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Tuning Morphology, Surface, and Nanocrystallinity of Rare Earth Vanadates by One-Pot Colloidal Conversion of Hydroxycarbonates

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

We show that particle size, morphology, nanocrystallinity, surface area, and defect density of (Y,Eu)VO₄ structures can be tuned by one-pot colloidal conversion of rare earth hydroxycarbonates in water/ethylene glycol (EG) suspensions. Using small angle X-ray scattering, transmission electron microscopy and dynamic light scattering, we show how volume fractions of EG direct the amorphous to crystalline conversion at 1 atm / 95 °C by controlling size and aggregation of hydroxycarbonate precursors. A template effect due to a Kirkendall-type conversion occurs for low EG contents, yielding solids with high densities of oxygen defects, as demonstrated by O₂ uptakes in thermogravimetry and X-ray photoelectron spectroscopy profiles. Starting from small and aggregated hydroxycarbonates high-porosity (Y,Eu)VO₄ nanoparticles were produced with expanded unit cells and short-range (<100 Å) crystalline ordering. We explored the effects of synthesis on the textural, microstructure, and defects of (Y,Eu)VO₄ solids, which were further correlated to the spectroscopic profiles of Eu³⁺-activated samples. We show that the ratios between Eu³⁺ ⁵D₀ internal quantum yields and particle diameters can be directly correlated to the particle surface areas, opening new perspectives for theoretical detailing of f-f luminescence in YVO₄ solids, and enabling accurate tuning of structure and applicability of colloidal vanadate nanoparticles for sensing and catalysis applications.

Introduction

Luminescent rare earth (RE) orthovanadates (REVO₄) are studied for more than a half century for their highly efficient emissions and wide applicability as light emitting materials.^{1,2} The high chemical stability, low crystallization temperatures, and the possibility to afford multiple and intense lanthanoid (Ln³⁺) emissions under both ultraviolet (UV) and near infrared excitation make these solids highly promising for emerging nanoscale applications. New functionalities such as nanothermometry,^{3,4} bio-imaging,⁵ detection of reactive oxygen species,⁶⁻⁸ multifunctional sensing,^{9,10} and photo-^{11,12} and biomimetic catalysis¹³ require an understanding of the correlation between luminescence mechanisms and microstructure in these solids. Given the effects of morphology, surface state, nanocrystallinity, and defect chemistry on such applications,¹⁴ development of simple and mild methods allowing the controlled production of colloidal REVO₄ nanoparticles is also of paramount importance for understanding and improving the properties of interest. In

addition, synthetic conditions also impact on the biocompatibility and toxicity of RE vanadates due to the strong dependence of the corona composition on the surface state of the nanoparticles, which is crucial for biologic sensing applications.^{15,16}

A very broad literature details the preparation of REVO₄ nanoparticles via hydrothermal treatments using surface ligands, surfactants or polymers such as oleates,¹⁷⁻¹⁹ poly(ethylene glycol),²⁰ poly(vinylpyrrolidone),²¹ poly(acrylic acid),^{9,22} and citrates,²³⁻²⁶ among others. In addition to safety issues and the general low accessibility to *in situ* conditions during the reactions, hydro- and solvothermal procedures often result in limited and empirical control of size, morphology, and microstructure. Hence, the simplicity of direct coprecipitation procedures^{4,7,27-29} is commonly preferred over polymer-mediated hydrothermal syntheses for REVO₄ nanoparticles. However, poor reproducibility is also an issue on coprecipitation protocols, as products may show strong variability in microstructure and morphology with the composition and even the batch of the precursors.³⁰

The use of colloidal templates emerged as powerful approaches to generate homogeneous and controllable nanoparticles,^{3,6,31-33} thus overcoming the drawbacks of conventional syntheses of REVO₄ materials. Whilst hard and soft templates³⁴ impose difficulties on the purification of the products, sacrificial templates^{3,6,31,35} can yield chemically pure and homogeneous solids, also directly determining size and shape of the final particles.

