Contents lists available at ScienceDirect



Progress in Natural Science: Materials International

journal homepage: www.elsevier.com/locate/pnsmi



## Original Research

# Environmentally-friendly harvesting TiO<sub>2</sub> nanospheres and V<sub>2</sub>O<sub>5</sub> microrods from spent selective catalytic reduction catalysts



Hua-Jun Chen<sup>a</sup>, Rui Wang<sup>a</sup>, Yan-Ling Yang<sup>b,\*</sup>, Xiao-Lei Shi<sup>c,d</sup>, Siyu Lu<sup>e</sup>, Zhi-Gang Chen<sup>c,d,\*</sup>

<sup>a</sup> School of Environment and Chemistry, Luoyang Institute of Science and Technology, Luoyang, 471000, China

<sup>b</sup> School of Materials Science and Engineering, Shaanxi Key Laboratory of Green Preparation and Functionalization for Inorganic Materials, Shaanxi University of Science

and Technology, Xi'an, 710021, China

<sup>c</sup> Centre for Future Materials, University of Southern Queensland, Springfield Central, QLD, 4300, Australia

<sup>d</sup> School of Mechanical and Mining Engineering, The University of Queensland, QLD, 4072, Australia

<sup>e</sup> Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou, 450001, China

#### ARTICLE INFO

Keywords: TiO<sub>2</sub> nanospheres V<sub>2</sub>O<sub>5</sub> microrods Hydrothermal Spent selective catalytic reduction catalyst

#### ABSTRACT

Spent selective catalytic reduction (SCR) catalysts are defined as hazardous wastes because of the toxicity of  $V_2O_5$  to the ecological environment. Recycling of  $V_2O_5$  and TiO<sub>2</sub> from the spent SCR catalysts has strikingly social and environmental benefits as well as economic values. In this work, a "NaOH + Na<sub>2</sub>CO<sub>3</sub>" system was employed to recycle 99.2% of anatase/rutile TiO<sub>2</sub> nanospheres with a nanospherical morphology from the spent SCR catalysts by a simple sintering-leaching process. The observed photocatalytic performance of anatase/rutile TiO<sub>2</sub> nanospheres was higher than that of the other TiO<sub>2</sub> recovered from the spent SCR catalysts, commercial TiO<sub>2</sub>, and chemosynthetic TiO<sub>2</sub>, which can be ascribed to the enhanced separation of photo-excited electron/hole in a direct Z-scheme of anatase/rutile TiO<sub>2</sub> homostructures. Additionally, high-purity  $V_2O_5$  microrods with high H<sub>2</sub>S removal performance were efficiently prepared by a hydrothermal method in the leaching solution, which is superior to the traditional method including NH<sub>4</sub>VO<sub>3</sub> precipitation and solvent extraction as the present method can recycle vanadate from low-grade filtrate with a 99.6% of recovery rate. This study develops an alternative method for controlling pollution of vanadate to soil and water and recycling of valuable metals.

## 1. Introduction

Selective catalytic reduction (SCR) technology is widely used to reduce  $NO_x$  emission [1,2], while  $V_2O_5$ -supported  $TiO_2$  is mainly used material [3–6]. With the promotion of SCR denitration technology in cement, glass, steel, and thermal power industry, increasing amounts of the spent SCR catalysts are generated and bring severe environment pressure because of the toxicity of  $V_2O_5$  to ecological environment [7,8].

Recycling of  $V_2O_5$  and TiO<sub>2</sub> from the spent SCR catalysts can prevent environmental pollution and avoid wastes of the valuable resources. Recently, various hydrometallurgical processes, such as acid leaching [9], alkaline leaching [10], salt leaching [11], and bioleaching [12], together with roasting as a pre-treatment step, have been used to recycle  $V_2O_5$  and TiO<sub>2</sub> from the spent SCR catalysts. Choi et al. [13] reported V and W can be recycled from the spent SCR catalysts by a Na<sub>2</sub>CO<sub>3</sub> roasting-leaching process. The leaching rate of W increases rapidly as functions of the Na<sub>2</sub>CO<sub>3</sub> addition, time, and temperature. However, the leaching rate of V is only 40% in the entire experiment, leading to the wasting of V as well as the environmental pollution of toxic V, which is ascribed to the formation of calcium vanadate (CaV<sub>2</sub>O<sub>6</sub>). Yang et al. [14] extracted W and V from the spent SCR catalysts by a roasting-leaching method. The leaching solutions of W and V were enriched by using an ion-exchange and NaOH elution process, then 96.2% of W and 93.4% of V were separated by an ammonium salt precipitation method from the enriched solutions. In addition, nano-sized TiO<sub>2</sub> and sodium titanate (Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) microrods with superior adsorption capacity for heavy metal ions were recycled from the leached residue. During those roasting-leaching process, V2O5 can transform into soluble species and separate vanadate from TiO<sub>2</sub>, then TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> can be prepared from filter residue and filtrate, respectively [15].

