



Article

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



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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-hydroxyl-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 pK_a = 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].

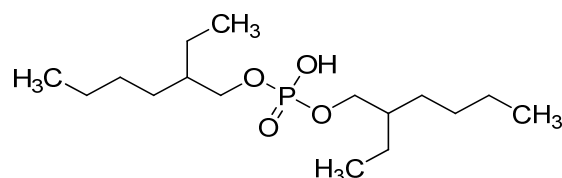


Figure 1. The structure of di(2-ethylhexyl) phosphoric acid (D2EHPA).

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 ν_{OH} 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–CH₂ vibrations in the Zr–D2EHPA complex shift higher than in D2EHPA, and the deviations are 41 cm^{−1} and 105 cm^{−1}, respectively, demonstrating that Zr(IV) complexed with D2EHPA and the complex is formed [1,4].

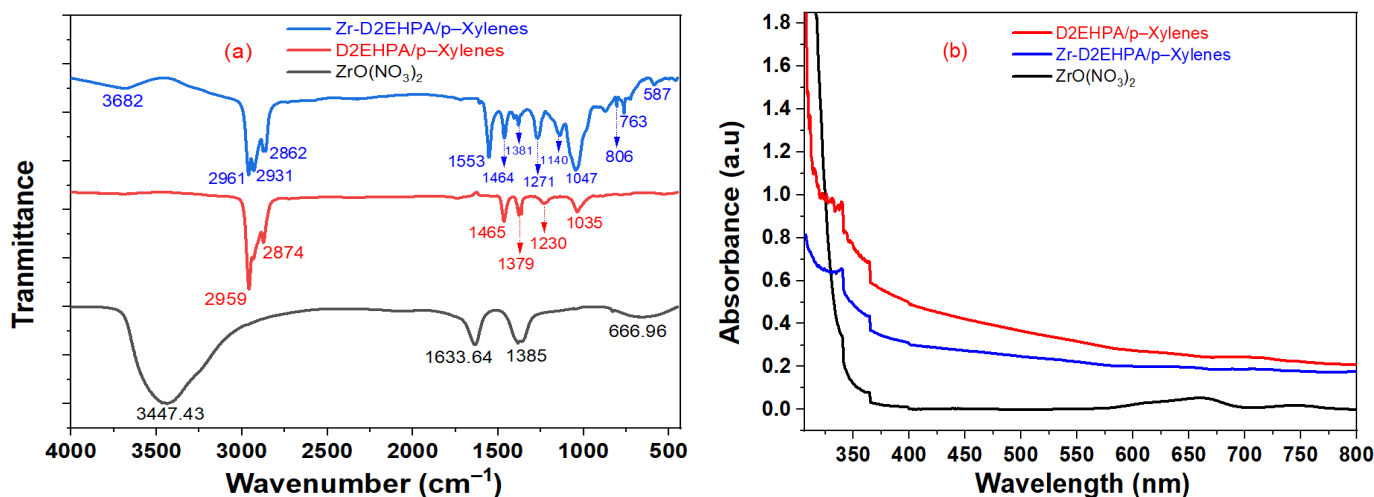


Figure 2. (a) FT-IR spectra and (b) UV-Vis spectra of ZrO(NO₃)₂; D2EHPA/p-xylenes; and Zr-D2EHPA/p-xylenes.

The above apparent changes confirmed the bonding between the P=O group of D2EHPA with ZrO²⁺ 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(NO₃)₂ salt and the D2EHPA/p-xylenes solvent. These changes indicate the strong coordination of the (O=P–OH) group of D2EHPA and ZrO²⁺ ion in HNO₃ media, which is in line with previously reported spectra [21]. The results also suggest the pivotal role of the (P–OH) bond in D2EHPA (H₂X₂) in the cationic exchange mechanism that allows for the extraction of ZrO²⁺. This mechanism can be illustrated by the following equation:



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 HNO₃ using 50% D2EHPA/p-xylenes. Stock organic solution D2EHPA was used in all the experiments. A 125 mL funnel containing 30 mL of the loaded organic (29.46 gL^{−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 HNO₃ 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 H₂SO₄ 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 H₂SO₄ acid) is required to decompose the complex. Initially before solvent extraction, the aqueous phase contained zirconium at a concentration of 30.00 gL^{−1}. In the organic phase, the Zr concentration was 29.88 gL^{−1} after extraction; after 2 cycles of contact by 6.0 M nitric for scrubbing and two