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†Electronic Supplementary Information (ESI) available: [Additional details on fitting of SAXS curves and luminescence overall quantum yields; additional TEM/SEM images, FTIR spectra, N₂ adsorption isotherms, additional XRD data, TGA results, XPS data, ⁵D₀ decay curve fits, calculated Eu³⁺ spectroscopic parameters]. See DOI: 10.1039/x0xx00000x

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Nanoscale

Some sacrificial template procedures may also yield hollow particles via the Kirkendall effect,^{6,31,36} which consists in the formation of voids due to the imbalance between incoming anion diffusivity and outgoing cation diffusivity at the template/solution interface.³⁷ Hollow nanoparticles show additional advantages of low volumetric mass density, increased defect density, and improved porosity, which is highly attractive for chemical sensing applications depending on the permeability of the particles against the dispersing medium.³⁸ RE hydroxycarbonates ($\text{RECO}_3\text{OH}\cdot x\text{H}_2\text{O}$)³⁹ have been described as efficient sacrificial precursors for REVO_4 particles,^{6,31,40–42} but these conversions generally require application of hydrothermal conditions and rather long reaction times. We recently demonstrated³ that the improved reactivity of low size (<100 nm) RE hydroxycarbonates enables colloidal conversion into REVO_4 in water at 1 atm. However, previous preparation of hydroxycarbonate templates imposes additional synthesis and purification steps, thus making the procedure less attractive compared to direct coprecipitations. We herein describe a fundamental study motivated by understanding the mechanisms of a one-pot colloidal conversion of hydroxycarbonates into REVO_4 and correlating spectroscopic properties to particle size, texture, and nanocrystallinity. Low particle size hydroxycarbonates were produced by homogeneous precipitation with urea in water/ethylene glycol and directly converted into REVO_4 nanoparticles without hydrothermal treatment or purification of intermediates. The volume fractions of ethylene glycol controlled the size and aggregation of hydroxycarbonate templates, which in turn resulted in the control of size, porosity, microstructure, and defect density of the final REVO_4 particles. We explored both the formation of RE hydroxycarbonates and their conversion in REVO_4 *in situ*, correlating conversion mechanisms to final structural and morphological properties. Finally, we evaluated how the surface areas and density of defects impacted the spectroscopic behaviour of the final particles by monitoring Eu^{3+} decay parameters. We therefore demonstrated a mild, scalable, and surfactant-free liquid-phase method for controlling size, morphology, porosity, and microstructure of REVO_4 nanoparticles, thus enabling further advance in tuning their properties for nanoscale sensing applications.

Experimental

Synthesis of (Y,Eu) VO_4 nanoparticles

Aqueous solutions of rare earth nitrates [$\text{Y}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$, 0.10 mol L⁻¹, pH=6] were prepared by dissolution of previously annealed (900 °C, 30 min) rare earth oxides (Y_2O_3 and Eu_2O_3 , 99.99%, Aldrich) with aqueous nitric acid (65% w/w) under heating at ~50 °C. The vanadate nanoparticles were prepared via colloidal conversion of RE hydroxycarbonates templates in a one-pot process. In a general procedure, 1 mmol of $\text{RE}(\text{NO}_3)_3$ [$\text{RE}=(\text{Y}_{0.95}\text{Eu}_{0.05})$, $(\text{Y}_{0.80}\text{Eu}_{0.20})$, or $(\text{Y}_{0.60}\text{Eu}_{0.40})$] in 10 mL of H_2O was diluted to 0.01 mol L⁻¹ with appropriate volumes of water and ethylene glycol at 25 °C. The final $\text{H}_2\text{O}/\text{EG}$ volume ratios were 3/2, 1/1, 1/2, and 1/3 (i.e. volume fractions of 40%, 50%, 67%,

