

Supporting Information

Upconversion Metal (Zr, Hf, Ta) Oxide Aerogels

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Materials

Zirconium (IV) propoxide solution (70%, Aldrich), hafnium (IV) *n*-butoxide (99%, Aldrich), tantalum (V) ethoxide (99.98 %, Aldrich), erbium (III) acetate hydrate (99.9%, Aldrich), ytterbium (III) acetate hydrate (99.95%, Aldrich), acetic acid (98%, Chimmed), hydrochloric acid (36%, Chimmed), propanol-2 (Chimmed).

Sol-gel synthesis

Sol-gel zirconia, hafnia, and tantalum oxide were produced by hydrolysis and polycondensation of zirconium propoxide, hafnium *n*-butoxide, and tantalum ethoxide respectively. To perform controlled hydrolysis, an esterification reaction route was chosen with acetic acid as a precursor.¹ The proportion of reagents for ZrO₂ production is as follows: zirconium propoxide 1.0 ml, isopropanol 9.5 mL, acetic acid 0.43 mL, hydrochloric acid 0.01 mL. In case of HfO₂: hafnium-butoxide 1.0 mL, isopropanol 6.0 mL, acetic acid 0.3 mL, hydrochloric acid 0.01 mL. For Ta₂O₅: tantalum (V) ethoxide – 0.160 mL, propanol-2 – 4.80 mL, acetic acid – 0.40 mL, hydrochloric acid – 0.03 mL.

Erbium acetate hydrate (1 mol%) and ytterbium acetate hydrate (1 mol%) were dissolved in propanol-2 under stirring at 60°C. Zirconium propoxide (hafnium *n*-butoxide, tantalum ethoxide) was added to the solution in the glove box under an inert (argon) atmosphere and stirring for 30 minutes at 60°C. Acetic acid and hydrochloric acid were added to the solution under permanent stirring for 4 hours at 60°C. The resulting mixture was poured into a polypropylene mold, which has a removable bottom. The form was placed into a closed container for 12 hours and covered by parafilm to seal the system and to avoid its drying and collapsing followed by aging.

Supercritical CO₂ (scCO₂) drying of the aerogels

Before the start the drying process the aged gels were soaked in propanol-2 for 48 hours to extract water from the sample, due to the availability of propanol-2 to dissolve in liquid CO₂, contrary to H₂O, and to prevent cracking and shrinkage. Finally, the gels, which were preliminarily immersed into fresh propanol-2, were put into an autoclave for supercritical drying.

The system E3100 Critical Point Dryer connected with E4860 thermostat (Quorum Technologies) was applied for supercritical carbon dioxide drying of the gels. The first stage of procedure was extraction of alcohol by liquid CO₂, because only the system of pure liquid CO₂

without propanol-2 can provide extinction of meniscus between liquid and gas phases in rather soft conditions (31°C and 73.7 bar).

Calcination of upconversion aerogels

The UCL appears due to the intercalation of Er³⁺ and Yb³⁺ ions into the crystalline structure of the aerogels matrix.² Embedding of ions occurs due to calcination of an aerogel in which amorphous structure changes to crystal one. Aerogels allow producing crack-free calcination in slow heating conditions. Thus, zirconia, hafnia, and tantalum oxide aerogels were placed in an oven and heated (2 °C/min) from room temperature to 800°C and baked for two hours. The oven was then cooled to ambient temperature and the aerogels were taken out for characterization.

Characterization

Textural characterization of the samples was studied at 77.4 K using a gas sorption analyzer Quantachrome NOVA 1200e. Prior to the analysis, the samples were pre-cleaned by heating under vacuum for 3 hours at 200°C to accelerate the degassing process. The surface area was analyzed using the Brunauer–Emmett–Teller (BET) method; pore size distribution and total pore volume were investigated by Brunauer-Joyner-Halenda (BJH) equations.

Rheological properties of the metal oxide gels were examined using rotational viscometer Fungilab EXPERT.

