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Upconversion metal (Zr, Hf, and Ta) oxide aerogels[†]

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A major obstacle in developing upconversion aerogels is the incompatibility of the highly-developed porosity and the crystal structure required for converting light to a shorter wavelength. We propose a novel method for creating a sol-gel procedure for synthesizing metal (Zr, Hf, and Ta) oxide upconverison aerogels uniformly doped with Er³⁺ and Yb³⁺ by precisely adjusting the calcination conditions.

Upconversion nanomaterials doped with rare-earth elements (REEs), when excited by continuous-wave near-infrared (NIR) light, exhibit a unique luminescence with high energy transforming NIR radiation in visible and ultraviolet (UV) regions.^{1,2} Attractive properties of rare-earth element based nanomaterials comprise exceptionally narrow emission bands, large Stoke's shifts, and long lifetimes accompanied by the absence of blinking, which offers utilization for biophotonic and photonic applications.³ Among a large number of materials that possess upconversion luminescent characteristics, aerogels have not been developed to date, but they are attracting the attention of many researchers.4,5 Aerogels are materials with specific textural features - an open pore structure and a large specific surface area. Aerogels are synthesized through a wellknown sol-gel method with a subsequent supercritical (sc) drying process. The supercritical drying process leads to the formation of supercritical fluid mixtures in the gel pores without reducing any liquid phase. Thus, the drying procedure enables avoiding any intermediate vapor-liquid transition and surface tensions in the gel pores, protecting the gel structure from the pore collapse phenomenon (i.e., changes in the macroscopic level) during solvent elimination.⁶ Moreover, intrinsically biocompatible metal oxide gels used to produce corresponding functional metal oxide aerogels

impart smart properties, which enables the development of novel practical applications. 7

Due to their many excellent properties, materials based on upconversion-luminescent aerogels potentially can find a variety of practical applications, ranging from the areas of optics such as random lasers,⁸ displays,⁹ and inks for security printing^{10,11} (e.g., banknotes and bonds) to medicine, including biosensors,¹² catalysts,¹³ and materials for diagnostics and drug sorption.¹⁴ In addition, upconversion luminescence (UCL) via NIR excitation is highly advantageous for biomedical use due to its intensive and deep penetration in living tissues without any autofluorescence of the tissues since the exciting NIR light is located in the second biological transparency window.¹⁵ Furthermore, in contrast to UV excitation, NIR light treatment causes less photo damage to the living tissues and, hence, develops efficient realization of upconversion processes with remarkably higher sensitivity of the signal-to-noise ratio, and therefore, quantitative analysis.^{16,17} In this regard, employing upconversion may offer budding prospective options for bioimaging.17-19

A number of research studies reported luminescent composites obtained from aerogels by assembling luminous agents into the aerogel pores.^{20,21} Additionally, in their previous research, Kitamoto et al. manufactured composite materials based on an anatase aerogel doped with upconversion nanoparticles, aiming to apply the obtained composites as a photocatalyst.^{22,23} In these studies, UCL originates from the dispersing phase of REE-doped nanoparticles, which precipitate in the matrix owing to the instability of REE when mixed with the sol-gel anatase system over the gelation process. In contrast, in the present work, REE erbium (Er³⁺) and ytterbium (Yb^{3+}) ions intercalate into the structure of ZrO_2 , HfO_2 , and Ta₂O₅ aerogels, so that the materials obtained at one stage of synthesis become stable and homogenous. These features are provided by the development of a specific protocol, which consists of the following steps: firstly, sol-gel synthesis, then, CO_2 supercritical drying and, finally, the calcination procedure.

One of the most significant challenges in the production of upconversion aerogels concerns the inclusion of REE ions

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Fig. 1 Schematic illustration of the synthesis of upconversion metal oxide aerogel.

homogeneously into the crystalline lattice without losing the porous structure.²⁴ Moreover, the embedded REE ions need to be spread evenly over the entire matrix volume in order to act as luminescent centers. As noted, the intercalation of these elements by high-temperature calcination usually results in the degradation of the majority of matrices.²⁵ Therefore, zirconia, hafnia, and tantalum oxide matrices are employed since they perfectly fit the development of highly luminescent materials due to their chemical, photochemical, and thermal stability combined with high refractive indices and low phonon energies.^{26–28} Additionally, Gómez *et al.* reported on possible UCL in REE doped zirconia and hafnia nanocrystals.²⁹

The synthesis process of an upconversion metal oxide aerogel is schematically illustrated in Fig. 1. Sol–gel zirconia, hafnia, and tantalum oxide were produced by the hydrolysis–polycondensation reaction through a controlled hydrolysis reaction route. This allowed the REE ions to distribute uniformly, while the following stage of aerogel production – sc drying resulted in the formation of heat-resistant aerogels. Final calcination lead to the introduction of Er^{3+} and Yb^{3+} ions into the crystal structure of matrices since the zirconium, hafnium, and tantalum radii are comparable to the radii of the REE involved (for details of the experimental part see the ESI†).

