

Supplemental materials

Chemical Characteristics of Zirconium Chloride and Nanoparticles Zirconium Oxide Driving Toxicity on *Lemna minor*

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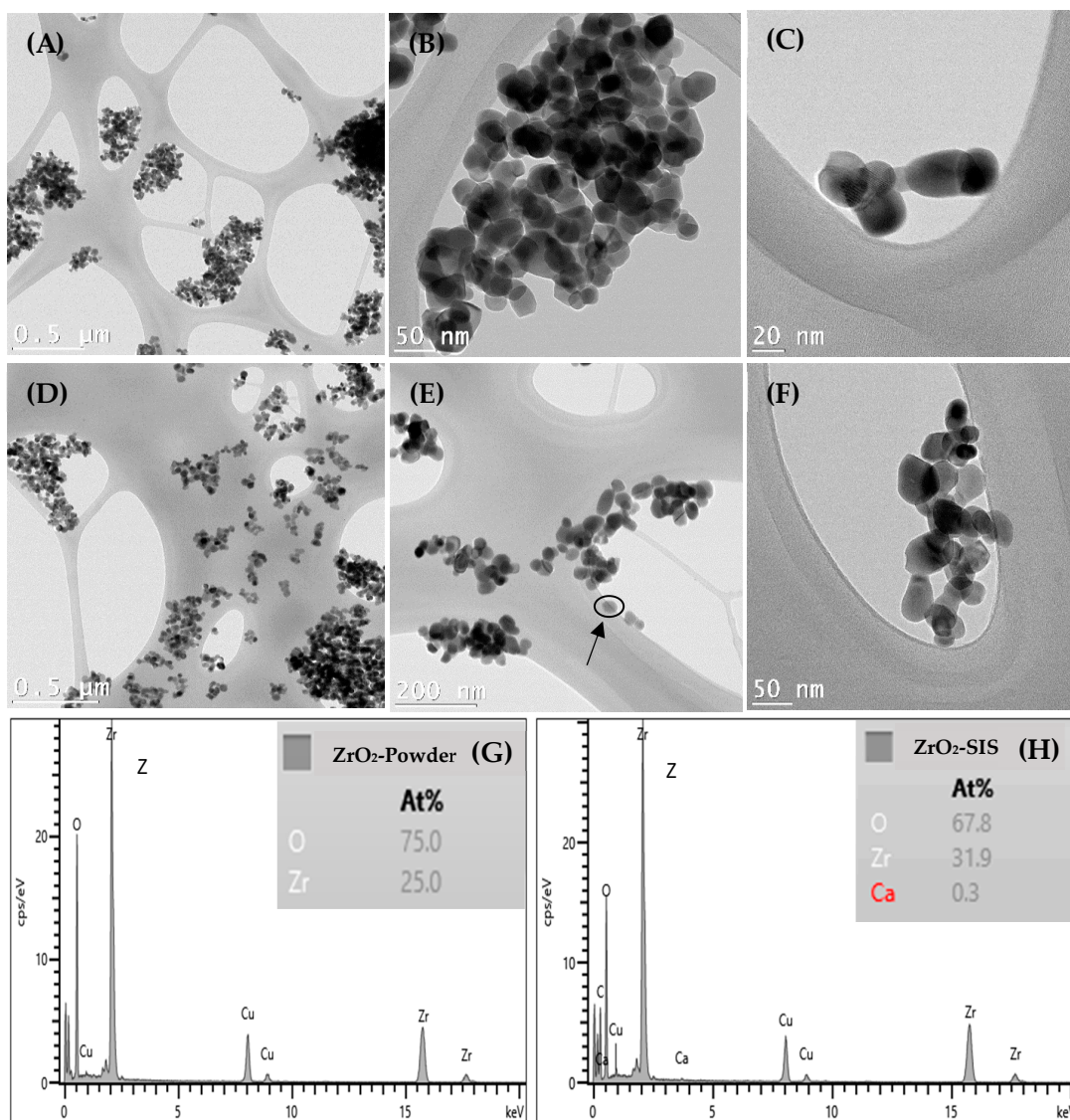