X-ray diffraction patterns were measured by Bruker D8 Advance using Cu-K radiation ($\lambda = 1.54 \text{ \AA}$). Scanning was conducted at 2θ speed 0.5° per minute. Crystallite sizes were determined from X-ray line broadening using Scherrer equation. Volume fractions of tetragonal and monoclinic zirconia, monoclinic hafnia, and orthorhombic tantalum oxide were calculated from integrated peak intensities.

Transmission electron microscopy was conducted by high-resolution transmission electron microscopy (HR-TEM) JEM-2010 (JEOL, Japan).

Photoluminescence, transmittance, and reflection of samples were measured using Ocean Optics QE Pro spectrometer. Excitation for photoluminescence measurements was provided by mercury lamp HBO 100 supplied with a set of filters for measuring photoluminescence. Excitation for transmittance, and reflection measurements was provided by HAL 100 white light pump. Full transmittance of samples was additionally measured using Labsphere integrating sphere coated with spectralon. Optical micrographs were obtained using Carl Zeiss Axio Imager.A2m microscope. The 980 nm excitation light source was an infrared laser module LSI980 - 2000 (980nm 2000mW) kit with power supply, display and power adjustment.

Results

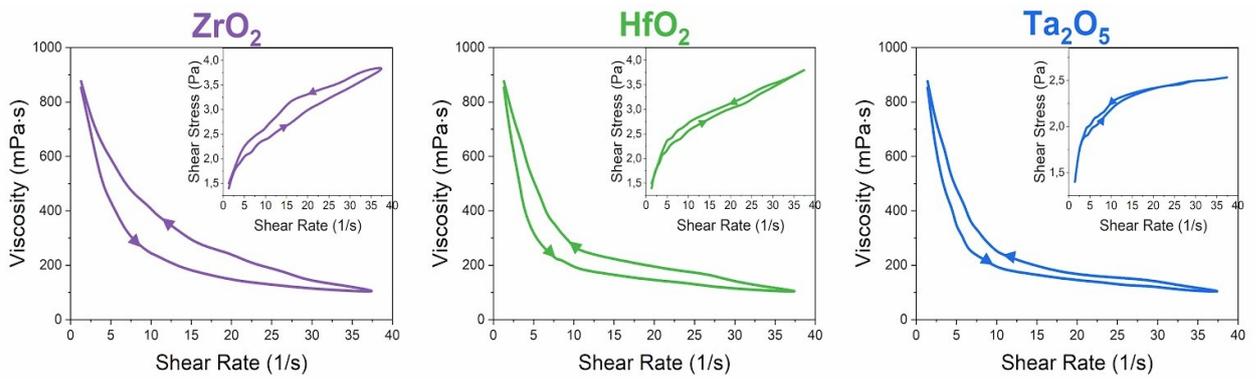


Fig. S1 Rheological data for the as-made gels; the insets show the dependence of shear stress on shear rate for metal oxide gels.

Fig. S1 shows the rheological curves for the gels of zirconium, hafnium and tantalum oxides. The similarity of the behavior for all systems is observed. These data strongly suggest that systems have very similar structure. According to the shape of the curves, the gels obtained can be ascribed to non-Newtonian pseudoplastic materials.

Additionally, the presence of a hysteresis loop on the rheological curves is a characteristic feature of thixotropy, or in other words, the ability of the system to restore its structure while reducing the shear rate. Furthermore, the presence of interlayers of the medium in the places of contact between the particles causes a relatively small strength and pronounced plastic properties of the structures.

