Purification and Characterization of High Purity Nano Zirconia by Liquid-Liquid Extraction Using D2EHPA/p-Xylenes

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Abstract: In this paper, Zr(IV) nitrate solution decomposed from Viet Nam zircon concentrate was the source of zirconium extraction by liquid-liquid extraction (L.L.E). The FT-IR and UV-Vis spectra confirmed the extraction of Zr(IV) by D2EHPA/p-xylenes. There were four stages for the purification of impurities from the Zr matrix. First, the extraction of elements in 3.0 M HNO₃ by 50% D2EHPA/p-xylenes was conducted. Second, two scrubbing cycles of impurities using 6.0 M HNO₃, 76.5% of the total amount of Zr(IV) were retained in the organic phase, and 23.5% remained in the aqueous phase. Third, the stripping of a macro amount of zirconium from loaded D2EHPA has been effectively carried out using 1.5 M H₂SO₄ with a stripping efficiency of 99.6%. Fourth, concentrated ammonia was added to the solution Zr(IV) after stripping extraction to form precipitate for calcination at 550 °C for the final products. The refined products were characterized by X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), EDS, XRF, and diffuse reflectance spectroscopy. The ZrO₂ has high purity, is nanospherical, and has a uniform sphere-like morphology with small grain size of less than 30 nm and a bandgap value of about 3.30 eV.

Keywords: high purity; nanospherical; ZrO₂; extraction; D2EHPA; p-xylenes

1. Introduction

High-purity zirconium exhibits superior mechanical properties such as high corrosion resistance and low neutron cross-section and is thus often used in nuclear applications. In nature, two common forms of Zr–ZrSiO₄ and ZrO₂– are often exploited in titanium mines. In Viet Nam, titanium mines are mainly distributed in Ha Tinh, Thua Thien Hue, and Binh Thuan provinces, and most of Viet Nam’s zircon minerals are exported to foreign countries, mainly in raw form (content about 62.28% ZrO₂) or in zircon concentrate form (content > 65% ZrO₂), and in modest amounts compared to the total amount of ore mined.

According to the relevant studies, Zr(IV) can be effectively extracted from acid medium by some extractants diluted in kerosene, benzene, and toluene, such as bis (2-ethylhexyl) phosphoric acid (D2EHPA) [1], N,N,N′,N′–tetraoctyldiglycolamide (TODGA) [2], N–n–Octylaniline [3], 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) [4], di (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [5], 2-hydroxy-5-nonyl-acetophenone (LIX84-IC) [6], tributyl phosphate (TBP) [7], 1-phenyl-3-methyl-4-benzoyl-5-pyrazone (PMBP), trioctyl phosphin oxide (TOPO or Cyanex 921) [8,9], di isobutyl ketone (DIBK) and P204 [10], bis (2-ethylhexyl)-1-(2-ethylhexylamino) propylphosphonate (BEAP) [11], Cyanex 923 [12–14], and Cyanex 921 [15].
The Zr(IV) was quantitatively separated higher than 99% of the matrix in HNO₃ media by PMBP/xylenes [16], D2EHPA/xylenes [17] to determine the trace rare earth and trace other impurities in pure ZrO₂ or zircalloys by the ICP-MS method. In some other studies, D2EHPA was rated as an effective organophosphorus compound for the separation of Zr(IV), Hf(IV), In(III), V(IV), and other metal ions from acid solutions. D2EHPA (C₁₆H₃₄PO₃(OH), M = 322.43 g mol⁻¹) has pKₐ = 3.2 in methanol and contains good stability, high selectivity, affordability, and low solubility in acidic aqueous solutions with a phosphoryl group in its molecular structure (Figure 1) [18–20].

![Figure 1. The structure of di(2-ethylhexyl) phosphoric acid (D2EHPA).](image)

In our previous study, we investigated the separation of the Zr matrix by solvent extraction using PC88A diluted in toluene for the determination of impurities and obtained ZrO₂ nanostructure [21].

Furthermore, nano ZrO₂ has many industrial applications such as for the fabrication of nanophosphor with color tunable photoluminescence and enhanced photocatalytic efficiency [22], enhanced efficiency for the separation of some ions from wastewater [23], the synthesis of sintered WC-bronze-based diamond composites [24], the anti-corrosion effect of ZrO₂ nano-modified coating on a steel surface in hot mixed acid solution [25], the studied properties of deposition Ni-Co-ZrO₂ for ultrasonic-assisted electrochemical [26], synthetic ZrO₂ doped multi-elements for photodegradation of indigo carmine within the conditions of visible-light [27], the hydrogenation of CO₂ to methanol by ZnO-ZrO₂ solid solution catalyst [28], using Pt/CeO₂-ZrO₂-ZnO catalysts for complete toluene oxidation [29], synthetic nano-ZrO₂–SnO₂ for enhanced photocatalytic properties for the photodegradation of an azo dye [30], the preparation of TiO₂/ZrO₂ nanocomposites for photocatalysis activity in the environment [31], and the synthesis ZrO₂/CeO₂ nanocomposite for photocatalytic organic reactions under visible light [32].