75% of EG in water). The mixtures were homogenized with stirring, and 125 mmol (7.5 g) of urea was added to each to form clear solutions, which were heated under ambient pressure at 95 °C for 2 h. The conductivity of the reaction mixtures was monitored *in situ* using a Hanna EC215 conductometer with a HI 76303 probe with temperature correction. Samples of RE hydroxycarbonate particles were acquired for characterization centrifugation (10000 rpm). In the one-pot procedures, 1 mmol of ammonium metavanadate (NH_4VO_3 , 99%, Aldrich) dissolved in 20 mL of a $\text{H}_2\text{O}/\text{EG}$ mixture (3/2, 1/1, 1/2, or 1/3 v/v) was rapidly added to the suspension containing the hydroxycarbonate intermediates. The $\text{H}_2\text{O}/\text{EG}$ volume ratio of the reaction mixture was kept constant during this procedure. The suspensions were stirred for 2 h at 100 °C. The final particles were separated by centrifugation (10000 rpm) and washed with deionized water until conductivities below ~100 $\mu\text{S cm}^{-1}$ were observed. The vanadate nanoparticles were resuspended in deionized water (50–60 mmol L⁻¹) for storage or dried in vacuum at 25 °C over silica for 72 h for further characterization. Solids with compositions $(\text{Y}_{0.80}\text{Eu}_{0.20})\text{VO}_4$ and $(\text{Y}_{0.60}\text{Eu}_{0.40})\text{VO}_4$ were also prepared in the same conditions for further comparison of luminescent properties. Two-step conversions of hydroxycarbonates into vanadates were also performed for comparison. In these cases, hydroxycarbonate particles were obtained according to the procedure described above in a $\text{H}_2\text{O}/\text{EG}=3/2$ (v/v) mixture. These particles were purified by centrifugation after 2 h of reaction prior to the addition of the metavanadate solution. After the purification, the hydroxycarbonate particles were resuspended in H_2O at 100 °C, and a solution containing 1 mmol of NH_4VO_3 (0.05 mol L⁻¹) was added with stirring. After 2 h at 100 °C, the vanadate particles were isolated and purified as described above.

Characterisation

Powder X-ray diffraction (XRD) was performed on a Shimadzu 7000 diffractometer using $\text{Cu-K}\alpha_{1/2}$ radiation (0.15418 nm, 2° min⁻¹) at 25 °C. Experimental data were fitted using the MAUD package⁴³ to determine lattice parameters, crystalline coherence lengths and strain. Temperature-dependent (30–800 °C) XRD profiles were measured on Bruker D8 Avance using $\text{Cu-K}\alpha_{1/2}$ radiation and equipped with a VANTEC-1 solid state detector and an Anton Parr XRK900 heating chamber. Scanning electron microscopy images (SEM, ESI⁺) were acquired on a FEI Quanta FEG 250 operating at 20 kV, with samples deposited onto mica slices and metallized with iridium (15 mA, 120 s). Transmission electron microscopy (TEM) images were measured on a Carl Zeiss Libra 120 (LaB₆, 120 kV) and a TECNAI G2F20 HRTEM (FEG, 200 kV) microscopes by deposition of particle suspensions (~1 mmol L⁻¹) onto C-covered copper grids (Ted Pella C1822-F). Dynamic light scattering (DLS) and ζ potential profiles were acquired on Malvern Zetasizer Nano ZS using suspensions (0.5 mmol L⁻¹) in Milli-Q water after homogenization with ultrasound (20 kHz, 40 W).

Small-angle X-ray scattering (SAXS) profiles were measured on Xenocs Xeuss 2.0 equipped with a Cu-K α source collimated by two sets of scatterless slits and a Pilatus 300k detector to record the scattered signal. Measurements were made with a sample to detector distance of 2.481(5) m with suspensions mounted into 1 mm diameter borosilicate glass capillaries. *In situ* acquisition of time-dependent SAXS profiles of reaction mixtures enabled kinetical monitoring of both formation of hydroxycarbonates and their conversion into REVO $_4$ particles. Details on measurement corrections and modelling are presented in the ESI † . Thermogravimetry analyses were performed on a Seiko TGA-DTA equipment under synthetic air or N $_2$ atmosphere at a 10 °C min $^{-1}$ heating rate. For N $_2$ adsorption-desorption measurements, samples were dried for 24 h in vacuum at room temperature and further degassed at 60 °C (10 °C min $^{-1}$). Isotherms were obtained on an ASAP 2020 equipment and data were treated according to the Brunauer-Emmett-Teller (BET) and Barrett-Jones-Halenda (BJH) methods. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD using monochromatic Al-K α excitation (1486.7 eV) with detection at 90° with respect to the surface. Data were treated using the CasaXPS package applying Voigt peaks and Shirley backgrounds for all regions. Fourier-transform infrared (FTIR) spectra were measured on attenuated total reflection (ATR) mode over a diamond crystal on an Agilent Cary 360 spectrometer (4 cm $^{-1}$ resolution). Luminescence spectra was measured with aqueous (H $_2$ O or D $_2$ O 99% Aldrich) colloids (25 mmol L $^{-1}$) in 2 mm length quartz cuvettes on a Horiba FL3-22-IR320 spectrofluorometer using a Hamamatsu R928P photomultiplier detector and a xenon arc lamp (450 W) as excitation. Luminescence decay curves were measured using a pulsed Xe lamp (150 W) and a Horiba FluoroHub A+ TCSPC lifetime controller. Luminescence overall quantum yields of particle suspensions in H $_2$ O and D $_2$ O were estimated comparatively using a Horiba Quanta ϕ integrating sphere and 2-aminopyridine (Aldrich, 99.9%, 10 $^{-5}$ mol L $^{-1}$ in 0.1 mol L $^{-1}$ aqueous H $_2$ SO $_4$) as an internal standard⁴⁴ in 10 mm path quartz cuvettes. Additional details on the determination of quantum yields are described in the ESI † .