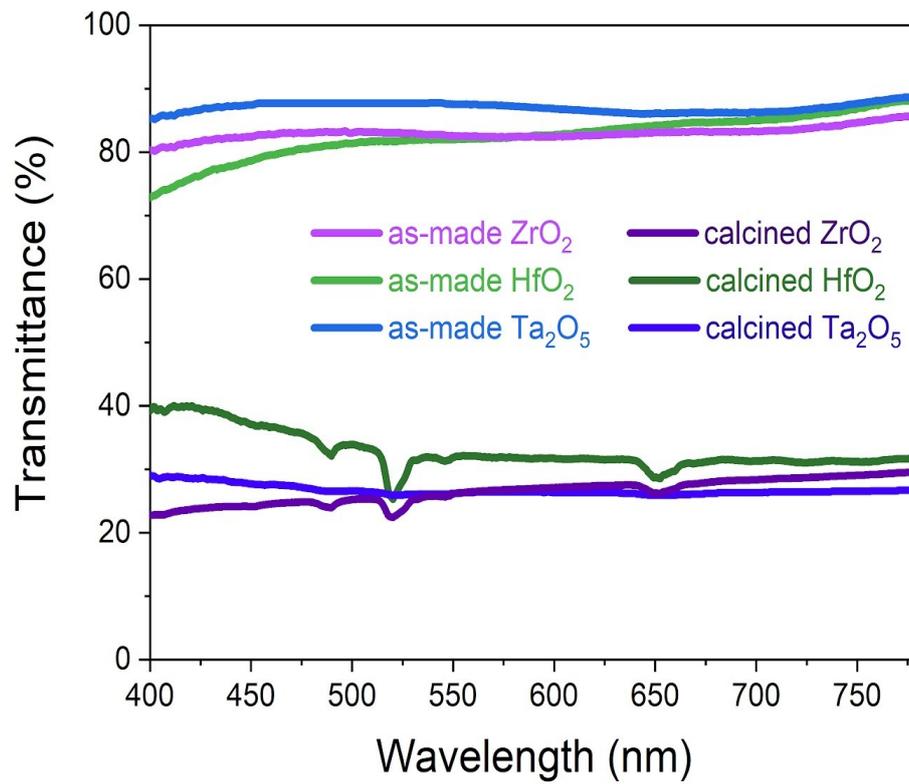


Fig. S2 Full transmittance spectra of as-made and calcined aerogels measured with integrating sphere.

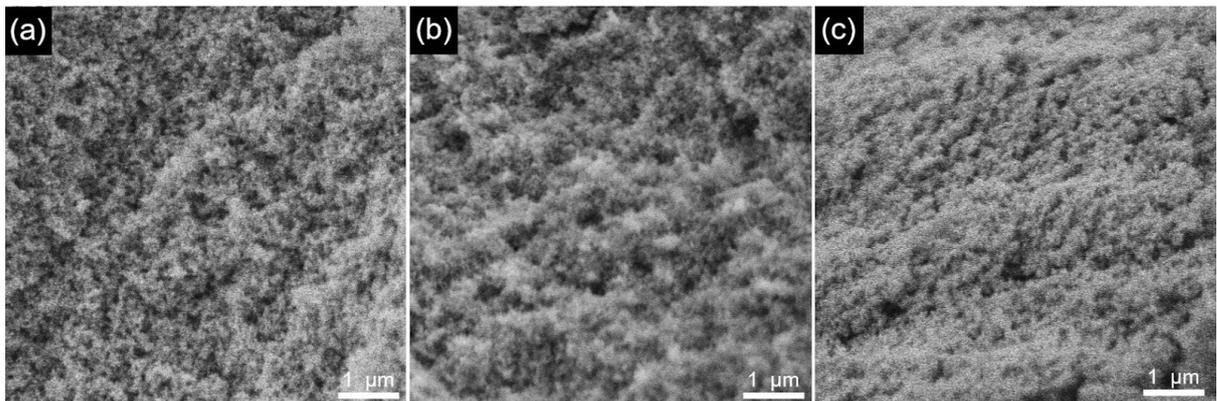


Fig. S3 SEM images of the calcined ZrO₂ (a), HfO₂ (b), and Ta₂O₅ (c) aerogels.