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):

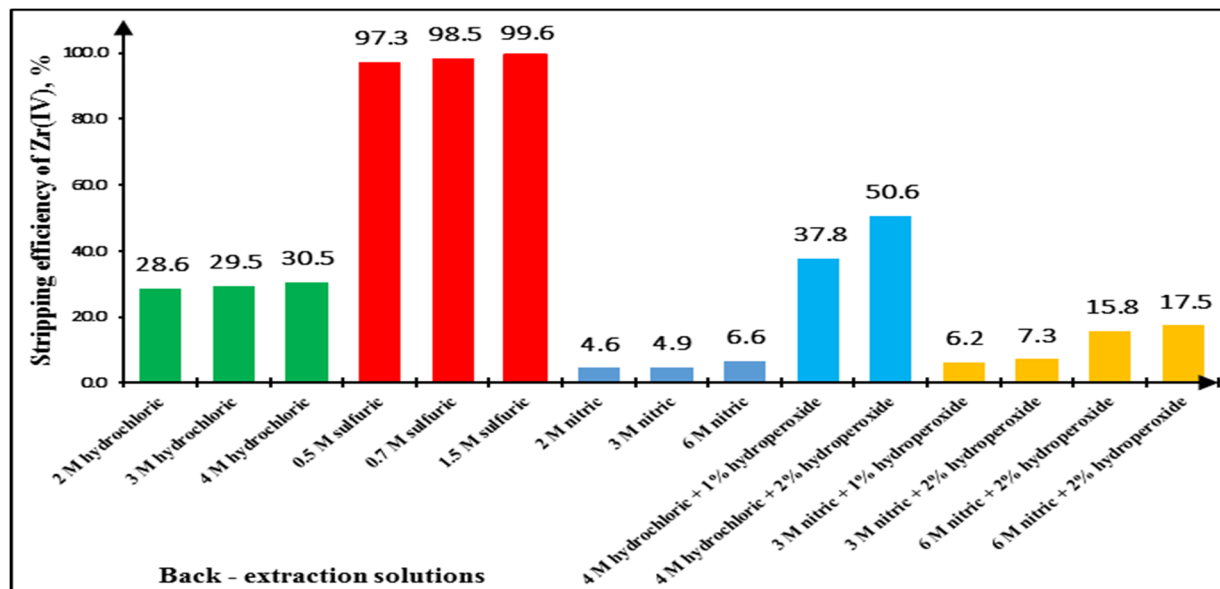
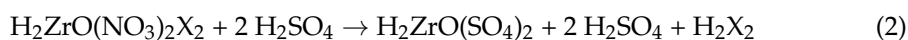


Figure 3. Back-extraction efficiency (%) of Zr(IV) from loaded organic phase with 15 agents.

2.3. Separation of Impurities and Purification of ZrO_2

Based on the stripping results of Zr(IV) in Section 2.2, 6.0 M HNO_3 solutions have been used for two scrubbing cycles of impurities after L.L.E containing 30.00 gL^{-1} Zr(IV) and $0.5 \mu\text{gL}^{-1}$ of each impurity from 3.0 M HNO_3 . 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 HNO_3 , two scrubbing cycles by 6.0 M HNO_3 , and two stripping cycles by 1.5 M H_2SO_4 using 50% D2EHPA/p-xylenes.

Impurities	Li, Mg, K, Ca, Rb, Na, Sr, Ba, Cu, Al, Ga, Tl, 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 ZrO_2

The TGA diagram of the obtained ZrO_2 after L.L.E by D2EHPA/p-xylenes is presented in Figure 4. The $\text{Zr}(\text{OH})_2(\text{NH}_4)_2(\text{SO}_4)_2$ sample may be decomposed by the following Equation (3):



