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# Detection of reactive oxygen species (ROS) and investigation of efficient visible-light-responsive photocatalysis via nanoscale PbSe sensitized $TiO_2$

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ABSTRACT

In this study, a novel visible-light-responsive PbSe–$TiO_2$ nanocomposite photocatalysts were successfully synthesized through a facile sonochemical-assisted method, and characterized by XRD, SEM–EDX, TEM, and DRS to confirm its structure, morphology, composition, and optical property. In decolorization of rhodamine B, a significant enhancement in the reaction rate was observed with PbSe–$TiO_2$ composite, compared to the pure $TiO_2$. The generation of reactive oxygen species was detected through the oxidation reaction from 1,5-diphenyl carbazide (DPCI) to 1,5-diphenyl carbazone (DPCO). The high photocatalytic activity can be attributed to the synergetic effect of PbSe nanoparticles and $TiO_2$ by extending the spectral response of $TiO_2$ to visible region and also help to reduce the charge recombination. Finally, the possible mechanism for generation of reactive oxygen species under visible light irradiation was proposed as well.


## 1. Introduction

In most of the industrial wastewater treatment, adsorption by activated carbon, advanced chemical oxidation, enhanced coagulation and photochemical processes are commonly employed technologies for removal of refractory pollutants from industrial wastes. The advance of photochemical processes has made the decomposition of synthesized refractory organics sustainable, especially with the advent of semiconductor photocatalysts [1,2]. Several semiconductors have been developed to exhibit photocatalytic behavior. The most commonly referenced semiconductors for waste degradation are $TiO_2$, ZnO, CdS, etc. [1]. $TiO_2$ is of great interest mainly due to its unique properties, such as high photoactivity and size dependent optical properties [1]. However, $TiO_2$ is a wide band gap semiconductor (band gap around 3.2 eV), which adsorbs light only in the UV region. To overcome this problem, various materials, like dyes and metallic nanoparticles, have been used as sensitizer to increase the photoactivity of $TiO_2$ in the visible range.

Compared with other materials, semiconductors have attracted considerable interest in the past two decades because of their applications in single electron transistors [3], lasers [4], light emitting diodes [5], and infrared photodetectors [6] operating at lower currents and higher temperatures. Semiconductors have two unique advantages: (1) their band gap can be modified by varying the size to tune the visible response; (2) they can utilize hot electrons to generate multiple charge carriers with a single high energy photon [7]. Various semiconductors, including $ZnFe_2O_4$ [8], PbS [9], $Bi_2S_3$ [10], CdSe [11,12], and InP [13], have been investigated to sensitize $TiO_2$ as a visible light absorber. However, there is no report on the utilization of PbSe/$TiO_2$ photocatalyst systems for environmental purification under visible light irradiation. According to other's studies, PbSe is one kind of potential semiconductor to sensitize $TiO_2$ as a visible light absorber due to its excellent catalytic performance. Manga et al. [14] reported high-performance broadband photodetector using solution-processible PbSe–$TiO_2$–graphene hybrids which act as light harvesting photoactive materials from the UV to IR regions of the electromagnetic spectrum. Néstor et al. [15] reported sensitization of $TiO_2$ with PbSe quantum dots by SILAR: how mercaptophenol improves charge separation. It is well known that the synthesis of nanomaterials with uniform size, shape and high crystallinity is one of the important challenging problems. There are various kinds of synthesis methods available for the preparation of nanomaterials such as hydrothermal, microwave synthesis, sol–gel, micro emulsion and the polyol technique. But each method has its own drawbacks such as long reaction time, non-uniform shape and size, particle agglomeration and high cost

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of the solvent medium. Recently, the sonochemical synthesis became an imperative for the preparation of nanomaterials with uniform size and shape with shorter reaction time. In sonochemical synthesis, interaction occurs between energy and matter, where the applied ultrasound incident on the liquid surface, there is a three step process that takes place including the formation, growth and finally implosive collapse of bubbles. This collapsing of bubbles produces an intense heat and high pressure within a very short time. In this process, temperatures up to 5000 K and pressures greater than 20 MPa are created, and subsequently cooled at high cooling rates of $10^{10}$ K/s [16]. These conditions are induced reactions such as oxidation, reduction, hydrolysis, dissolution, and decomposition [17]. The high intensity shockwaves could be facilitating to prevent particle agglomeration and rapid crystal growth. Hence, considering the advantage of using sonochemical method here we have adopted the same for the synthesis of PbSe–$TiO_2$ nanocomposite. Subsequently, heat treatment was used to tune the morphology of $TiO_2$ particles. Finally the structural, morphological, visible light photocatalysis properties of the prepared PbSe–$TiO_2$ were investigated.

## 2. Experimental

### 2.1. Materials

Lead chloride ($PbCl_2$), selenium metal powder and ammonium hydroxide ($NH_4OH$, 28%) were purchased from Dae Jung Chemicals & Metal Co., Ltd, Korea. Anhydrous purified sodium sulfite ($Na_2SO_3$, 95%) was purchased from Duksan Pharmaceutical Co., Ltd, Korea. The titanium (IV) *n*-butoxide (TNB, $C_{16}H_{36}O_4Ti$) as a titanium source for the preparation of $TiO_2$ nanoparticles was purchased from Kanto Chemical Company (TOKYO, Japan). The Rh.B ($C_{28}H_{31}ClN_2O_3$, 99.99+%) was used as model pollutant which purchased from Duksan Pure Chemical Co., Ltd, Korea. All chemicals used without further purification and all experiments were carried out using distilled water.