\* Corresponding authors. *E-mail addresses:* yangyanling@sust.edu.cn (Y.-L. Yang), zhigang.chen@usq.edu.au (Z.-G. Chen).

https://doi.org/10.1016/j.pnsc.2021.10.002

Received 20 July 2021; Received in revised form 22 September 2021; Accepted 8 October 2021 Available online 30 October 2021

<sup>1002-0071/© 2021</sup> Chinese Materials Research Society. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/bync.nd/4.0/).

## Table 1

Chemical components of the spent SCR catalysts.

components	TiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	Etc.
Contents (wt. %)	79.80	1.23	10.26	5.36	2.35	0.56	0.23	0.21



Fig. 1. An illustration of the preparation of anatase/rutile TiO2 nanospheres and V2O5 microrods from the spent SCR catalysts.

The activity of recovered TiO<sub>2</sub> depends on the morphology, the spherical TiO<sub>2</sub> in the spent SCR catalysts can easily melt down and agglomerate together to form bulky materials in the process of high temperature and strongly alkaline roasting, which degrade the activity of recovered TiO<sub>2</sub>. Therefore, it is difficult to prepare TiO<sub>2</sub> nanospheres with high photocatalytic performance from the spent SCR catalysts using conventional roasting techniques. In the past decades, WO3-TiO2 sheet [16], TiO<sub>2</sub> rods [17], and titanate [14] have been recycled from the spent SCR catalysts by conventional roasting-leaching methods. In addition, the concentration of vanadate in filtrate is usually less than the solubility of NH<sub>4</sub>VO<sub>3</sub> precipitation. The enrichment steps, such as ionic-exchange and extraction, are necessary to precipitate NH<sub>4</sub>VO<sub>3</sub>. Hence, it is pivotal to develop an environmentally-friendly technology with a high recovery rate that can prepare TiO<sub>2</sub> nanospheres from the spent SCR catalysts, harvest vanadate from low-grade filtrate to address the pollution of vanadate, and promote the sustainability of SCR catalysts industry.

In this work, to maintain nanospherical morphology of TiO<sub>2</sub> in the spent SCR catalysts and prepare TiO<sub>2</sub> nanospheres with high photocatalytic activity, a "NaOH + Na<sub>2</sub>CO<sub>3</sub>" system was employed to dispose the spent SCR catalysts as well as recycling of valuable metals via a simple sintering-leaching process. Furthermore, a hydrothermal method with a high recovery rate was developed to address the difficulty of harvesting vanadate from the low-grade filtrate. This study develops an environmentally-friendly disposal of the spent SCR catalysts as well as the preparation of anatase/rutile TiO<sub>2</sub> nanospheres and V<sub>2</sub>O<sub>5</sub> microrods with great potential industrial applications.

## 2. Materials and methods

#### 2.1. Chemicals and materials

The spent SCR catalysts used in this study were collected from a thermal power plant in Henan province of China. Chemical components of the spent SCR catalysts were analyzed by titrimetry and the results are shown in Table 1. The mainly effective compositions are TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>. The analytical grade reagents including NaOH, Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> (98 wt% in H<sub>2</sub>O), HNO<sub>3</sub> (69 wt% in H<sub>2</sub>O), H<sub>3</sub>PO<sub>4</sub> (85 wt% in H<sub>2</sub>O), FeSO<sub>4</sub>·7H<sub>2</sub>O, phenolphthalein (C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>), N-Phenylanthranilic acid (C<sub>13</sub>H<sub>11</sub>NO<sub>2</sub>), ethylene diamine tetra acetic acid (EDTA, C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>), sulfosalicylic acid (C<sub>7</sub>H<sub>6</sub>O<sub>6</sub>S·2H<sub>2</sub>O), and NH<sub>3</sub>•H<sub>2</sub>O (25 wt% in H<sub>2</sub>O) were obtained

from Shanghai Chemical Reagents Co., Lit. All reagents without additional purification and deionized (DI) water were used in all processes.

## 2.2. Sintering and leaching of the spent SCR catalysts

The sintering and leaching process is shown in Fig. 1. The spent SCR catalysts were firstly shredded to screen through mesh size of 200 after air swept to remove the dust from the surface. The mixtures, consisted of the as-shredded spent SCR catalysts, Na<sub>2</sub>CO<sub>3</sub> and NaOH at a mass ratio of 11:10:1, were sintered for 90 min at 500 °C in a muffle furnace. The sintered products were transferred to a beaker in which a certain volume of DI water was added. The beaker was agitated on a magnetic stirrer at room temperature for 2 h, and the filtration was adopted for solid-liquid separation.