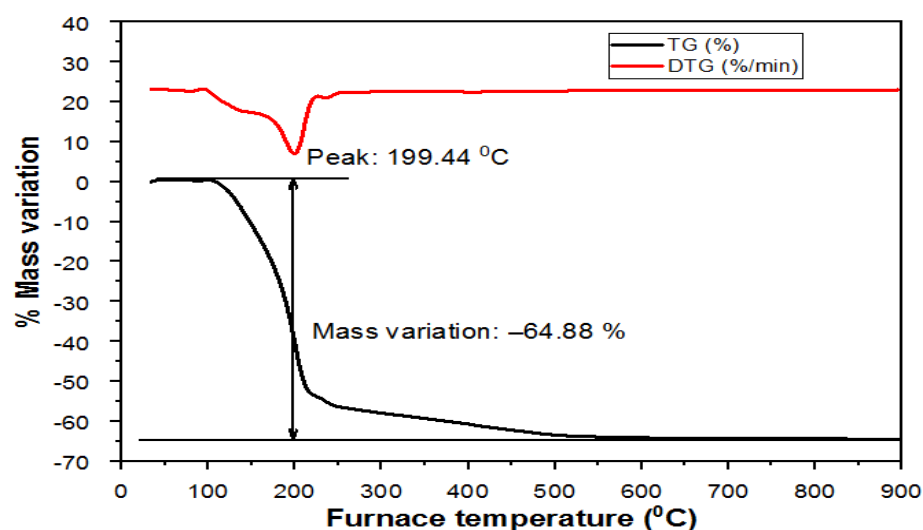


Figure 4. TGA diagram of zirconium compound.

On the thermal analysis diagram (Figure 4) of the sample $\text{Zr}(\text{OH})_2(\text{NH}_4)_2(\text{SO}_4)_2$, 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_2O 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 $2\theta = 24.44^\circ$; 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 $2\theta = 34.07^\circ$; 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].

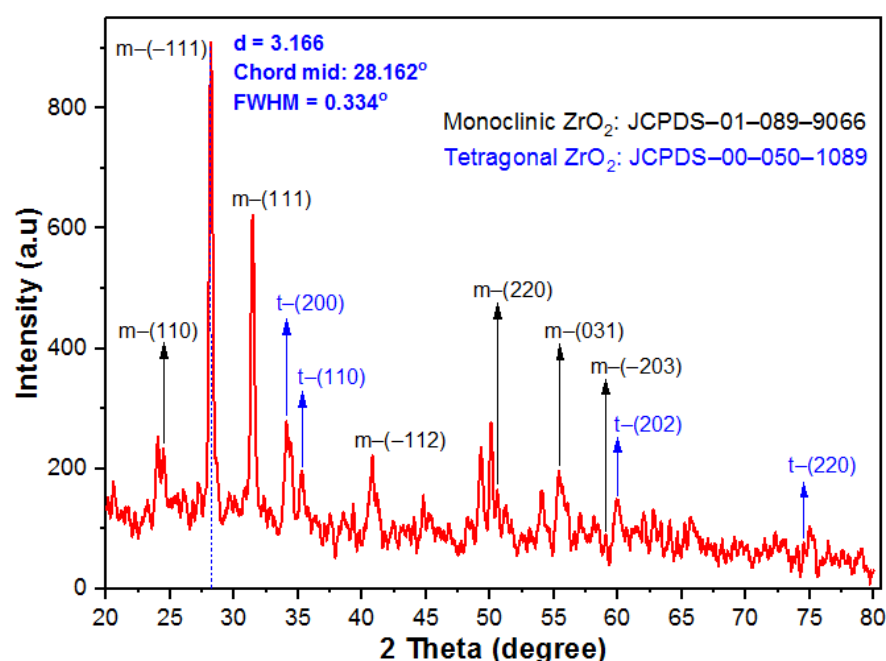


Figure 5. XRD pattern of obtained ZrO_2 after L.L.E by D2EHPA/p-xylenes at 550 °C.

Further examination as the major component of characteristic peaks, which is obtained using the Debye Scherer Formula (4):

$$\bar{r} = \frac{0.9 * \lambda}{\beta * \cos\theta} \quad (4)$$

where the X-ray wavelength is λ (1.54056 nm), the Full-Width at Half-Maximum (FWHM) of the diffraction peak is β , and the diffraction angle is θ . Peak at $2\theta = \sim 28.162^\circ$ ($d = 3.166$ 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 .