Results and Discussion

Formation of RE hydroxycarbonates.

Submicrometric RE hydroxycarbonate particles are already reported to act as sacrificial templates to yield RE vanadate hollow structures via the Kirkendall effect.^{6,31,41} These procedures usually require hydrothermal conditions and result in large vanadate particles. By contrast, the use of nanosized hydroxycarbonates as templates enables production of smaller size vanadate particles at milder conditions.³ However, reduced template sizes impose higher solubilities and higher degrees of aggregation, which induces intermediate mechanisms of particle growth and eventual loss the template effect. The balance between the Kirkendall effect-driven crystallization and

the partial redissolution of template particles can therefore be used to modify size, porosity, and microstructure of REVO $_4$ nanoparticles (Figure 1), which is of great interest for applications based on their luminescence.

We firstly evaluated systematically how the amount of ethylene glycol (EG) affected the formation of the RE hydroxycarbonate templates. Whilst homogeneous precipitation of RE hydroxycarbonates with urea in water yields 300-400 nm particles (Fig. S2),⁶ the use of polyols usually limits their size.^{3,45} The volume fraction of polyols affects the rate of hydrolysis of urea as well as the solubility and aggregation of the hydroxycarbonate particles. In our case, variation of the volume fraction of EG volume fraction from 40% (H $_2$ O/EG=3/2 vol./vol.) to 75% (H $_2$ O/EG=1/3) resulted in significant changes in size and shape of the hydroxycarbonate templates (Figure 1). A 3/2 ratio yielded homogeneous spherical particles with mean hydrodynamic diameter of 77 $\pm$ 18 nm. Partially aggregated spherical particles of $\sim$ 20-30 nm diameter were detected with volume fractions of 1/1 (28 $\pm$ 8 nm) and 1/2 (19 $\pm$ 4 nm, Fig. 1). When the volume fraction of EG was further increased, the formed hydroxycarbonates consisted of <10 nm structures which strongly aggregated in suspension, resulting in a bimodal hydrodynamic diameter distribution seen by DLS [50 $\pm$ 14 and 161 $\pm$ 68 nm, Fig. 1(b)]. The produced hydroxycarbonates templates were non-crystalline particles regardless of the H $_2$ O/EG ratio applied. The four templates showed a composition denoted by (Y $_{0.95}$ Eu $_{0.05}$)CO $_3$ OH $\cdot$ xH $_2$ O, x=0.9-1.9 (TGA, Fig. S3, Table S1) with the characteristic^{3,6} set of FTIR signals of RE hydroxycarbonates [(Fig. S4), 3700-2700 cm $^{-1}$ (vOH); 2940 and 2880 cm $^{-1}$ (nCH $_2$, EG) 1640 cm $^{-1}$ (δ HOH); 1505 and 1385 cm $^{-1}$ (v $_3$ CO $_3^{2-}$ + n $_3$ NO $_3$); 1087 cm $^{-1}$ (v $_1$ CO $_3^{2-}$ +vC-O EG); 1045 cm $^{-1}$ (vC-O, EG) 842, 739, and 677 cm $^{-1}$ (v $_2$ and v $_4$ CO $_3^{2-}$)]. Fitting of time-dependent SAXS profiles (Figure 2a,d,g,i and Fig. S5-S7) provided further insights on the formation of the RECO $_3$ OH $\cdot$ xH $_2$ O particles from homogeneous precursors in H $_2$ O/EG mixtures.