Although the use of D2EHPA as an extractant for the recovery of Zr(IV) has been widely studied, the literature concerning its application for the purification of nano ZrO₂ is scarce. Therefore, in this research, we aimed to investigate the synthesis of high-purity nano ZrO₂ by L.L.E using D2EHPA from Vietnamese zircon mineral since reduction costs are associated with purchased or imported high-purity zirconium resources from foreign countries. The results are an addition to the application of high-purity ZrO₂ nanomaterials in nuclear reactors and the synthesis of composites based on zirconium for photocatalysis and photoluminescence.

2. Results and Discussion

2.1. FT-IR and UV-Vis Spectra

The Fourier-Transform-Infrared (FT-IR) and Ultraviolet-Visible (UV-Vis) spectra of ZrO(NO₃)₂, D2EHPA/p-xylenes, and Zr–D2EHPA/p-xylenes are shown in Figure 2a,b.

FT-IR spectra (Figure 2a) showed the broad band centered at 3444.43 cm⁻¹ and a band at 1633.64 cm⁻¹ corresponding to the νOH stretching and bending vibrations, respectively, due to the presence of adsorbed water or surface hydroxyl groups; frequencies were present in bands at 1553 cm⁻¹ in the Zr–D2EHPA complex. Moreover, the absorption band at 1230 cm⁻¹ for P=O vibration in D2EHPA was changed into 1271 cm⁻¹ in the complex. Especially, the absorption band at 1035 cm⁻¹ for P–O–CH₂ vibration in D2EHPA is split into two bands at 1140 cm⁻¹ and 1047 cm⁻¹ in the complex. In addition, the appearance of band at 587 cm⁻¹ can be attributed to Zr–O vibration mode, confirming the formation of the Zr–D2EHPA complex [33,34]. It is clearly shown that the wave numbers of the P=O and
P–O–CH\textsubscript{2} vibrations in the Zr–D2EHPA complex shift higher than in D2EHPA, and the deviations are 41 cm\textsuperscript{−1} and 105 cm\textsuperscript{−1}, respectively, demonstrating that Zr(IV) complexed with D2EHPA and the complex is formed [1,4].

The above apparent changes confirmed the bonding between the P=O group of D2EHPA with ZrO\textsuperscript{2+} ion. The results are in line with previously reported results [1].

Figure 2b indicates that the UV-Vis spectrum of the Zr–D2EHPA complex is very different to the UV-Vis spectra of ZrO(NO\textsubscript{3})\textsubscript{2} salt and the D2EHPA/p-xylenes solvent. These changes indicate the strong coordination of the (O=P–OH) group of D2EHPA and ZrO\textsuperscript{2+} ion in HNO\textsubscript{3} media, which is in line with previously reported spectra [21]. The results also suggest the pivotal role of the (P–OH) bond in D2EHPA (H\textsuperscript{+}) in the cationic exchange mechanism that allows for the extraction of ZrO\textsuperscript{2+}. This mechanism can be illustrated by the following equation:

$$\text{ZrO}^{2+} + 2\text{HNO}_3 + \text{H}_2\text{X}_2 \rightarrow \text{H}_2\text{ZrO(NO}_3)_2\text{X}_2 + 2\text{H}^+$$  \hspace{1cm} (1)

2.2. Effect of Stripping Solutions

Zr(IV) was back-extracted by stripping agents to the aqueous phase after being extracted in 3.0 M HNO\textsubscript{3} using 50% D2EHPA/p-xylenes. Stock organic solution D2EHPA was used in all the experiments. A 125 mL funel containing 30 mL of the loaded organic (29.46 gL\textsuperscript{−1}) of Zr(IV) and stripping solution at ratios was contacted and shaken vigorously at room temperature for 60 min. After 30 min of equilibration, it was separated into two phases, and analyzed Zr(IV) was analyzed in the aqueous phase because Zr is the subject of the analysis. The stripping efficiencies of zirconium from loaded D2EHPA/p-xylenes with 15 back-extraction solutions are presented in Figure 3.