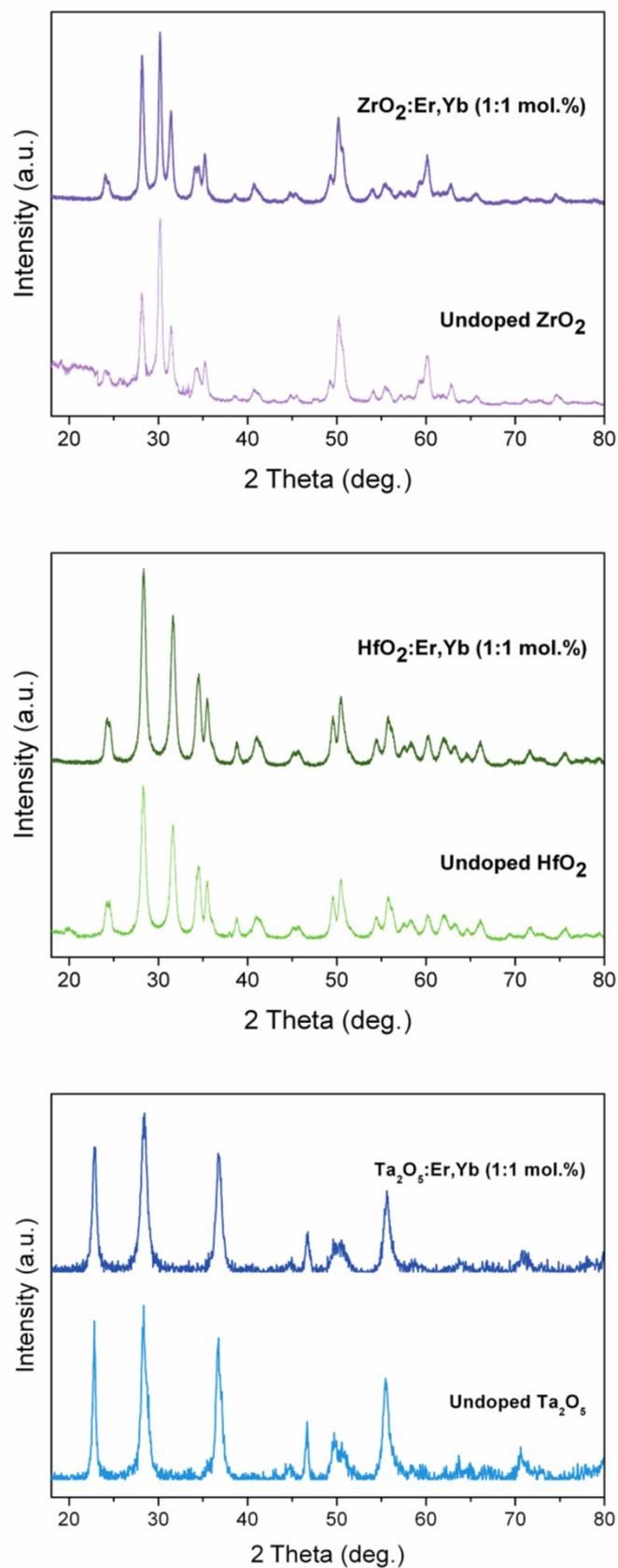


Fig. S4 XRD pattern of REE doped and undoped calcined zirconia, hafnia and tantalum oxide aerogels.

Table S1 Crystallite sizes of REE doped and undoped zirconia, hafnia and tantalum oxide aerogels after calcination.

Aerogel phase	Average CSR size (nm)
ZrO ₂ undoped tetragonal	15
ZrO ₂ doped tetragonal	17
ZrO ₂ doped monoclinic	20
HfO ₂ undoped	13
HfO ₂ doped	19
Ta ₂ O ₅ undoped	16
Ta ₂ O ₅ doped	13