To demonstrate the appearance and consistency of the gels, samples were obtained in vials (Fig. 2(a, c and e)), where it can be seen that the proposed method for the synthesis allows the production of stable and transparent zirconia, hafnia, and tantalum oxide gels. The rheological data for the as-prepared gels can be found in the ESI[†] (Fig. S1). After the gels were aged, they were subjected to sc drying (details can be found in the ESI[†]). Photos of the aerogels are shown in Fig. 2(b, d and f).



Fig. 2 The appearance of zirconia gel (a) and aerogel (b); hafnia gel (c) and aerogel (d), and tantalum oxide gel (e) and aerogel (f).

The UCL appears due to the intercalation of Er^{3+} and Yb^{3+} ions into the atomic structure of the aerogel matrix.³⁰ The embedding of ions occurs due to calcination of aerogels, during which an amorphous structure changes to a crystalline one. Calcination allows the production of crack-free aerogels with a transmittance of up to 40% (as seen from the ESI,† Fig. S2) under slow heating conditions.

Structural changes of the zirconia, hafnia, and tantalum oxide aerogels together with xerogels (taken for comparison) were investigated at 200 and 800 °C calcination temperatures, respectively. The nitrogen adsorption-desorption isotherms of the samples are shown in Fig. 3. No doubt, the drying method is one of the ways to change the pore shape and pore size distribution in the metal oxide nanoparticles obtained by the sol-gel method. The nitrogen sorption results indicate essential distinctions in the characteristic features of the measured isotherms. This is manifested in the hysteresis behavior of an adsorptive and in the values of the pore volume and surface area of porous solid metal oxide nanoparticles obtained by different drying procedures. The nitrogen sorption isotherms of the metal oxide nanoparticles belong to the Type IV isotherm of IUPAC classification given for many mesoporous adsorbents. Isotherms of this type have the same overall shape as the usual Type II isotherms obtained for nonporous or macroporous adsorbents up to the value of relative pressure p/p_0 at which capillary condensation results in a hysteresis loop and adsorption growth. The nitrogen sorption isotherms



Fig. 3 Nitrogen adsorption-desorption diagrams of the aerogels after different temperature treatments.

Table 1 The textural characteristics of $ZrO_2,\,HfO_2,\,and\,Ta_2O_5\,xerogels$ and aerogels

	Surface area	Pore volume	Pore size	Density
Sample	$\overline{A_{\rm BET}}$, m ² g ⁻¹	$V_{\rm BJH}$, cm ³ g ⁻¹	D _{BJH} , nm	ρ , g cm ⁻³
ZrO ₂ aerogel 200 °C	350	1.358	3.2	0.65
ZrO ₂ aerogel 800 °C	80	0.393	5.2	1.77
ZrO ₂ xerogel 800 °C	17	0.096	3.9	4.11
HfO ₂ aerogel 200 °C	266	1.070	1.4	0.85
HfO ₂ aerogel 800 °C	80	0.226	3.2	3.07
HfO ₂ xerogel 800 °C	17	0.071	3.9	5.10
Ta ₂ O ₅ aerogel 200 °C	135	0.281	1.3	2.56
Ta ₂ O ₅ aerogel 800 °C	45	0.029	1.0	7.18
Ta ₂ O ₅ xerogel 800 °C	5.7	0.005	0.8	8.67

of aerogels exhibit no limiting adsorption at high p/p_0 values and can be attributed to the pseudo-type II isotherms. Such isotherms, according to Kenneth S. W. Sing,³¹ may be attributed to macromesopores, which are not completely filled. Their adsorption curve entirely repeats the path of the Type II adsorption isotherm, but the desorption curve follows a different path, leading to hysteresis limited by the area of the multilaver adsorption. Physical properties of the samples such as surface area, total pore volume, and pore size distribution were determined and are shown in Table 1. Clearly, the drying method affects the type of the sorption isotherm and, hence, the shape of the capillarycondensation hysteresis loop. Therefore, the textural parameters of the samples vary appreciably. For instance, the specific surface area and the pore volume of the aerogels exceed the same values for the xerogels by almost 3 to 4 times – 80 and 17 $m^2 g^{-1}$, respectively (Table 1). The surface area and pore volume of the as-prepared amorphous aerogels decreased but their densities increased upon heating. Moreover, a well-developed and uniform surface of the aerogel samples is observed from the SEM images (Fig. S3, ESI[†]).

The XRD and HR-TEM analyses for doped zirconia, hafnia, and tantalum oxide aerogels after calcination are shown in Fig. 4. The XRD patterns display the transformation of the amorphous material into the crystalline one after calcination at 800 °C. Consequently, a combination of the monoclinic structure (space group $P2_1/a$) (JCPDS card no. 37-1484) and the tetragonal structure (space group $P\bar{4}m2(115)$) (JCPDS card no. 17-923) was formed for zirconia, the monoclinic structure (space group $P2_1/a$) was formed for hafnia (JCPDS card no. 30-104), and the orthorhombic structure (space group C2mm(38)) was formed for tantalum oxide (JCPDS card no. 01-089-2843). HR-TEM images (Fig. 4(b, d and f)) show the form and the size of the aerogel particles that have the domain organization of nanocrystals and are in good agreement with XRD data. Additionally, as seen in Fig. S4 (ESI[†]), XRD patterns indicate that REE-doped samples have no impurity phases, and all reflections of doped oxides correspond correctly to the reflections of undoped ones. Moreover, the crystallite sizes determined by the well-known Debye-Scherrer formula from the XRD data correlate well with the HR-TEM data (see Table S1, ESI[†]).