The use of D2EHPA for the separation of zirconium is justified by previous stripping studies, suggesting that scrubbing extraction using 6.0 M HNO\textsubscript{3} solutions is the most appropriate process to remove, determine impurities, and separate the Zr(IV) matrix. By two cycles, back-extraction with 1.5 M H\textsubscript{2}SO\textsubscript{4} at 60 min contact phases and a phase ratio O:A (v/v) as 1:1, about 99.6% Zr(IV) was quantitatively stripped. A highly acidic, antioxidant, or combination thereof stripping solution (such as H\textsubscript{2}SO\textsubscript{4} acid) is required to decompose the complex. Initially before solvent extraction, the aqueous phase contained zirconium at a concentration of 30.00 gL\textsuperscript{−1}. In the organic phase, the Zr concentration was 29.88 gL\textsuperscript{−1} after extraction; after 2 cycles of contact by 6.0 M nitric for scrubbing and two

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![Figure 2](image-url)
cycles of contact by 1.5 M sulfuric for stripping, the Zr concentration was 22.95 gL⁻¹ in the aqueous phase. The following equation illustrates the back-extraction of Zr(IV):

\[
H_2ZrO(NO_3)_2X_2 + 2 H_2SO_4 \rightarrow H_2ZrO(SO_4)_2 + 2 H_2SO_4 + H_2X_2
\]  

(2)

Figure 3. Back-extraction efficiency (%) of Zr(IV) from loaded organic phase with 15 agents.

2.3. Separation of Impurities and Purification of ZrO₂

Based on the stripping results of Zr(IV) in Section 2.2, 6.0 M HNO₃ solutions have been used for two scrubbing cycles of impurities after L.L.E containing 30.00 gL⁻¹ Zr(IV) and 0.5 μgL⁻¹ of each impurity from 3.0 M HNO₃. The results of the separation of Zr(IV) and other impurities are shown in Table 1.

Table 1. ICP-MS for the number of impurities in the two phases after one extraction cycle by 3.0 M HNO₃, two scrubbing cycles by 6.0 M HNO₃, and two stripping cycles by 1.5 M H₂SO₄ using 50% D2EHPA/p-xylenes.

| Impurities | Li, Mg, K, Ca, Rb, Na, Sr, Ba, Cu, Al, Ga, Ti, Sc, B, Cd, Ag, Zn, Pb, Bi, Co, Ni, Se, Mn, V, As, Ce, Nd, Pr, La, Sm, Eu, Pm, Tb, Gd, Er, Ho, and Dy | Lu, Yb, Tm | Y | Fe, Ti | Hf | Zr |
|------------|------------------------------------------------------------------------------------------|------------|---|------|----|----|
| Aqueous phase, % | ≈100                                                                                   | 95.6       | 96.5 | 69.2 | 32.7 | 23.5 |
| Organic phase, % | Not detected                                                                            | 4.40       | 3.50 | 31.8 | 68.3 | 76.5 |

According to the results shown in Table 1, with the above separation process, the recovery of 41 impurities was higher than 95%, and the recovered zirconium was about 76.5%. Therefore, 50% D2EHPA/p-xylenes can be effectively used in the manufacturing technology high-purity zirconium materials.

2.4. Characterization of Obtained ZrO₂

The TGA diagram of the obtained ZrO₂ after L.L.E by D2EHPA/p-xylenes is presented in Figure 4. The Zr(OH)₂(NH₄)₂(SO₄)₂ sample may be decomposed by the following Equation (3):

\[
Zr(OH)_2(NH_4)_2(SO_4)_2 \rightarrow ^\rho ZrO_2 + 2SO_2 + 2NH_3 + O_2 + 2H_2O
\]  

(3)
2.4. Characterization of Obtained ZrO$_2$

The TGA diagram of zirconium compound is shown in Figure 4. On the thermal analysis diagram (Figure 4) of the sample Zr(OH)$_2$(NH$_4$)$_2$(SO$_4$)$_2$, there is the large mass reduction effect on the TGA curve. The total loss is large, at about 64.88%, approximating the theoretical result (65.52%). This occurs due to the release of gases such as SO$_2$, NH$_3$, O$_2$ and H$_2$O from the original sample. The weight of the sample is almost constant at temperatures higher than 550 °C. The sample undergoes complete thermal decomposition to form the final product, ZrO$_2$.

The XRD diffraction pattern for obtained ZrO$_2$ is observed in Figure 5. The result indicates the relatively amorphous state of the sample when being heated at 550 °C, major ZrO$_2$ monoclinic phase (m). The formation of the monoclinic ZrO$_2$ phase (JCPDS Card No. 01-089-9066) was evidenced by reflection peaks at 2θ = 24.44°; 28.16°; 31.43°; 40.80°; 50.60°; 55.34°; and 59.87°, corresponding to the characteristic spacing between m-(110); m-(111); m-(112); m-(220); m-(031); and m-(−203). In addition, the presence of tetragonal ZrO$_2$ phase (t) peaks at 2θ = 34.07°; 35.24°; 60.02°; and 74.51° can be assigned to the crystal planes t-(200); t-(110); t-(202); and t-(220) of the tetragonal structure (JCPDS Card No. 00-050-1089) [35–38].