## 2.3. Preparation of TiO<sub>2</sub> nanospheres

The filter residue was added into DI water and pH of the solutions was controlled using HCl solution. The mixture was agitated on magnetic stirrer at room temperature for 2 h, and ions including Fe<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, etc., were dissolved in water and separated from TiO<sub>2</sub> nanospheres. TiO<sub>2</sub> nanospheres were washed repeatedly with a dilute solution of HCl to remove excess residues, and further dried at 120 °C for 2 h followed by calcining at 500 °C for 2 h.

#### 2.4. Evaluation of photocatalysis

To evaluate the photocatalytic performance of TiO<sub>2</sub> nanospheres prepared from the spent SCR catalysts, photocatalytic degradation of 2,4dinitrophenol was performed under Xenon light. 10 mg TiO<sub>2</sub> nanospheres were dispersed in 100 mL aqueous solution of 2,4-dinitrophenol (20 mg L<sup>-1</sup>). The mixture was irradiated under Xenon light. The residual concentration of 2,4-dinitrophenol solution ( $c_t$ ) was analyzed by spectrophotometry during photocatalysis. The degradation ratio of 2,4-dinitrophenol was calculated by Equation (1).

Degradation ratio = 
$$\frac{c_e - c_t}{c_e} \times 100 \%$$
 (1)

The equation of the first-order kinetics (Equation (2)) was adopted to simulate the degradation kinetics of 2,4-dinitrophenol.



Fig. 2. (a-b) TEM images of the spent SCR catalysts (a) and as-prepared  $TiO_2$  nanospheres (b). (c) HRTEM image of the as-prepared  $TiO_2$  nanospheres. (d) XRD patterns of the spent SCR catalysts and as-prepared  $TiO_2$  nanospheres. (e) Illustration of the preparation of  $TiO_2$  nanospheres. (f) Photocatalytic performance and degradation kinetics of the as-prepared  $TiO_2$  nanospheres for 2,4-dinitrophenol. (g) Schematic descriptions the migration of photo-excited electron/hole in the as-prepared  $TiO_2$  nanospheres.



where k is the rate constant of the first-order kinetics in the process of photocatalysis of 2,4-dinitrophenol.

#### 2.5. Preparation of V2O5 microrods

pH of alkaline filtrate was firstly adjusted to 11–12 by using a solution of H<sub>2</sub>SO<sub>4</sub>, and then MgCl<sub>2</sub> was added to filtrate to separate MgSiO<sub>3</sub> precipitation from the filtrate. The precipitate was filtered after 2 h. Secondly, pH of above filtrate was adjusted to 1.8 by using a solution of H<sub>2</sub>SO<sub>4</sub> [18], and then the filtrate was transferred to a 100 mL Teflon-lined kettle and heated at 120 °C for 36 h. The hydrothermal products were collected by centrifugation, washed with DI water, and dried in an oven. After calcination at 500 °C for 2 h in a muffle furnace, brown V<sub>2</sub>O<sub>5</sub> microrods were obtained.

## 2.6. $H_2S$ removal performance

100 mg  $V_2O_5$  microrods were dispersed in 100 mL sour water (provided by Luoyang Sinopec Technologies Co., Lit) with the initial concentration of 1300 mg L<sup>-1</sup>. The mixture was agitated on a magnetic stirrer at room temperature and solid-liquid separation was achieved by centrifugation. The residual concentration of H<sub>2</sub>S in sour water was analyzed by iodometry [18].

#### 2.7. Sample characterization

The phase compositions of  $TiO_2$  nanospheres and  $V_2O_5$  microrods were studied by X-ray diffraction (XRD, D8 Focus, Bruker, Germany), and morphology of  $TiO_2$  nanospheres and  $V_2O_5$  microrods were assessed by field-emission scanning electron microscope (FESEM, Sigma HD, Zeiss, Germany) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20, FEI, America).

## 3. Results and discussion

#### 3.1. Preparation and evaluation of TiO<sub>2</sub> nanospheres

Fig. 2(a) presents a typical TEM image of the spent SCR catalysts. As can be seen, the spent SCR catalysts compose of TiO2 nanospheres and their surface is wrapped by other ingredients, exhibiting core-shell nanostructure with a thickness of  $\sim$ 2.5 nm for the shell. Fig. 2(b) presents a typical TEM image of the as-prepared TiO<sub>2</sub> products after the recycling. Compared with the spent SCR catalysts, the surface of the asprepared TiO<sub>2</sub> products is very clean and uniform without any impurities. Especially, most of them remain the nanosphere morphology. This is different from the other recycled TiO<sub>2</sub> rods [14,17], sheets [16], and particles [19] because of the agglomeration and meltdown of original TiO<sub>2</sub> nanospheres. The agglomeration of TiO<sub>2</sub> nanosphere deteriorates the liberation of soluble species during the leaching process, and further reduces the purity of the recycled TiO<sub>2</sub> products. The results suggest that our "NaOH + Na<sub>2</sub>CO<sub>3</sub>" sintering system can not only help to maintain the nanosphere morphology of TiO<sub>2</sub> in the spent SCR catalysts, but also recycle 99.2% of TiO<sub>2</sub> from the spent SCR catalysts. The diameter of the as-prepared TiO<sub>2</sub> nanospheres is slightly less than that of the spent SCR catalysts due to the removal of the impurity shell.