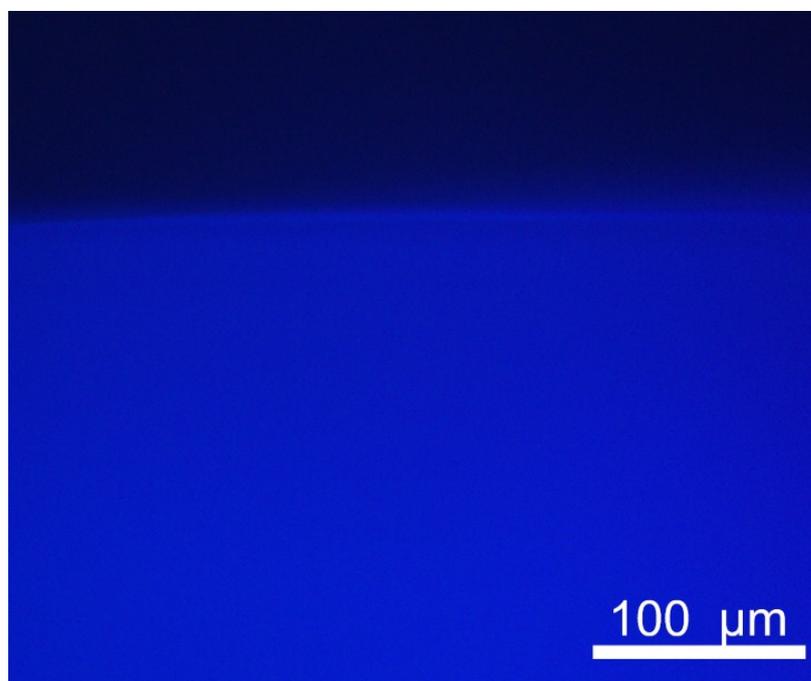


Fig. S5 Optical micrograph of as-synthesized zirconia aerogel in photoluminescence microscope under excitation with mercury lamp.

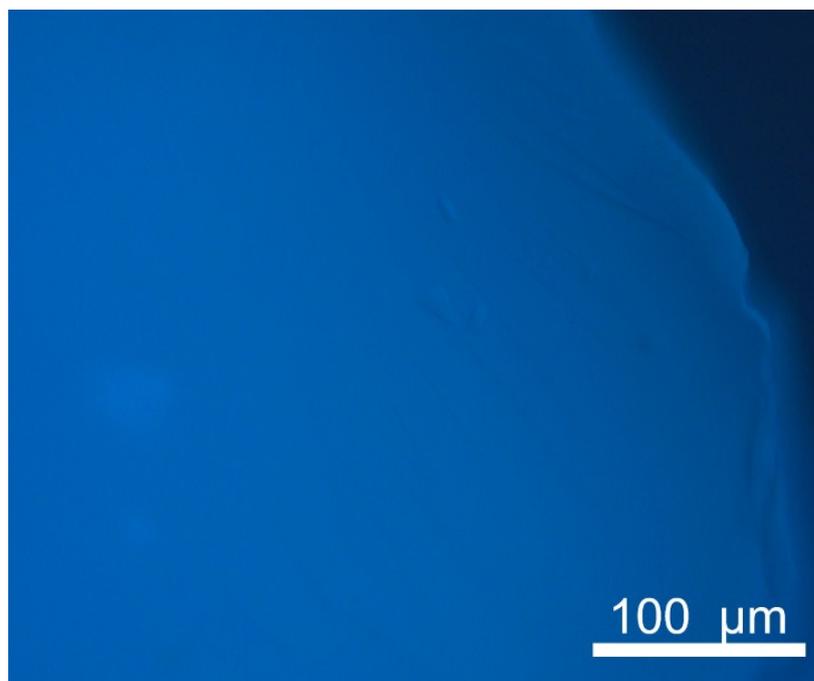


Fig. S6 Optical micrograph of as-synthesized hafnia aerogel in photoluminescence microscope under excitation with mercury lamp.