![Figure 4. TGA diagram of zirconium compound.](image)

![Figure 5. XRD pattern of obtained ZrO$_2$ after L.L.E by D2EHPA/p-xylanes at 550 °C.](image)
Further examination as the major component of characteristic peaks, which is obtained using the Debye Scherer Formula (4):

\[
\tau = \frac{0.9 \times \lambda}{\beta \times \cos \theta}
\]

where the X-ray wavelength is \(\lambda\) (1.54056 nm), the Full-Width at Half-Maximum (FWHM) of the diffraction peak is \(\beta\), and the diffraction angle is \(\theta\). Peak at \(2\theta \approx 28.162^\circ\) (\(d = 3.166\) and the plane \((-111)\)) with \(\beta = 0.334^\circ\); the crystallite size of the formed ZrO\(_2\) was about 24.25 nm, which is obtained using Debye Scherer and consistent with previous results [15,21].

The detailed microstructures and morphology of ZrO\(_2\) were analyzed by SEM and TEM, as shown in Figures 6 and 7a,b. First of all, SEM images (Figure 6) and TEM images (Figure 7a,b) of the ZrO\(_2\) nanoparticles, respectively, show the shape of the nano-scale spheres. These confirmed the role of D2EHPA as an effective surfactant and a great extractant for the synthesis of purity nano ZrO\(_2\).

**Figure 6.** SEM images of ZrO\(_2\) nanoparticles after L.L.E by D2EHPA/p-xylenes.

**Figure 7.** (a,b) TEM images and (c,d) particle size distribution of ZrO\(_2\) nanoparticles after L.L.E by D2EHPA/p-xylenes.
The normal distribution curves of the particle size for TEM images of the ZrO$_2$ sample are monitored in Figure 7c,d. Accordingly, the particle size of purity ZrO$_2$ was distributed, with the average particle size being 25–30 nm. This result is consistent with the particle crystallite size calculated from Scherer’s equation.

The energy-dispersive X-ray spectrum (Figure 8) and the X-ray fluorescence data (Figure 9) are recorded for the quantitative determination of the trace elements to evaluate the product purity.

![Figure 8](https://example.com/figure8.png)

**Figure 8.** The EDS spectrum of ZrO$_2$ product after L.L.E by D2EHPA/p-xylene.

![Figure 9](https://example.com/figure9.png)

**Figure 9.** The XRF analysis for purified zirconia.

From EDS (Figure 8) and XRF (Figure 9) analysis of the obtained product, it is clear that the produced zirconium oxide is highly purified has the an absence of impurities. The results show that ZrO$_2$’s main elements are Zr (69.29%) and O (30.71%) in final sample. This result reaffirms that the zirconia product after purification by D2EHPA/p-xylene has very high purity and is consistent with the XRD pattern in Figure 5.

Compared with Cyanex 921, ZrO$_2$ products were purer in this study [15]. Compared with PC88A, the acidity of the extractant D2EHPA (pK$_a$ = 3.2) is different (pK$_a$ = 4.1). Both D2EHPA and PC88A have characteristic bonding of the (–P=O) and (P–O–CH$_2$) groups,
which are bonded strongly with Zr(IV). The results show that D2EHPA displays efficient separation of impurities and plays a role as a control agent for size and morphology, obtained purity ZrO$_2$ nanoparticles, and PC88A by L.L.E [21].

Figure 10a,b illustrates the transformation of the DRS curve and the Kubelka-Munk energy curve of the obtained ZrO$_2$. The absorption wavelength shifts of the ZrO$_2$ are determined about 375 nm, so the ZrO$_2$ is absorbed in the UV light region. The bandgap energy ($E_g$) of ZrO$_2$ is identified as being about 3.300 eV, which is much lower than previous studies of about 3.670–5.850 eV [27,36–42].