Fig. 2(c) presents a HRTEM image of the as-prepared TiO<sub>2</sub> nanospheres. 0.35 nm and 0.32 nm lattice fringes affiliate to the d spacings of (101) plane of anatase  $TiO_2$  and (110) crystal plane of rutile  $TiO_2$  [20]. Fig. 2(d) displays the XRD patterns of the spent SCR catalysts and as-prepared TiO2 nanospheres. In the XRD pattern of the spent SCR catalysts, the diffraction peaks can be indexed to the anatase TiO<sub>2</sub> (No. 21-1272), and no additional peak is indexed to other ingredients, because of the low crystallinity and well dispersion of other ingredients on the TiO<sub>2</sub> surface [21–24]. The as-prepared TiO<sub>2</sub> nanospheres comprise of anatase phase (No. 21-1272) and rutile phase (No. 21-1276) [25], which is in agreement with the HRTEM analysis. The diffraction peaks at 25.4° and 27.4° can be indexed to (101) planes of anatase and (110) plane of rutile TiO2. XRD patterns of the spent SCR catalysts and as-prepared TiO<sub>2</sub> products indicate that anatase TiO<sub>2</sub> partially transform into rutile at 500 °C [26,27]. In addition, the phase content was calculated according to XRD patterns of the as-prepared TiO<sub>2</sub> nanospheres using Jade analysis software. The content of anatase and rutile phase TiO<sub>2</sub> are 69.8 wt% and 30.2 wt% in the as-prepared TiO<sub>2</sub> nanospheres, respectively. The phase conversion of TiO<sub>2</sub> nanospheres helps the liberation of soluble species occupied interstitial positions of TiO<sub>2</sub> lattice and improves the purity of recycled TiO<sub>2</sub> products. The results of XRD and HRTEM consistently indicate that anatase/rutile TiO<sub>2</sub> nanospheres can be completely separated from the spent SCR catalysts. According to above results, a synthetic processing of anatase/rutile TiO2 nanospheres is illustrated in Fig. 2(e). As previously discussed, our "NaOH + Na<sub>2</sub>CO<sub>3</sub>" system is used to transform impurity shell including vanadate and metasilicate into soluble species in a muffle furnace. The reaction mechanism can be expressed by the following equations:

$$V_2O_5 + 2NaOH \xrightarrow{\Delta} 2NaVO_3 + H_2O$$
(3)

$$\begin{split} M_{2}(\text{SiO}_{3})_{n} + n\text{N}a_{2}\text{CO}_{3} \xrightarrow{\Delta} n\text{N}a_{2}\text{SiO}_{3} + M_{2}\text{O}_{n} + n\text{CO}_{2} &\uparrow (\text{M} \\ &: \text{Fe}, \text{Al}, \text{ Ca}, \text{ Mg} \cdots) \end{split} \tag{4}$$

As can be seen, the insoluble vanadium and metasilicate react with NaOH and Na<sub>2</sub>CO<sub>3</sub> at high temperatures to form soluble species, leading to the volumetric expansion of impurity shell during alkaline sintering. The shell of soluble vanadate and metasilicate breaks into pieces and anatase/rutile TiO<sub>2</sub> nanospheres are released from the spent SCR catalysts during the leaching process.

Photocatalytic performance and degradation kinetics of the asprepared  $TiO_2$  nanospheres for 2,4-dinitrophenol were evaluated and the results are shown in Fig. 2(f). As can be seen in Fig. 2(f), the

#### Table 2

A comparison of photocatalytic performance of anatase/rutile  $TiO_2$  nanospheres with other  $TiO_2$  recovered from the spent SCR catalysts, commercial  $TiO_2$  and chemosynthetic  $TiO_2$  photocatalysts.

