

Figure 3 shows the SEM images of TiO_2 nanoparticles and Se-doped TiO_2 nanoparticles doped with 3 % Se. SEM image (Figure 3a) of the pure TiO_2 shows spherical particles that are formed by the accumulation of small spherical particles of dispersed sizes with a diameter less than 100 nm. However, these aggregates maybe associated with the drying process necessary for the SEM sample preparation. It is observed that Se doping does not influence the morphology of TiO_2 materials.

Table 1. Composition of Se-doped TiO_2

	Dopant concentration in doped samples (% w/w)			
	0 %	1 %	3 %	5 %
Oxygen	35. 77	34. 13	40. 02	39. 09
Selenium	0	0.2 >	0. 41	0. 41
Titanium	64. 23	65. 87	59. 57	60. 50



(a) (b)

Figure 3. SEM images of pure TiO_2 (a) and TiO_2 doped with 3 % selenium (b)

The XRD patterns of pure and doped TiO_2 powders are shown in Figure 3. XRD data for all samples, suggested the presence of pure anatase phase of TiO_2 for all samples which indicated the incorporation of Se^{4+} into the TiO_2 lattice. In the present study, with changes in the Se-doped TiO_2 dosage no change occurs in nanoparticles phase. But in Li *et al.* , an increase in selenium dosage leads to the formation of the rutile phase in titanium oxide nanoparticles prepared by sol-gel method. The titanium oxide nanoparticles are preferred in terms of photocatalytic ability of the anatase phase [15].

The crystallite size of prepared particles was 52.6, 44.0, 43.8 and 44.2 nm for the dopant concentrations of 0, 1, 3 and 5 %, respectively. Therefore, selenium doping initially reduced the crystalline size of nanoparticles and then the change in the content of doped material has not affected it.

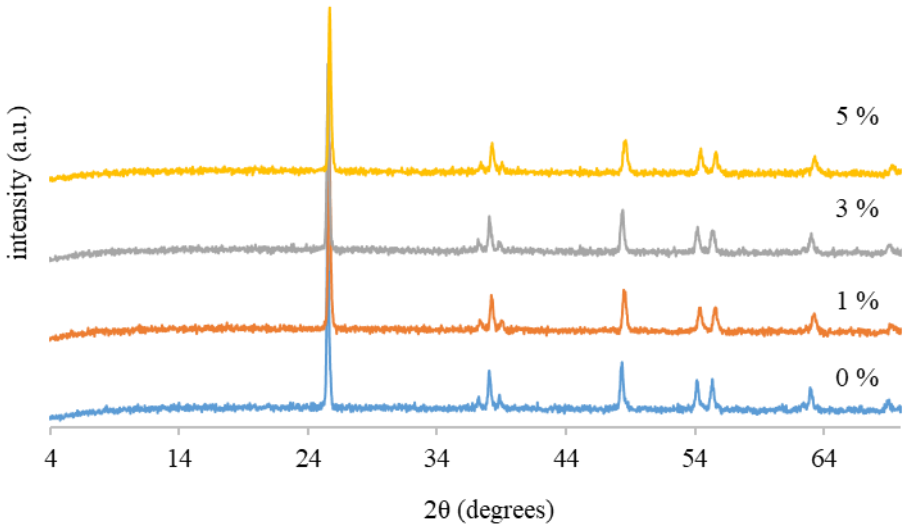


Figure 3. The XRD patterns of pure and doped TiO_2 powders

As discussed before, increasing the doping content in the starting precursor to 3% enhances the photocatalytic activity. However, the sample doped with 3 % Se exhibited the same photocatalytic activity of 5 doped TiO_2 samples. These results are consistent with Lee *et al.* (2009) [15].

According to the SEM results, more than 3 % doping of Se does not influence the morphology and crystalline size of TiO_2 materials and Se concentration did not show any sugnificant impact. Furthermore, the prepared Se-doped TiO_2 shows higher visible light absorption and lower band gaps. The above mentioned content suggests that the photocatalytic activities of Se doped TiO_2 may be enhanced by increasing the dopant concentration up to 3 % and activated by visible light. More dopant agent increase did affect the physicochemical properties of nanoparticles and subsequently their photocatalytic activities.

Conclusions

It has been shown that Se-doped TiO_2 nanoparticles photocatalytic activity with visible light can be synthesized by a facile molten salt technique. It was found that Se doping could not affect the morphology of TiO_2 nanoparticles. The photocatalytic activity of Se-doped TiO_2 nanoparticles on degradation of MO under visible light irradiation was better than pure TiO_2. Since these Se-doped TiO_2 nanoparticles achieved an efficient visible light photo activity in the photo degradation, they might have a good applicability in waste water treatment.

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