Compared with some recent studies [27,35–40], we abstracted some main points regarding the synthesis method and characterization of the obtained ZrO$_2$, as shown in Table 2.
| Ref. [27] | Ref. [35] | Ref. [36] | Ref. [37] | Ref. [38] | Ref. [39] | Ref. [40] | This Research |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|--------------|
| Method    | Microwave mediated solvothermal process | Hydrothermal process | Plasma electrolytic oxidation (PEO) | Hydrothermal route | Sol-gel Technology | Thermal oxidation | Liquid-liquid extraction |
| Resources | ZrOCl₂·8H₂O | Commercial ZrO₂ (yellow powder) | Zirconium foils | ZrOCl₂·8H₂O | Metallic Zr films | ZrSiO₄ (Thua Thien Hue, Vietnam) |
| Conditions | 0.7 g ZrOCl₂·8H₂O+20 mL 1,4-butanediol; stirred 15 min; heated in microwave at 180 °C; 800 W power; 10 min; dried at 100 °C; 24 h | 10 M NaOH; 150 °C; 85 h | Constant current density of 100 mA/cm², at 20 °C; 0.1 M citric acid; 600 s | 96% ethanol; 0.4 M Zr(IV); 60 °C; 30 min | 300–500 °C | 50% D2EHPA/p-xylene; extraction 3.0 HNO₃; scrubbing 6.0 M nitric; stripping 1.5 M sulfuric |
| Optimum heating temperature | Heated under refluxing and stirring at 180 °C; 4 h | 110 °C for 6 h | 600–1000 °C for 1 h | 550 °C for 3 h |
| Phase formed | t-ZrO₂ zirconia nanowires | Single phase t-ZrO₂ | 72% (cubic and tetragonal); 28% monoclinic | ZrO₂ films; mainly composed monoclinic | pure m-ZrO₂ | ZrO₂ thin films on glass or quartz substrates | m-ZrO₂ and polycrystalline, thin films | t-ZrO₂ and m-ZrO₂ |
| Particle crystallite size | 10.69 nm | 23.55 nm | 19–27 nm | 24.25 nm |
| The average particle size | Average 80 nm, length of over 10 µm | 30 nm | 32.5 nm | Thicknesses of 40–120 nm; refractive index 1.86–2.08 | Refractive index 2.05–2.02 | 25–30 nm |
| Bandgap value and purity of nano ZrO₂ | E<sub>g</sub> = 5.33 eV | E<sub>g</sub> = 3.67–5.0 eV | XRD (99.45% ZrO₂; 0.11% SiO₂ and another) | E<sub>g</sub> = 3.76–6.2 eV | E<sub>g</sub> = 4.28 eV | E<sub>g</sub> = 5.0–5.2 eV | E<sub>g</sub> = 5.42–5.46 eV | E<sub>g</sub> = 3.300 eV; EDS (69.29% Zr; 30.71% O); XRF (100% ZrO₂) |
3. Experimental Procedure

3.1. Preparation of the High-Purity ZrO$_2$ Nano

Sample ZrO$_2$ nanoparticles were synthesized by the liquid-liquid extraction method. All chemicals were purchased from Merck, Darmstadt, Germany (purity > 99%) and were used without further treatment: D2EHPA (95%), p-xylenes, zirconyl chloride (ZrOCl$_2$), and multi-elements standard solutions (1000 µg mL$^{-1}$), (HCl, HNO$_3$, H$_2$SO$_4$, HF, H$_2$O$_2$, and NH$_3$) concentrated solutions, and ultra water 18 MΩ. Viet Nam ZrSiO$_4$ mineral with chemical composition was composed of ZrO$_2$ (65.17%), SiO$_2$ (33.04%), Fe$_2$O$_3$ (0.004%), TiO$_2$ (0.10%), and Al$_2$O$_3$ (1.01%).

First, 2.3188 g of ZrSiO$_4$ powder (65.17%, from Thua Thien Hue province, Viet Nam) was measured and introduced into a mixture of 10 mL of concentrated HNO$_3$, 5 mL of concentrated HCl, and 5 mL of concentrated HF. Then, the mixture was boiled at 180 °C in a steel bomb for 24 h, followed by the addition of 5 mL of concentrated HNO$_3$ to remove excess HF acid and SiF$_4$. Afterwards, the solution was added to 25 mL by 0.3 M and 3.0 M HNO$_3$ while still maintaining slow heating. The Zr(IV) content in each solution was approximately 30 g L$^{-1}$.

The separation and purification of Zr(IV) by D2EHPA/p-xylenes solvent was done as follows: the equal volumes of the aqueous phase (containing 30 g L$^{-1}$ Zr(IV) in 3.0 M HNO$_3$ media) and the organic phase (50% extractant) were shaken for 60 min and for balance for 30 min. Then, the separation of the two phases and the scrubbing of the elements from organic phase for 2 cycles by 6.0 M HNO$_3$ were carried out, along with the merging of the aqueous phase and the scrubbing solutions. Finally, 5 mL of the mixture aqueous phase was added (25% nitric + 20% perchloric), heated to drying, internal standard indium (In) was added, and 0.3 M nitric solutions were dissolved to determine elements by ICP-MS (NexION300Q, PerkinElmer, USA).

After the back-extraction of the two cycles for the highest recovery of Zr(IV), drop by drop ammonia solutions into the aqueous phase to pH = 9, forming a precipitate. The precipitate was then centrifuged, washed with deionized water, and dried at 60 °C. Finally, the prepared sample was heated at 550 °C for 3 h, and allowed to cool to room temperature, for further characterization.