Figure S1: Transmission electron microscopic (TEM) and energy dispersive X-ray spectroscopy (EDS) analyses of zirconium oxide nanoparticles (NP-ZrO₂). A, B, C: TEM images of pure commercial NPs; D, E, F: TEM images of NPs after dissolution in SIS culture medium; G: EDS analysis as well as the atomic percentage (%) elemental composition (At) before dissolution of NPs powder; H: EDS analysis as well as the atomic percentage (%) elemental composition (At) after dissolution of NPs in SIS medium. The white bar is 0.5 μm, 200 nm, 50 nm, and 20 nm. The presence

of Zr and O confirms the ZrO_2 composition, and the appearance of Ca after dissolution (0.3%) likely comes from the SIS medium, indicating potential interaction or surface adsorption. The Cu (copper) and C (carbon) peaks in both spectra are attributed to the TEM grid and carbon film used for sample preparation, not the NPs themselves. The TEM analyses of NP- ZrO_2 were conducted at the Centre de Caractérisation des Matériaux (CM2) of École Polytechnique de Montréal. Pure commercial NP- ZrO_2 samples were prepared by dispersing a small amount of commercial powder in methanol, followed by ultrasonic bath treatment for uniform dispersion. The resulting suspension was then transferred to a copper grid covered with a film based on 'lacey carbon.' For the analysis, a JEM-2100 F model microscope from JEOL was employed with an acceleration voltage of 200 kV. The images obtained had a bright background with a resolution of approximately 0.1 nm. The EDS utilized was a TEM Xplore (Oxford). High-resolution images were obtained using a Gatan Ultrascan 1000 camera, and data acquisition was performed using digital micrograph software.

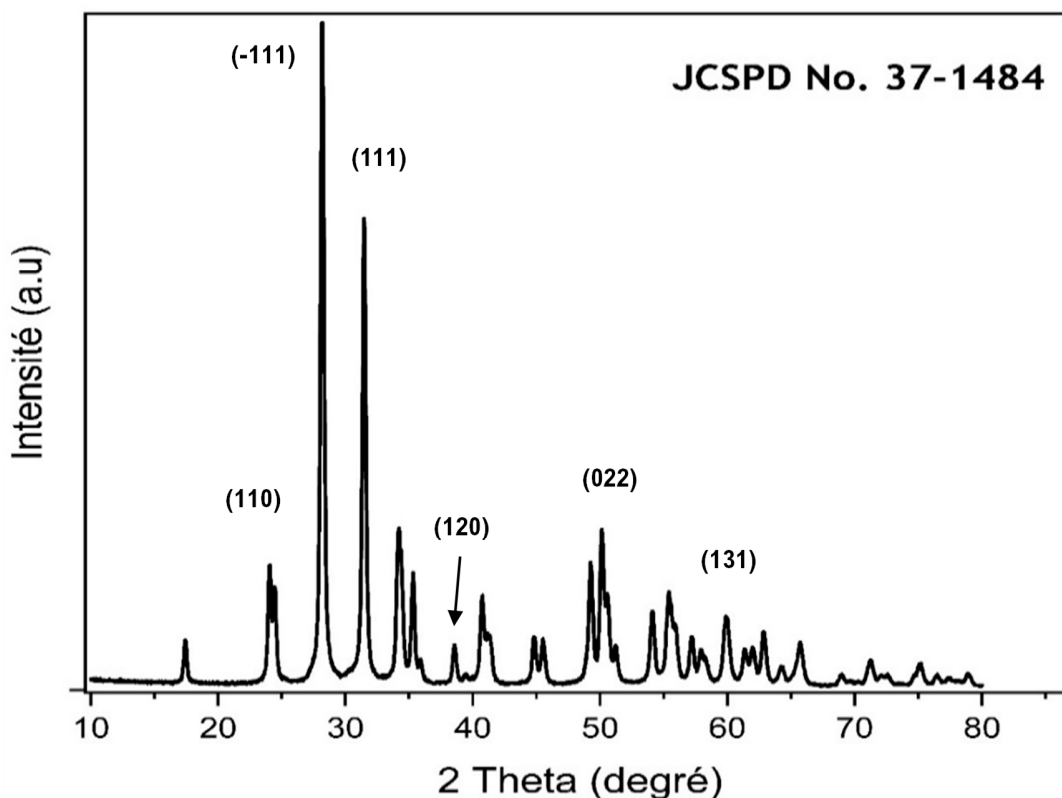


Figure S2: X-ray diffraction (XRD) analysis of zirconium oxide nanoparticles (NP- ZrO_2) determined the crystalline state of nanoparticles (NPs). No pre-treatment of samples was necessary. The NPs were deposited on a glass slide, which was then positioned on a sample holder. The Bruker D8 Advance X-ray diffractometer was utilized for characterizing the commercial NP- ZrO_2 powder. A minimal amount of powder within a capillary tube with a 0.2 mm diameter was adequate for the generation of the diffractogram. The observed X-ray diffraction peaks confirm the formation of the monoclinic phase of NP- ZrO_2 , corresponding to JCSPD No. 37-1484. The XRD