Samples	Solution	Light source	Rate constant of first-order kinetic	Ref.
0.2 g L <sup>-1</sup> , anatase/rutile TiO <sub>2</sub> nanospheres, recovered from spent SCR catalvst	20 mg L <sup>-1</sup> , 2,4- dinitrophenol, 100 mL	150 W Xenon light	$\begin{array}{l} k=0.0603\\ min^{-1} \end{array}$	Our sample
WO <sub>3</sub> -TiO <sub>2</sub> sheet, recovered from spent SCR catalyst	10 mg L <sup>-1</sup> , methyl orange, 50 mL	30-W UV lamp (365 nm)	0.03721 min <sup>-1</sup>	[16]
1.3 g L <sup>-1</sup> , TiO <sub>2</sub> rods, recovered from spent SCR catalyst	10 mg L <sup>-1</sup> , rhodamine B, 150 mL	450 W xenon lamp	0.0035 min <sup>-1</sup>	[17]
0.2 g L <sup>-1</sup> , P25, commercial TiO <sub>2</sub> from Evonik-Degussa	25 mg L <sup>-1</sup> , reactive red 2, 50 mL	150W xenon lamp	0.00263 min <sup>-1</sup>	[39]
0.2 g L <sup>-1</sup> , anatase TiO <sub>2</sub> , commercial TiO <sub>2</sub> from Ishihara Sangyo	20 mg L <sup>-1</sup> , phenol, 500 mL	20W fluorescent lamp	0.00168 min <sup>-1</sup>	[40]
$0.2 \text{ g L}^{-1}$ , TiO <sub>2</sub> particles, prepared by precipitation	10 mg L <sup>-1</sup> , methylene blue, 100 mL	150 W halogen lamp	0.0050 min <sup>-1</sup>	[41]
0.2 g $L^{-1}$ , bean- like TiO <sub>2</sub> particles, prepared by solvothermal method	10 mg L <sup>-1</sup> , methylene blue, 100 mL	150 W Xenon lamp with the filter of 420 nm	0.03013 min <sup>-1</sup>	[42]
8.0 g $L^{-1}$ , TiO <sub>2</sub> particles, prepared by sol- gel method	38.8 mg L <sup>-1</sup> , 2,4-dinitro- phenol, 150 mL	Sunlight	$\begin{array}{l} k=0.0286\\ min^{-1} \end{array}$	[43]

concentration of 2,4-dinitrophenol solution ( $c_t$ ) decreases when the reaction time is prolonged and 99.9% of 2,4-dinitrophenol was oxidized in 120 min. The oxidation reaction of 2,4-dinitrophenol complies with first-order kinetics and the first-order kinetics rate constant of photocatalysis is 0.0603 min<sup>-1</sup>. The result indicates that anatase/rutile TiO<sub>2</sub> nanospheres possess powerful photocatalytic ability and can be utilized as photocatalysts for practical applications.

The photocatalytic degradation of the as-prepared  $TiO_2$  nanospheres for 2,4-dinitrophenol has been repeated 5 times, the standard deviation was calculated to evaluate the photocatalytic stability of the as-prepared  $TiO_2$  nanospheres. As shown in Fig. 2(f), the standard deviation is less than 0.63, indicating photocatalytic activity of the as-prepared  $TiO_2$ nanospheres hardly change for 5 cycles. The results show that the asprepared  $TiO_2$  nanospheres achieve high stability and activity, which can be ascribed to the higher dispersibility and photochemical stability of the as-prepared  $TiO_2$  nanospheres.

The transfer of photo-excited electron/hole in anatase/rutile  $\text{TiO}_2$  nanospheres is shown in Fig. 2(g). Anatase and rutile  $\text{TiO}_2$  construct a direct Z-scheme homostructure system [7,20,28–32]. The electrons in the conduction band of anatase  $\text{TiO}_2$  recombine with the holes in the valence band of rutile  $\text{TiO}_2$ . Therefore, electrons in the conduction band of rutile  $\text{TiO}_2$  and holes in the valence band of anatase  $\text{TiO}_2$  are spatially separated. The photo-excited hole in the valence band of anatase  $\text{TiO}_2$  reacts with H<sub>2</sub>O to form •OH. Simultaneously, photo-excited electrons in the conduction band of rutile  $\text{TiO}_2$  react with O<sub>2</sub> to form  $\bullet \text{O}_2^-$ .  $\bullet \text{OH}$  and

H.-J. Chen et al.



Fig. 3. (a–b) Effect of hydrothermal temperature and time on recycle rate of  $V_2O_5$  microrods during hydrothermal process. (c) XRD pattern of the as-prepared  $V_2O_5$  microrods. (d) SEM image of the as-prepared  $V_2O_5$  microrods. (e) TEM image of the as-prepared  $V_2O_5$  microrods. (f) HRTEM image of the as-prepared  $V_2O_5$  microrods. (g) The comparison of conversion rate of  $H_2S$  in sour water between the as-prepared  $V_2O_5$  microrods and commercial  $V_2O_5$  powder. (h) The  $H_2S$  removal kinetics of the as-prepared  $V_2O_5$  microrods and commercial  $V_2O_5$  powders.

 $\bullet O_2^-$  can directly/indirectly oxidize 2,4-dinitrophenol into CO<sub>2</sub>, H<sub>2</sub>O, and others [33–38].