3.2. Characterization of Obtained ZrO$_2$

FT-IR was recorded in the range of 4000–400 cm$^{-1}$ with the help of FT-IR (Spectrum Two, PerkinElmer, Akron, OH, USA) using KBr pellets to identify the functional groups present in the sample. The UV-Vis absorption spectrum was recorded using the UV-1700 PharmaSpec, Shimadzu, Kyoto, Japan spectrophotometer. The X-ray powder diffraction patterns were characterized using the XRD, D8 Advance, Bruker, Germany diffractometer at room temperature (Cu–K$_x$ radiation, $\lambda = 0.15406$ nm) with nickel filter at a scan rate of 2°/min. The TGA diagram (Setaram Labsys Evo, France) of the zirconium compound was analyzed by differential thermal analysis from room temperature to 900 °C with a heating rate of 10 °C/min in the air. EDS (module ISIS 300 Oxford England) and XRF (ElementEye JSX-1000S EDXRF/JEOL, USA) were the determined elements in the product final.

The morphology of the ZrO$_2$ nanoparticles was evaluated by using emission scanning electronic microscope (Nova NanoSEM450-FEI-HUS-VNU, USA) operating at 5 kV. The surface morphology and microstructure of the nanocomposites were characterized by transmission electron microscopy (TEM) made with a JEOL, JEM 1010, JEOL Techniques, Tokyo, Japan operating at 200 kV. For the TEM analyses, the powders were dispersed in ethanol by sonication for 5 min. The UV-visible diffuse reflectance spectra were recorded with Carry 5000 spectroscopy.

4. Conclusions

In this investigation, the obtained ZrO$_2$ was successfully synthesized by the liquid-liquid extraction method using D2EHPA/p-xylenes from zircon concentrate in Viet Nam. The best properties of the ZrO$_2$ included high purity, nanoparticles, uniform sphere-like
morphology, small grain size less than 30 nm, and a distribution and bandgap of about 3.300 eV. The high-purity zirconia, a resource for the synthesis of photocatalysts (composites based on ZrO₂ matrix), is used for the degradation of a wide range of organic pollutants in wastewater and in various high technology fields.

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**References**

1. Biswas, R.K.; Hayat, M.A. Solvent Extraction of Zirconium(IV) from Chloride Media by D2EHPA in Kerosene. *Hydrometallurgy* 2002, 63, 149–158. [CrossRef]
2. Saleh, A.S. Solvent extraction of Zr(IV) and Hf(IV) with N,N,N′,N′-tetraoctyldiglycolamide. *J. Radioanal. Nucl. Chem.* 2012, 292, 1109–1114. [CrossRef]
3. Rajmane, M.M.; Sargar, B.M.; Mahamuni, S.V.; Anuse, M.A. Solvent Extraction Separation of Zirconium(IV) from Succinate Media with N-n-Octylaniline. *J. Serbian Chem. Soc.* 2006, 71, 223–234. [CrossRef]
4. Reddy, B.R.; Kumar, J.R.; Reddy, A.V.; Priya, D.N. Solvent Extraction of Zirconium(IV) from Acidic Chloride Solutions Using 2-EthylHexyl Phosphonic Acid Mono-2-EthylHexyl Ester (PC-88A). *Hydrometallurgy* 2004, 72, 303–307. [CrossRef]
5. Reddy, B.R.; Kumar, J.R.; Reddy, A.V. Liquid-Liquid Extraction of Tetravalent Zirconium from Acidic Chloride Solutions Using Cyanex 272. *Anal. Sci.* 2004, 20, 501–505. [CrossRef] [PubMed]
6. Reddy, B.R.; Rajesh, K.J.; Varada, R.A. Solvent Extraction of Zirconium(IV) from Acid Chloride solutions using LIX 84-IC. *Hydrometallurgy* 2004, 74, 173–177. [CrossRef] [PubMed]
7. Blazheva, I.V.; Fedorov, Y.S.; Zilberman, B.Y.; Mashirov, L.G. Extraction of Zirconium with Tributyl Phosphate from Nitric Acid Solutions. *Radiochemistry* 2008, 50, 256–260. [CrossRef]
8. Wang, L.Y.; Lee, M.S. A Review on the Aqueous Chemistry of Zr (IV) and Hf (IV) and Their Separation by Solvent Extraction. *J. Ind. Eng. Chem.* 2016, 39, 1–9. [CrossRef]
9. Wang, L.Y.; Lee, H.Y.; Lee, M.S. Solvent Extraction of Zirconium and Hafnium from Hydrochloric Acid Solutions Using Acic Organophosphorous Extractants and Their Mixtures with TOPO. *Mater. Trans.* 2013, 54, 1460–1466. [CrossRef]
10. Xu, Z.; Wang, L.; Wu, M.; Xu, Y.; Chi, R.; Li, P.; Zhao, J. Separation of Zirconium and Hafnium by Solvent Extraction Using Mixture of DIBK and P204. *Hydrometallurgy* 2016, 165, 275–281. [CrossRef]
11. Chen, S.; Zhang, Z.; Kuang, S.; Li, Y.; Huang, X.; Liao, W. Separation of Zirconium from Hafnium in Sulfate Medium Using Solvent Extraction with a New Reagent BEAP. *Hydrometallurgy 2017*, 169, 607–611. [CrossRef]
12. Amaral, J.; Antônio de Morais, C. Study of Zirconium and Hafnium Separation by Solvent Extraction Technique from Nitric and Hydrochloric Solutions with Acid, Basic and Neutral Extractants. *World J. Eng. Technol.* 2016, 4, 138–150. [CrossRef]
13. Gordon, M.R. Solvent Extraction in Hydrometallurgy: Present and Future. *Tsinghua Sci. Technol.* 2006, 11, 137–152.
14. Yudaev, P.A.; Kolpinskiaya, N.A.; Chistyakov, E.M. Organophosphorous Extractants for Metals. *Hydrometallurgy 2021*, 201, 105558. [CrossRef]
15. El Shafie, A.S.; Daher, A.M.; Ahmed, I.S.; Sheta, M.E.; Moustafa, M.M. Extraction and separation of nano-sized zirconia from nitrate medium using Cyanex 921. *Int. J. Adv. Res.* 2014, 2, 2956–2970.
16. Shi-zhong, C. Determination of Trace Rare Earth Impurities in High Purity Zirconium Dioxide by Inductively Coupled Plasma Mass Spectrometry after Separation by Solvent Extraction. *Metall. Anal.* 2006, 26, 7–10.
17. Panday, V.K.; Becker, J.S.; Dietze, H.J. Trace Impurities in Zircalloys by Inductively Coupled Plasma-Mass Spectrometry after Removal of the Matrix by Liquid Liquid Extraction. *At. Spectros.* 1995, 16, 97–101.
18. Shenkay, L.; Fuchung, C. Determination of Trace Elements in Zirconium Base Alloy by Inductively Coupled Plasma Mass Spectrometry. *Spectrochim. Acta Part B* 1990, 45, 527–535.
19. Zheng, R.; Bao, S.; Zhang, Y.; Chen, B. Synthesis of Di-(2-Ethylhexyl) Phosphoric Acid (D2EHPA)-Tributyl Phosphate (TBP) Impregnated Resin and Application in Adsorption of Vanadium (IV). Minerals 2018, 8, 206. [CrossRef]