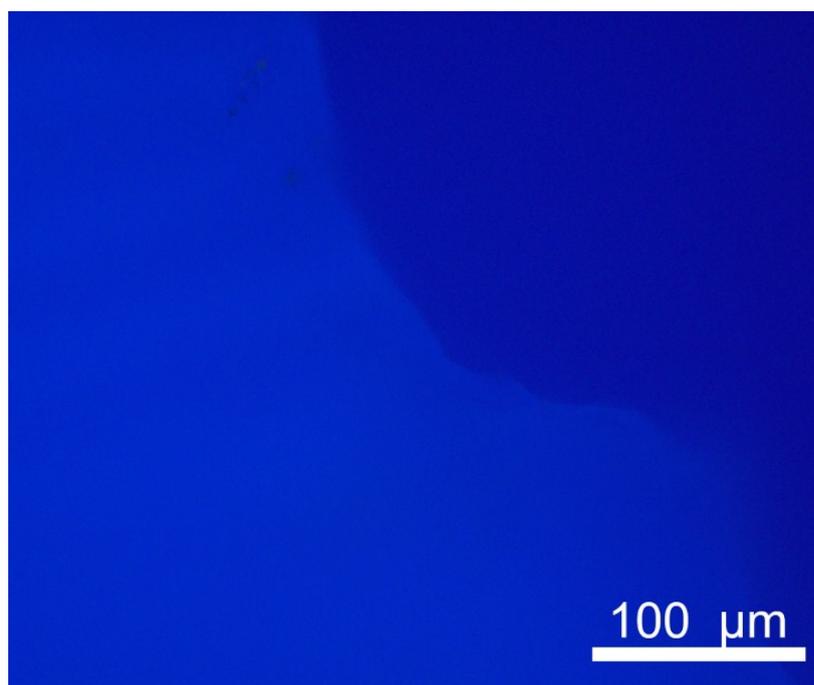


Fig. S7 Optical micrograph of as-synthesized tantalum oxide aerogel in photoluminescence microscope under excitation with mercury lamp.

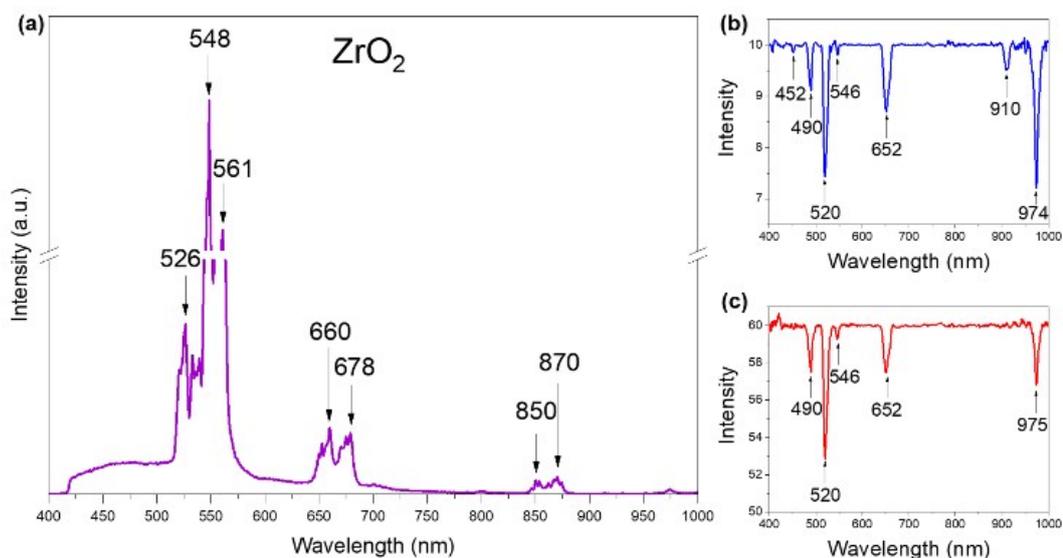


Fig. S8 Photoluminescence (a), transmittance (b) and reflection (c) spectra of doped zirconia aerogel after calcination.