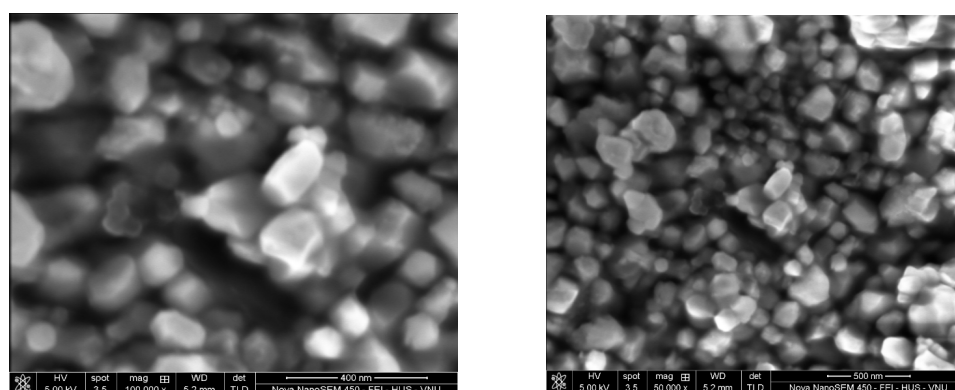


Figure 6. SEM images of ZrO_2 nanoparticles after L.L.E by D2EHPA/p-xylenes.

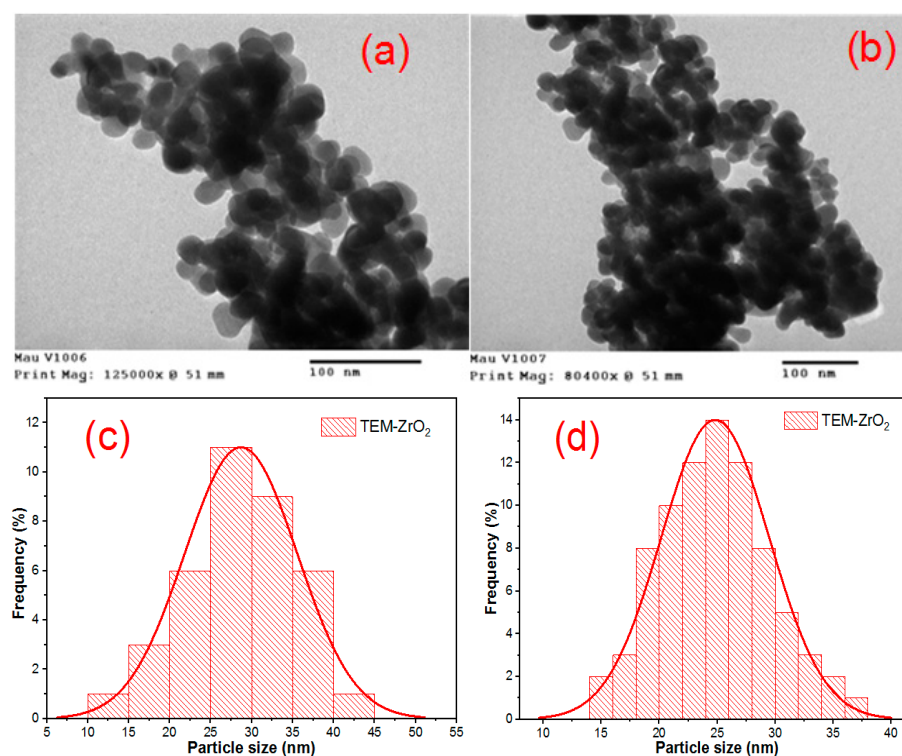


Figure 7. (a,b) TEM images and (c,d) particle size distribution of ZrO_2 nanoparticles after L.L.E by D2EHPA/p-xylenes.

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.