20. Tsai, H.-S.; Tsai, T-H. Extraction Equilibrium of Indium (III) from Nitric Acid Solutions by Di (2-Ethylhexyl) Phosphoric Acid Dissolved in Kerosene. Molecules 2012, 17, 408–419. [CrossRef]

21. Chu, M.N.; Nguyen, L.T.H.; Mai, X.T.; Van Thuan, D.; Bach, L.G.; Nguyen, D.C.; Nguyen, D.C. Nano ZrO2 Synthesis by Extraction of Zr (IV) from ZrO(NO3)2 by PC88A, and Determination of Extraction Impurities by ICP-MS. Metals 2018, 8, 851. [CrossRef]

22. Vidya, Y.S.; Gurushanthan, K.; Nagabhushana, H.; Sharma, S.C.; Anantharaju, K.S.; Shivakumara, C.; Suresh, D.; Nagaswarupa, H.P.; Prashanth, S.C.; Anilkumar, M.R. Phase Transformation of ZrO2; Tb3+ Nanophosphor: Color Tunable Photoluminescence and Photocatalytic Activities. J. Alloy Compd. 2015, 622, 86–96. [CrossRef]

23. Mahmoud, M.E.; Abdou, A.H.E.; Sobhy, M.E. Engineered Nano-Zirconium Oxide-Crosslinked-Nanolayer of Carboxymethyl Cellulose for Speckleation and Adsorptive Removal of Cr(III) and Cr(VI). Powder Technol. 2017, 321, 444–453. [CrossRef]

24. Sun, Y.; Wu, H.; Li, M.; Meng, Q.; Gao, K.; Liu, B. The Effect of ZrO2 Nanoparticles on the Microstructure and Properties of Sintered WC–Bronze-Based Diamond Composites. Materials 2016, 9, 343. [CrossRef] [PubMed]

25. Xu, W.; Wang, Z.; Han, E.-H.; Wang, S.; Liu, Q. Corrosion Performance of Nano-ZrO2 Modified Coatings in Hot Mixed Acid Solutions. Materials 2018, 11, 934. [CrossRef] [PubMed]