### 2.2. Synthesis of PbSe–$TiO_2$ nanocomposite

$TiO_2$ nanoparticles were prepared according to our previous work [18]. The detailed process is described as follows: firstly, $TiO_2$ precursors were prepared with the molar ratios of ethanol: $H_2O$: TNB = 35:15:4, finally the suspension was sonicated at room temperature for 2 h using a Controllable Serial-Ultrasonic apparatus (Ultrasonic Processor, VCX 750, Korea). The final products were filtered and washed repeatedly and then vacuum dried at 373 K. The dried catalyst was ground in a ball mill and calcined at 773 K for 1 h to get $TiO_2$ nanoparticles.

For the synthesis of PbSe–$TiO_2$ nanocomposites, the sodium selenosulfite ($Na_2SeSO_3$) solution and $Pb(NH_3)_4^{2+}$ solution was prepared. $Na_2SO_3$ (5 g) and selenium metal powder (0.5 g) were dissolved in 30 mL distilled water and refluxed for 1 h to form $Na_2SeSO_3$ solution in a particular situation. Meanwhile, 2 mM $PbCl_2$ was dissolved in 20 mL distilled water. $NH_4OH$ (4 mL) was added to the solution and the mixture was stirred till it dissolved completely to form $Pb(NH_3)_4^{2+}$ solution. Then 0.5 g $TiO_2$ nanoparticles was added to the $Pb(NH_3)_4^{2+}$ solution, followed by stirring for 2 h under ambient temperature for adsorption of $Pb(NH_3)_4^{2+}$ on the surface of $TiO_2$ nanoparticles. Finally, the $Pb(NH_3)_4^{2+}/TiO_2$ solution and a certain amount of $Na_2SeSO_3$ solution were mixed together following by ultrasonicated for several hours. The sonochemical synthesis time was adjusted to prepare different PbSe–$TiO_2$ nanocomposites. The obtained PbSe–$TiO_2$ samples were labeled as PT1, PT2, and PT3, respectively. For comparison, another photocatalyst PbSe was prepared using similar procedure without adding $TiO_2$.

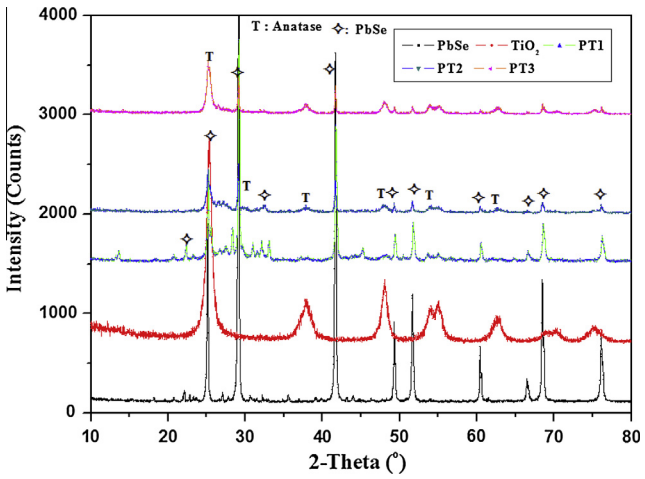
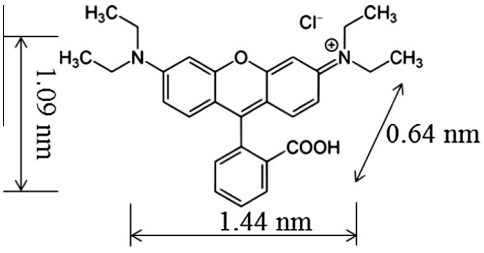



**Fig. 1.** XRD patterns of pure PbSe, $TiO_2$ nanoparticles and PbSe–$TiO_2$ composite.

### 2.3. Characterization

The Brunauer–Emett–Teller (BET) surface area of PbSe–$TiO_2$ composite was evaluated from the $N_2$ adsorption isotherms at 77 K using a BEL Sorp Analyzer (BEL). X-ray diffraction (XRD, Shimadz XD-D1) result was used to identify the phase with Cu Kα radiation. Scanning electron microscopy (SEM, JSM-5600) was used to observe the surface state and structure of PbSe–$TiO_2$ composite using an electron microscope. The element mapping over the desired region of PbSe–$TiO_2$ composite was detected by an energy dispersive X-ray (EDX) analysis attached to SEM. UV–vis diffuse reflectance spectra (DRS) were obtained using an UV–vis spectrophotometer (Neosys-2000) by using $BaSO_4$ as a reference and were converted from reflection to absorbance by the Kubelka–Munk method.

**Table 1**
The molecular structure and absorbance maximum ($\lambda_{max}$) of organic dyes.

| Organic dyes | Molecular structure | $\lambda_{max}$ |
|---|---|---|
| Rhodamine B (Rh.B) |  | 554 nm |