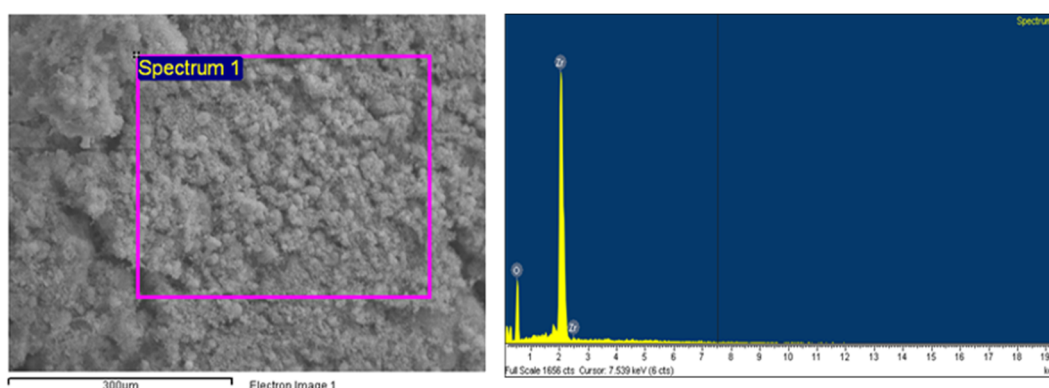


Figure 8. The EDS spectrum of ZrO_2 product after L.L.E by D2EHPA/p-xylenes.

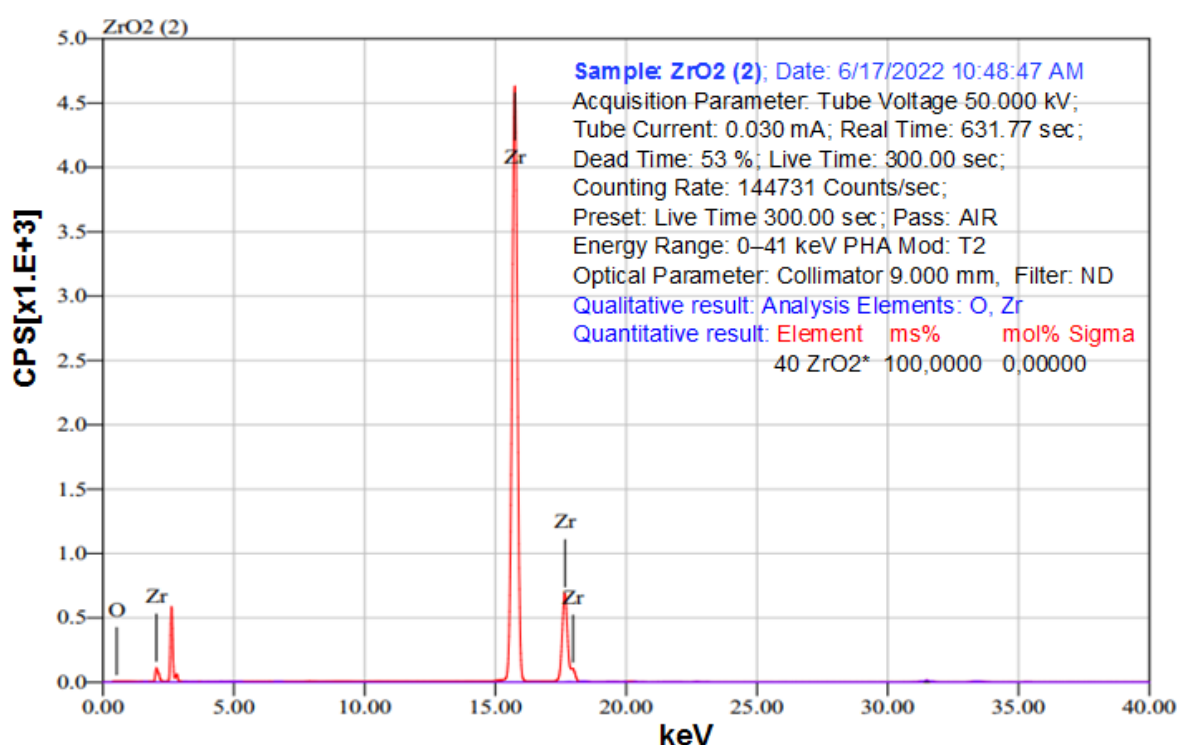


Figure 9. The XRF analysis for purified zirconia.