In addition, photocatalytic performance of anatase/rutile  $TiO_2$  nanospheres was compared with the reported photocatalysts and summarized in Table 2. As can be seen, the first-order kinetics rate constant of anatase/rutile  $TiO_2$  nanospheres is faster than that of the reported photocatalysts including other  $TiO_2$  recovered from the spent SCR catalysts [16,17], commercial  $TiO_2$  [39,40], and chemosynthetic  $TiO_2$  photocatalysts [41,42]. The higher photocatalytic performance of the as-prepared  $TiO_2$  nanospheres is mainly derived from their higher

specific surface areas and separation rate of photo-excited electron/hole. Firstly, the specific surface area of as-prepared  $TiO_2$  nanospheres is greater than that of  $TiO_2$  rods,  $TiO_2$  sheets, and  $TiO_2$  particles. Secondly, a direct Z-scheme homostructure system constructes in the as-prepared  $TiO_2$  nanospheres. Namely, the electrons in the conduction band of anatase  $TiO_2$  recombine with the holes in the valence band of rutile  $TiO_2$ , then electrons in the conduction band of rutile  $TiO_2$  and holes in the valence band of anatase  $TiO_2$  are spatially separated. Therefore, the photocatalytic performance of the as-prepared  $TiO_2$  nanospheres is better than that of commercial  $TiO_2$  and chemosynthetic  $TiO_2$  photocatalysts.

The results indicate that our anatase/rutile  $TiO_2$  nanospheres possess powerful photocatalytic ability and could be utilized as photocatalyst for practical applications.

## 3.2. Preparation and H<sub>2</sub>S removal of V<sub>2</sub>O<sub>5</sub> microrods

After removal of silicate from filtrate, V<sub>2</sub>O<sub>5</sub> can be prepared by a hydrothermal method from filtrate. Fig. 3(a-b) plot the effect of hydrothermal temperature and time on recovery rate of V<sub>2</sub>O<sub>5</sub> during hydrothermal process. The recovery rate of V2O5 increases from 33.3% to 99.6% as temperature increases from 60  $^\circ C$  to 120  $^\circ C$  and then remains steady. With the increase of hydrothermal time, recycle rate of V<sub>2</sub>O<sub>5</sub> increases rapidly and then levels off. Therefore, the optimum hydrothermal temperature and time are 120 °C and 36 h, respectively. The experimental results indicate that the recovery rate of hydrothermal method is higher than that of the reported recovery methods including NH<sub>4</sub>VO<sub>3</sub> precipitation [44,45], solvent extraction [46-48], and their combination [49-51]. Fig. 3(c) presents the XRD pattern of the recovered products. The diffraction peaks at 15.3°, 20.3°, 21.7°, 26.1°, 31.0° and 34.3° can be indexed to (200), (001), (101), (110), (301) and (310) planes of V<sub>2</sub>O<sub>5</sub> (No. 41–1426) according to the international centre for diffraction data. No additional peak can be detected in XRD patterns of  $V_2O_5$ , indicating high purity of the recovered products. Fig. 3(d) shows a typical SEM image of the recovered products, which exhibit high dispersibility and a uniform rod-like morphology with diameters ranging from 300 to 400 nm. These results suggest high-purity V<sub>2</sub>O<sub>5</sub> microrods can be efficiently prepared by the hydrothermal method. Firstly, V<sub>2</sub>O<sub>5</sub> precipitation generates through the hydrolysis of vanadate under the hydrothermal condition. Then, driven by the minimization of the total energy of the system, the primary V<sub>2</sub>O<sub>5</sub> precipitation aggregate together through Ostwald ripening to form the micrometer-sized V2O5 microrods under hydrothermal conditions [52]. Fig. 3(e) presents a typical TEM image of the as-prepared V2O5 microrods. As can be seen, a rod-like V2O5 with high dispersibility was recycled by hydrothermal method from filtrate. Fig. 3(f) presents a HRTEM image of the as-prepared V<sub>2</sub>O<sub>5</sub> microrods, and a 0.44 nm lattice fringe affiliates to the d spacings of (001) plane of V<sub>2</sub>O<sub>5</sub> microrods.

Sour water containing undesirable H<sub>2</sub>S is mainly produced from atmospheric and vacuum columns of oil refineries. Activities of the asprepared  $V_2O_5$  microrods and commercial  $V_2O_5$  powders were compared in terms of eliminating  $H_2S$  from sour water and the results are plotted in Fig. 3(g). The as-prepared V<sub>2</sub>O<sub>5</sub> microrods can eliminate completely H<sub>2</sub>S within 100 s, whereas only 88.7% H<sub>2</sub>S was eliminated by commercial V<sub>2</sub>O<sub>5</sub> powders. Furthermore, the analysis of standard deviation was applied to evaluate the stability of the as-prepared V<sub>2</sub>O<sub>5</sub> microrods. The experiments of eliminating H<sub>2</sub>S from sour water have been repeated 5 times. As shown in Fig. 3(g), standard deviation is less than 2.5 and the activity of the as-prepared V<sub>2</sub>O<sub>5</sub> microrods is almost unchanged for 500 s, indicating that the as-prepared V<sub>2</sub>O<sub>5</sub> microrods can achieve a high stability and activity, which can be ascribed to the higher dispersibility and specific area of the as-prepared V<sub>2</sub>O<sub>5</sub> microrods. The removal kinetic of H<sub>2</sub>S from sour water was furthermore simulated to compare the activity of the as-prepared V2O5 microrods with commercial V<sub>2</sub>O<sub>5</sub> powders. Fig. 3(h) shows that H<sub>2</sub>S removal kinetics of the asprepared V<sub>2</sub>O<sub>5</sub> microrods and commercial V<sub>2</sub>O<sub>5</sub> powders complies with first-order kinetics [53]. The kinetic constant of the as-prepared V<sub>2</sub>O<sub>5</sub> microrods is about 2.4 times greater than that of commercial V<sub>2</sub>O<sub>5</sub> powders, indicating the recycled V<sub>2</sub>O<sub>5</sub> microrods have great potentials in practical applications.