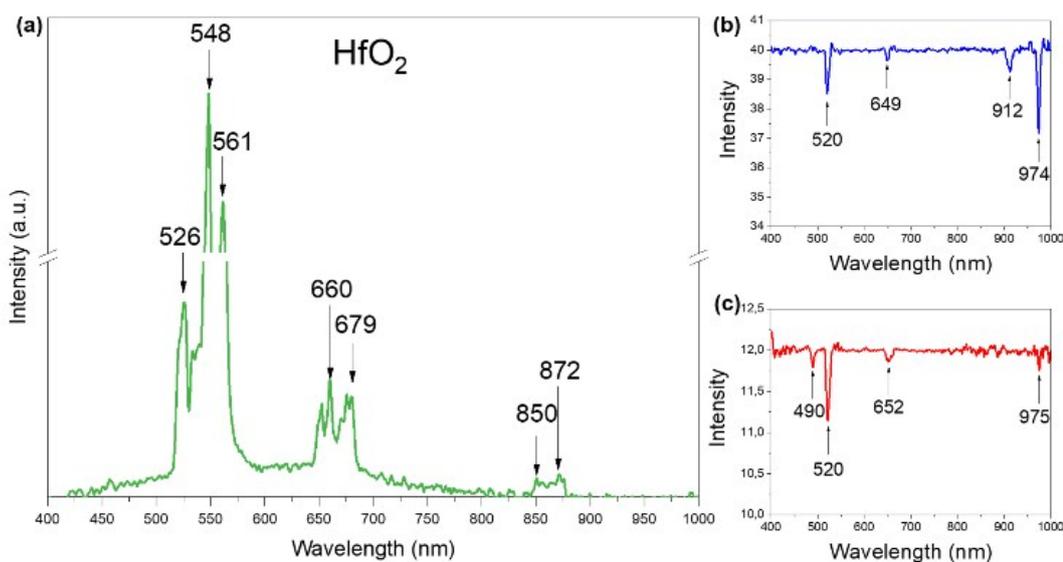


Fig. S9 Photoluminescence (a), transmittance (b) and reflection (c) spectra of doped hafnia aerogel after calcination.

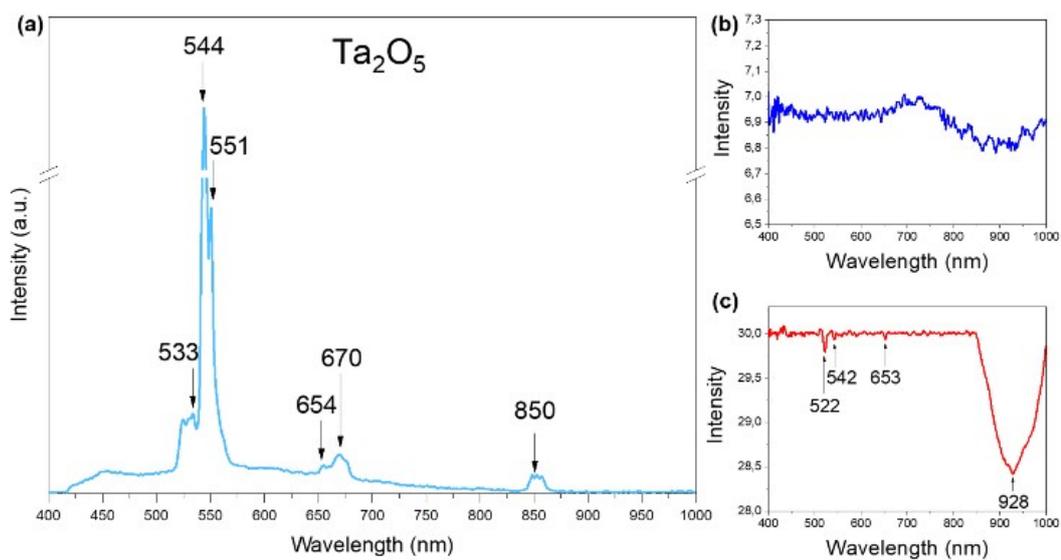


Fig. S10 Photoluminescence (a), transmittance (b) and reflection (c) spectra of doped tantalum oxide aerogel after calcination.

References

- 1 N. Agoudjil, S. Kermadi and A. Larbot, *Desalination*, 2008, **223**, 417–424.
- 2 M. K. Mahata, K. Kumar and V. K. Rai, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 2014, **124**, 285–291.