26. Wang, Y.; Zhou, X.; Liang, Z.; Jin, H. Characterization of Ultrasonic-Assisted Electrochemical Deposition of Ni-Co-ZrO2. Coatings 2018, 8, 211. [CrossRef]

27. Cao, H.; Qiu, X.; Luo, B.; Liang, Y.; Zhang, Y.; Tan, R.; Zhao, M.; Zhu, Q. Synthesis and room-temperature ultraviolet photoluminescence properties of Zirconia nanowires. Adv. Funct. Mater. 2014, 14, 243–246. [CrossRef]

28. Wang, J.; Li, G.; Li, Z.; Tang, C.; Feng, Z.; An, H.; Liu, H.; Liu, T.; Li, C. A Highly Selective and Stable ZnO-ZrO2 Solid Solution Catalyst for CO2 Hydrogenation to Methanol. Sci. Adv. 2017, 3, e1701290. [CrossRef]

29. Kim, M.Y.; Kamata, T.; Masui, T.; Imanaka, N. Complete Toluene Oxidation on Pt/CeO2-ZrO2-ZnO Catalysts. Catalysts 2013, 3, 646–655. [CrossRef]

30. Wang, X.; Zhai, B.; Yang, M.; Han, W.; Shao, X. ZrO2 Nanoparticles on the Microstructure and Properties of Zirconia Nanostructures. J. Alloys Compd. 2015, 621, 662–667. [CrossRef]

31. Chen, X.; Wang, X.; Fu, X. Hierarchical Macro/Mesoporous TiO2/SiO2 and TiO2/ZrO2 Nanocomposites for Environmental Photocatalysis. Energy Environ. Sci. 2009, 2, 872–877. [CrossRef]

32. Wang, X.; Zhao, B.; Yang, M.; Han, W.; Shao, X. ZrO2/CeO2 Nanocomposite: Two Step Synthesis, Microstructure, and Visible-Light Photocatalytic Activity. Mater. Lett. 2013, 112, 90–93. [CrossRef]

33. Agorku, E.S.; Kuvarega, A.T.; Mamba, B.B.; Pandey, A.C.; Mishra, A.K. Enhanced visible-light photocatalytic activity of multi-elements-doped ZrO2 for degradation of indigo carmine. J. Rare Earths 2015, 33, 498–506. [CrossRef]

34. Vuong, P.H.; Pham, V.H.; Phuong, D.T.; Nguyen, T.H.H.; Cao, X.T. The role of Cu2+ Concentration in Luminescence Quenching of Eu3+/Cu2+ Co-doped ZrO2 Nanoparticles. VNU J. Sci. Math.-Phys. 2019, 35, 72–77.

35. Mishra, S.; Debnath, A.; Muthe, K.; Das, N.; Parhi, P. Rapid synthesis of tetragonal zirconia nanoparticles by microwave-solvothermal route and its photocatalytic activity towards organic dyes and hexavalent chromium in single and binary component systems. Colloids Surfaces A Physicochem. Eng. Asp. 2020, 608, 125551. [CrossRef]

36. Behbahani, A.; Rowshanzamir, S.; Esmaeilifar, A. Hydrothermal synthesis of zirconia nanoparticles from commercial zirconia. Procedia Eng. 2012, 42, 908–917. [CrossRef]

37. Stojadinović, S.; Vasilić, R.; Radić, N.; Gričić, B. Zirconia films formed by plasma electrolytic oxidation: Photoluminescent and photocatalytic properties. Opt. Mater. 2015, 40, 20–25. [CrossRef]

38. Kumari, L.; Li, W.Z.; Xu, J.M.; Leblanc, R.M.; Wang, D.Z.; Li, Y.; Guo, H.; Zhang, J. Controlled Hydrothermal Synthesis of Zirconium Oxide Nanostructures and Their Optical Properties. Cryst. Growth Des. 2009, 9, 3874–3880. [CrossRef]

39. Borilo, L.P.; Spivakova, L.N. Synthesis and Characterization of ZrO2 Thin Films. Am. J. Mater. Sci. 2012, 2, 119–124. [CrossRef]

40. Sunke, V.; Suda, U. Structural and Optical Properties of Thermally Oxidized Zirconium Dioxide Films. Int. Lett. Chem. Phys. Astron. 2018, 77, 15–25. [CrossRef]

41. Reddy, C.V.; Babu, B.; Reddy, I.N.; Shim, J. Synthesis and characterization of pure tetragonal ZrO2 nanoparticles with enhanced photocatalytic activity. Ceram. Int. 2018, 44, 6940–6948. [CrossRef]

42. Oluwabii, A.T.; Acik, I.O.; Katerski, A.; Mere, A.; Krunks, M. Structural and electrical characterisation of high-k ZrO2 thin films deposited by chemical spray pyrolysis method. Thin Solid Films 2018, 662, 129–136. [CrossRef]