Fig. 5 shows the upconversion luminescence spectra of doped zirconia, hafnia and tantalum oxide aerogels obtained by the proposed method under excitation at 980 nm. The



Fig. 4 XRD patterns of REE doped aerogels before and after calcination: (a) ZrO_2 ; (c) HfO_2 ; and (e) Ta_2O_5 ; HR-TEM images of doped calcined aerogels: (b) ZrO_2 ; (d) HfO_2 ; and (f) Ta_2O_5 . Bright contrast pores inside the aerogels are clearly visible and marked with red lines.

position of the UCL peaks corresponds well to the well-known model of UCL in Er³⁺/Yb³⁺ co-doped nanomaterials.³² This illustrates the worthy performance of the offered method. Insets in the graphs show the photoluminescence microphotographs of these materials. Furthermore, the spectra of zirconia and hafnia match rather accurately, which means that the synthesis approach of the upconversion metal-oxide aerogels is universal since the nature of UCL originates from the REE ion interaction in the doped matrix and does not depend on the matrix itself.^{30,33} Finally, as seen in the ESI[†] (Fig. S5–S7), UCL was not observed in cases of as-synthesized samples, which states that REE ions intercalate into the atomic structure of the matrices after calcination and do not form phases of separate agglomerates after synthesis and sc drying. Thus, the obtained aerogels convert NIR light into visible green light via UCL as seen in Fig. 5(d)-(f). Obviously, there is a sharp peak at 487 nm present in the UCL of tantalum oxide, unlike in the UCL of the other two aerogels. Furthermore, the intensity ratio of the peaks at 546 nm and 559 nm in zirconia and hafnia UCL is almost the same, whereas in tantalum oxide it is completely different. Furthermore, the positions of the UCL peaks of zirconia and hafnia are identical to each other while the UCL peaks of tantalum oxide are slightly shifted, which can be explained by the difference in phase composition (Fig. 4) and crystallite sizes (Table S1, ESI[†]) of calcined oxides. Additionally, the valence of Ta differs from that of Zr and Hf, which affects the UCL peak positions.

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Fig. 5 Upconversion spectra of doped ZrO₂ (a), HfO₂ (b), and Ta₂O₅ (c) calcined aerogels under excitation at 980 nm; the insets show optical micrographs of ZrO₂ (a), HfO₂ (b), and Ta₂O₅ (c) calcined aerogels by photoluminescence microscopy under excitation with a mercury lamp; digital photographs of upconversion emission for doped ZrO₂ (d), HfO₂ (e), and Ta₂O₅ (f) calcined aerogels under NIR laser excitation at 980 nm.

In addition, as seen in the room-temperature photoluminescence (PL), transmittance and reflection spectra (Fig. S8-S10 in ESI[†]), the PL peaks reveal the transitions from the ${}^{4}I_{15/2}$ ground state to excited states of the Er³⁺ ions, which confirms that Er³⁺ ions can absorb visible light. The corresponding UV-VIS-NIR transmittance and reflection spectra prove that metal oxide aerogels are highly absorbing in the range of 400-1000 nm. Moreover, the transmittance and reflection spectra of zirconia and hafnia reveal a clear peak located at 974 nm, which corresponds to the $^2F_{7/2}$ \rightarrow $^2F_{5/2}$ transition of Yb^{3^+} ions demonstrating that Yb³⁺ ions absorb the pump light. Meanwhile, the transmittance and reflection spectra of tantalum oxide reveal a broad peak at 928 nm. In addition, the transmittance and reflection peaks corresponding to the transitions from the ${}^{4}I_{15/2}$ ground state to the excited states of the Er^{3+} ions indicate the energy transfer from Yb³⁺ to Er³⁺ ions being in good agreement with the peaks in the PL spectra.

In the present work, we have successfully demonstrated a feasible method for the production of monolithic aerogels demonstrating upconversion for the first time. Aerogels can be prepared by a simple and effective procedure. Introducing Er^{3+} and Yb^{3+} ions into the initial solution leads to upconversion properties in the final aerogel. We demonstrated that aerogels can be based on different matrices such as ZrO_2 , HfO_2 , and Ta_2O_5 , which points to the possible extension of the proposed synthesis method to a wide variety of metal oxides. The combination of aerogel properties, such as large surface area, bio-inertness and upconversion luminescence, allows us to assume that these materials can be used in a wide variety of applications ranging from optics and photonics to medicine.

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Conflicts of interest

There are no conflicts to declare.

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