From EDS (Figure 8) and XRF (Figure 9) analysis of the obtained product, it is clear that the produced zirconium oxide is highly purified and has the 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-xylenes 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 ($\text{pK}_a = 3.2$) is different ($\text{pK}_a = 4.1$). Both D2EHPA and PC88A have characteristic bonding of the ($-\text{P}=\text{O}$) and ($\text{P}-\text{O}-\text{CH}_2$) 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 ZrO₂ 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 ZrO₂. The absorption wavelength shifts of the ZrO₂ are determined about 375 nm, so the ZrO₂ is absorbed in the UV light region. The bandgap energy (E_g) of ZrO₂ 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].

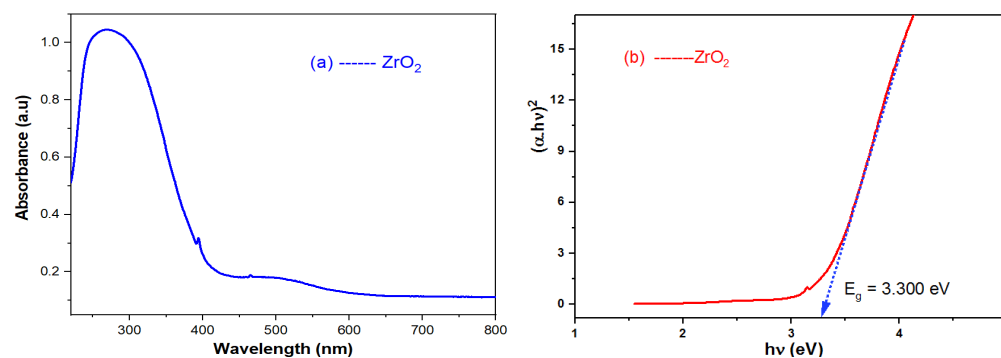


Figure 10. (a) The UV-Vis-DRS and (b) the Kubelka-Munk energy curve versus the band gap of obtained ZrO₂.

Compared with some recent studies [27,35–40], we abstracted some main points regarding the synthesis method and characterization of the obtained ZrO₂, as shown in Table 2.

Table 2. Comparison of purification method and characterization of ZrO₂ sample in previous studies.

	Ref. [27]	Ref. [35]	Ref. [36]	Ref. [37]	Ref. [38]	Ref. [39]	Ref. [40]	This Research
Method	Templates method	Microwave mediated solvothermal process	Hydrother-mal process	Plasma electrolytic oxidation (PEO)	Hydrother-mal route	Sol-gel Technology	Thermal oxidation	Liquid-liquid extraction
Resources		ZrOCl ₂ ·8H ₂ O	Commercial ZrO ₂ (yellow powder)	Zirconium foils		ZrOCl ₂ ·8H ₂ O	Metallic Zr films	ZrSiO ₄ (Thua Thien Hue, Viet Nam)
Conditions		0.7 g ZrOCl ₂ ·8H ₂ O+ 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/cm ² , 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-xylenes; extraction 3.0 HNO ₃ ; 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-ZrO ₂ zirconia nanowires	Single phase t-ZrO ₂	72% (cubic and tetragonal); 28% monoclinic	ZrO ₂ films; mainly composed monoclinic	pure m-ZrO ₂	ZrO ₂ thin films on glass or quartz substrates	m-ZrO ₂ and polycrystalline, thin films	t-ZrO ₂ and m-ZrO ₂
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 ZrO ₂	E _g = 5.33 eV	E _g = 3.67–5.0 eV	XRD (99.45% ZrO ₂ ; 0.11% SiO ₂ and another)	E _g = 3.76–6.2 eV	E _g = 4.28 eV	E _g = 5.0–5.2 eV	E _g = 5.42–5.46 eV	E _g = 3.300 eV; EDS (69.29% Zr; 30.71% O); XRF (100% ZrO ₂)

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 ($1000 \mu\text{g mL}^{-1}$), (HCl , HNO_3 , H_2SO_4 , HF , H_2O_2 , and NH_3) concentrated solutions, and ultra water 18 M Ω . Viet Nam ZrSiO_4 mineral with chemical composition was composed of ZrO_2 (65.17%), SiO_2 (33.04%), Fe_2O_3 (0.004%), TiO_2 (0.10%), and Al_2O_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 ($\text{Cu-K}\alpha$ radiation, $\lambda = 0.15406 \text{ nm}$) 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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