pattern shows several distinct peaks at specific 2θ angles, corresponding to the diffraction from various crystallographic planes within the NP-ZrO₂. The identified peaks at 2θ values are 24.04°, 28.17°, 31.46°, 38.54°, 51.11°, and 59.77°, corresponding to planes [110], [-111], [111], [120], [022], and [131], respectively. These peaks are finely resolved, indicating a very fine crystalline structure. Monoclinic NP-ZrO₂ were further analyzed using Wire 5.5 software with an excitation of 532 nm.

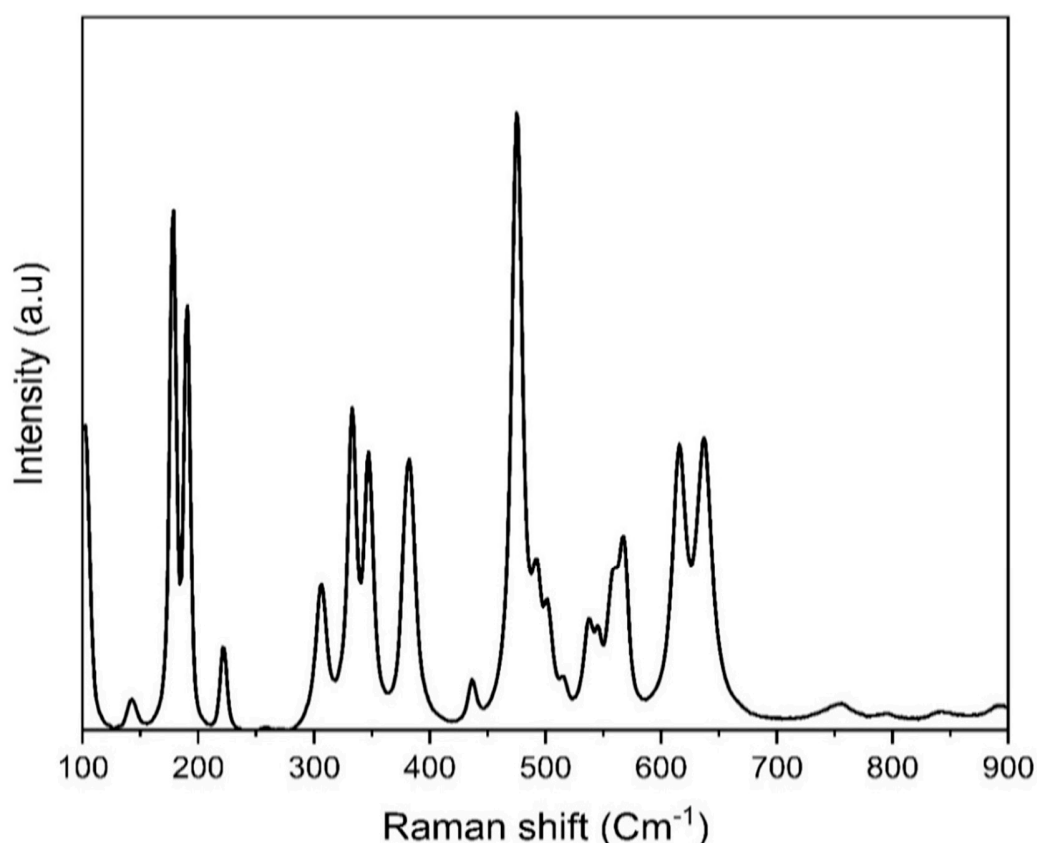


Figure S3: The Raman spectrum of zirconium oxide nanoparticles (NP-ZrO₂). The observed Raman active phonon modes were assigned to specific symmetries. The identified phonon modes include: 178-191 cm⁻¹ (Bg-Ag), 222 cm⁻¹ (Bg), 333 cm⁻¹ (Bg), 382 cm⁻¹ (Ag + Bg), 475 cm⁻¹ (Ag), and 637 cm⁻¹ (Ag). This Raman spectrum reveals information about the vibrational modes and crystalline phases present in the NP. Peaks labeled as Bg are observed at various Raman shifts, indicating the presence of monoclinic ZrO₂. Peaks labeled as Ag are also present, which are characteristic of both monoclinic and tetragonal phases. The presence of both Bg and Ag modes indicates that the sample contains a mixture of monoclinic and tetragonal phases of ZrO₂. The relative intensities of the peaks show the proportions of the different phases. The distinct vibrational bands correspond to the different crystal phases and their respective vibrational modes.