## 4. Conclusions

In this work, a "NaOH + Na<sub>2</sub>CO<sub>3</sub>" system is employed to recycle anatase/rutile TiO<sub>2</sub> nanospheres from the spent SCR catalysts via a simple sintering-leaching process. The results indicate that the "NaOH + Na<sub>2</sub>CO<sub>3</sub>" system can maintain nanospherical morphology of

 $TiO_2$  as well as recycle valuable metals from the spent SCR catalysts. Under the optimized condition of sintering and leaching, anatase/rutile  $TiO_2$  nanospheres are prepared from the spent SCR catalysts and show higher photocatalytic performance than that of the other  $TiO_2$  recovered from the spent SCR catalysts, commercial  $TiO_2$ , and chemosynthetic  $TiO_2$ photocatalysts. Such higher performance is ascribed to a direct Z-scheme in anatase/rutile  $TiO_2$  homostructures that can significantly suppress the recombination of photo-excited electron/hole. In addition, high-purity  $V_2O_5$  microrods with high  $H_2S$  removal performance can be also recycled from the low-grade filtrate by a hydrothermal method. Our study affords an environmentally-friendly disposal of the spent SCR catalysts to efficiently separate anatase/rutile  $TiO_2$  nanospheres and  $V_2O_5$  microrods with potential industrial applications as well as dispose environmental pollution of the spent SCR catalysts.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

The authors acknowledge financial support from the National Natural Science Foundation of China (51464020). ZGC thanks the financial support from the Australian Research Council.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.pnsc.2021.10.002.