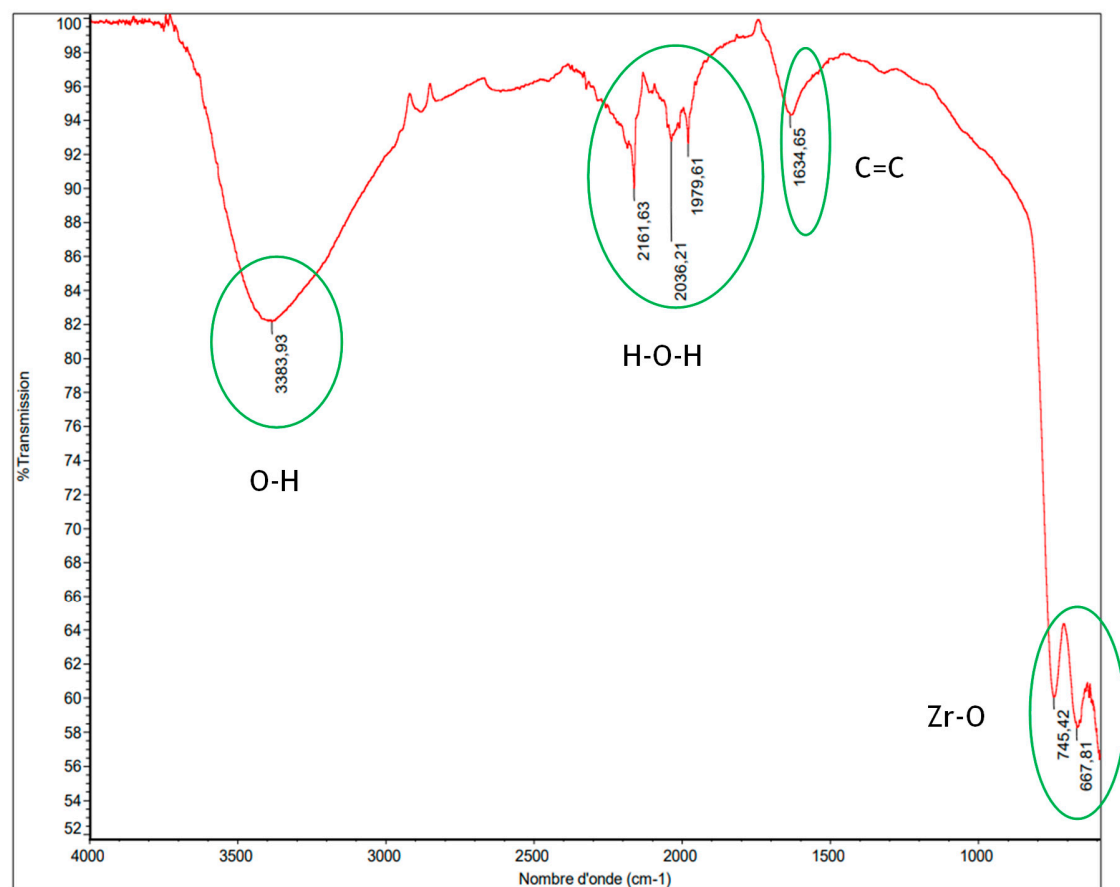


Figure S4: The FT-IR (Fourier Transform Infrared) spectrum of ZrO₂ nanoparticles (NP-ZrO₂) suspension in aqueous solution, providing insights into the functional groups and chemical bonds. The broad O-H stretching band around 3383.93 cm⁻¹ suggests the presence of surface hydroxyl groups. These groups can play a role in the surface chemistry and reactivity of the NPs, influencing their interactions with other substances. The H-O-H bending vibrations indicate that water molecules are adsorbed on the surface of the NPs, which is common due to their high surface area and affinity for water. The C=C stretching peak at 1634.65 cm⁻¹ suggests the presence of residual organic compounds in the sample. The Zr-O stretching peaks confirm the presence of zirconium oxide.