#### References

- [1] Z. Zhao, E. Li, Y. Qin, et al., J. Environ. Sci. 90 (2020) 119-137.
- [2] L. Chen, D. Weng, Z. Si, et al., Prog. Nat. Sci.: Mater 22 (4) (2012) 265-272.
- [3] L. Chen, J. Li, M. Ge, J. Phys. Chem. C 113 (50) (2009) 21177–21184.
- [4] K. Cheng, J. Liu, T. Zhang, et al., J. Environ. Sci. 26 (10) (2014) 2106-2113.
- [5] X. Chen, P. Wang, P. Fang, et al., Environ. Sci. Nano 4 (2) (2017) 437-447.
- [6] H. Chen, W. Tian, W. Ding, Sol. Energy 173 (2018) 1065–1072.
- [7] Y. Wang, M. Hong, W.-D. Liu, et al., Chem. Eng. J. 397 (2020) 125360.
- [8] Z. Ma, X. Wu, Y. Feng, et al., Prog. Nat. Sci.: Mater. 25 (4) (2015) 342-352.
- [9] E.A. Abdel-Aal, M.M. Rashad, Hydrometallurgy 74 (3) (2004), 189–19.
   [10] D. Chen, L. Zhao, Y. Liu, et al., J. Hazard Mater. 244 (2013) 588–595.
- [11] X.-S. Li, B. Xie, Int. J. Min., Met., Mater. 19 (7) (2012) 595–601.
- [11] A. O. E. D. Ale, Int. J. Mill, Meel, Match. 19 (7) (2012) 595 601.
   [12] D. Mishra, D.J. Kim, D.E. Ralph, et al., Hydrometallurgy 88 (1) (2007) 202–209.
- [13] I.-H. Choi, H.-R. Kim, G. Moon, et al., Hydrometallurgy 175 (2018) 292–299.
- [14] B. Yang, J. Zhou, W. Wang, et al., Colloid. Surface. A 601 (2020) 124963.
- [15] Y. Chen, Q. Feng, Y. Shao, et al., Int. J. Miner. Process. 79 (1) (2006) 42-48.
- [16] Q. Zhang, Y. Wu, L. Li, et al., ACS Sustain. Chem. Eng. 6 (9) (2018) 12502-12510.
- [17] Q. Zhang, Y. Wu, T. Zuo, ACS Sustain, Chem. Eng. 6 (3) (2018) 3091–3101.
- [18] N. Sahraeian, F. Esmaeilzadeh, D. Mowla, Ceram. Int. 47 (1) (2021) 923-934.
- [19] B. Ma, Z. Qiu, J. Yang, et al., Waste Biomass Valori 10 (10) (2019) 3037-3044.
- [20] X. Zou, Y. Yang, H. Chen, et al., Mater. Des. 202 (2021), 109542.
- [21] J. Yao, Y. Cao, J. Wang, et al., Hydrometallurgy 201 (2021), 1055766.
- [22] X.-L. Shi, H. Wu, Q. Liu, et al., Nanomater. Energy 78 (2020), 105195.
- [23] Y. Sun, Y. Yang, X.-L. Shi, et al., ACS Appl, Mater. Inter 13 (2021) 28359-28368.
- [24] Y. Deng, X. Gao, X.-L. Shi, et al., Chem. Mater. 32 (5) (2020) 2180–2193.
- [25] X. Zou, Y. Yang, H. Chen, et al., J. Colloid Interface Sci. 579 (2020) 463-469.
- [26] H.-J. Chen, Y.-L. Yang, M. Hong, et al., Sustain. Mater. Techno 21 (2019) e00105.
   [27] S. Agrawal, N. Dhawan, Sustain. Mater. Techno 27 (2021) e00246.
- [27] S. Agrawal, N. Dhawan, Sustain. Mater. Technol 27 (2021) e00246.
   [28] Y. Bi, Y. Yang, X.-L. Shi, et al., J. Mater. Sci. Technol. 83 (2021) 102–112.
- [20] H. Yang, C. He, L. Fu, et al., Ohn. Chem. Lett. (2021), https://doi.org/10.1016/j.cclet.2021.03.038. In press.
- [30] Y. Zheng, X.L. Shi, H. Yuan, et al., Mater. Today Phys. 13 (2020), 100198.
- [31] H. Wu, X.-L. Shi, W.-D. Liu, et al., Chem. Eng. J. 425 (2021), 130668.
- [32] J. Yu, C. He, C. Pu, et al., Chin. Chem. Lett. (2021), https://doi.org/10.1016/ i.cclet.2021.02.046. In press.
- [33] Y. Yang, H. Chen, X. Zou, et al., ACS Appl. Mater. Interfaces 12 (22) (2020) 24845–24854.
- [34] A. Zada, N. Ali, F. Subhan, et al., Prog. Nat. Sci.: Mater 29 (2) (2019) 138-144.
- [35] W. Yin, B. Wen, Q. Ge, et al., Prog. Nat. Sci.: Mater 29 (3) (2019) 335–340.
- [36] W. Ji, X.-L. Shi, W.-D. Liu, et al., Nanomater. Energy 87 (2021), 106171.
- [37] W. Meng, X. Liu, H. Song, et al., Nano Today 40 (2021), 101273.
- [38] L. Fu, R. Wang, C. Zhao, et al., Chem. Eng. J. 414 (2021), 128857.

#### Progress in Natural Science: Materials International 31 (2021) 858-864

- [39] D. Chatterjee, V.R. Patnam, A. Sikdar, et al., J. Hazard Mater. 156 (1) (2008) 435-441.
- [40] B. Tryba, A.W. Morawski, M. Inagaki, et al., Appl. Catal. B Environ. 63 (3) (2006) 215-221.
- [41] F. Bekena, D.-H. Kuo, Mater. Sci. Semicond. Process. 116 (2020), 105152.
- [42] Y. Ge, H. Luo, J. Huang, et al., Opt. Mater. 115 (2021), 111058.
- [43] H. Wang, H.-L. Wang, W.-F. Jiang, et al., Water Res. 43 (1) (2009) 204–210.
- [44] R.K. Biswas, M. Wakihara, M. Taniguchi, Hydrometallurgy 14 (2) (1985) 219-230. [45] L. Luo, T. Miyazaki, A. Shibayama, et al., Miner. Eng. 16 (7) (2003) 665–670.
- [46] J.R. Kumar, S.M. Shin, H.S. Yoon, et al., Separ. Sci. Technol. 49 (6) (2014) 819-828.
- [47] F. Yang, X. Li, L. Han, et al., Mining, Metall. Explor 37 (5) (2020) 1667-1672.
- [48] G.S.d. Rosa, T.R. Martiny, G.L. Dotto, et al., Sustain. Mater. Techno 28 (2021) e00276.
- [49] Z.-G. Deng, C. Wei, G. Fan, et al., T. Nonferr, Metal. Soc. 20 (1) (2010) 118-122.
- [50] R. Navarro, J. Guzman, I. Saucedo, et al., Waste Manag. 27 (3) (2007) 425-438.
- [51] Z. Liu, Y. Zhang, Z. Dai, et al., Front. Chem. Sci. Eng. 14 (5) (2020) 902–912.
- [52] H. Chen, D. Li, W. Ding, Sci. Adv. Mater. 10 (9) (2018) 1241–1249.
  [53] A. Houas, H. Lachheb, M. Ksibi, et al., Appl. Catal. B Environ. 31 (2) (2001) 145-157.