Gaussian volume-weighted radii after 120 min of homogeneous precipitations calculated from SAXS data agreed with observations from TEM and DLS, revealing average particle sizes about 120, 26, 22 and 9 nm, respectively, for H $_2$ O/EG volume ratios of 3/2, 1/1, 1/2, and 1/1. Additional information on the formation of hydroxycarbonates was provided by comparing the urea hydrolysis profile by conductivity and estimating the number of particles in suspension (Figure 3). The number of particles (N_p) per volume of sample was estimated from SAXS data by Eq.(1):⁴⁶

$$N_p = \frac{I_{q=0}}{\langle V_p^2 \rangle (\Delta\rho)^2} \quad (1)$$

where $I_{q=0}$ is the absolute intensity [i.e., $\lim_{q \rightarrow 0} I(q)$, being $I(q)$ the scattered intensity], and $\langle V_p^2 \rangle$ is the mean value of the square particle volume, calculated from SAXS fitting analysis. $(\Delta\rho)^2$ is the square of the scattering length density contrast between the dispersing medium (H $_2$ O/EG) and the particles (Table S2).

Figure 1. (a) Scheme of the synthesis of $(Y,Eu)VO_4$ nanoparticles from colloidal hydroxycarbonates. (b) DLS size-distributions (number-weighted) of $(Y_{0.95}Eu_{0.05})CO_3OH \cdot xH_2O$ (bars) and $(Y_{0.95}Eu_{0.05})VO_4$ (points) particles prepared via one-pot synthesis in different water/ethylene glycol (EG) volume ratios $[H_2O/EG = 3/2$ (top), $1/1$, $1/2$, and $1/3$ (bottom)]. (c) Dependence of hydrodynamic diameters (left) and ζ potentials (right) of $(Y_{0.95}Eu_{0.05})VO_4$ particles on the solvent composition (H_2O/EG) for the one-pot processes (empty symbols) and for the two-step synthesis (filled symbols, 0% vol. EG). (d-l) TEM images of (d,g,i,k) $(Y_{0.95}Eu_{0.05})CO_3OH \cdot xH_2O$ particles and (e,f,h,j,l) their respective $(Y_{0.95}Eu_{0.05})VO_4$ particles obtained at different H_2O/EG ratios. The histogram in (e) corresponds to DLS profile of particles obtained in water via the two-step process starting from the hydroxycarbonates shown in (d). Scale bars in TEM images correspond to 200 nm.

Conductivity profiles of urea solutions (1.25 mol L^{-1}) in the absence of RE cations (Fig. 3a,b) indicate how fast urea may hydrolyse to generate carbonate species for the precipitation of $RECO_3OH$ particles (Eq.(2) and (3):

Hydrolysis of urea stabilized after 40-60 min of reaction (Fig. 3a,b). Increasing volume fractions of EG reduced the time for highest hydrolysis rates (Fig. 3b). However, increasing EG contents lowered the extent of hydrolysis, as indicated by the reduction of conductivities after 120 min. Such a reduction cannot be related to the increase on solvent viscosity only (Fig. S8). The maximum rates of urea hydrolysis $[(dk/dt)_{max}]$ are not time-related to maximum rates of particle growth $[(dr/dt)_{max}]$ or particle formation $[(dN_p/dt)_{max}]$, which suggests nucleation and growth are not kinetically limited by the hydrolysis of urea.

Rates of change of numbers and radii (Fig. 3d) suggest lower correlation between $(dr/dt)_{max}$ and $(dN_p/dt)_{max}$ when smaller volume fractions of EG were applied. So, the nucleation steps of the $RECO_3OH \cdot xH_2O$ phases may occur during a large range of time, and particle formation still take place whereas initial

particles have undergone growth. This effect is more prominent for lower EG fractions ($3/2$, $1/1$), but it is also evidenced by the drop in the mean radii of particles observed during the formation of the hydroxycarbonates (Fig. 2c,f,i,l). The reduction in mean sizes generally coincides with the highest rates in the number of particles (Fig. 3(d)), which suggests that the drop in mean radii is due to the increased formation of particles with smaller size. This accounts for the non-monodisperse profiles observed on TEM (Fig. 1 and Fig. S9), on hydrodynamic diameters (Fig. 1b), and on FWHM of size distributions from SAXS (Fig. 2c,f,i,l). For higher EG volume fractions ($1/2$, $1/3$), the separation of maximum rates of change in radii and numbers become lower. This can be related to a reduced solubility of the $RECO_3OH \cdot xH_2O$ phase in such conditions, so particles formed are less prone to redissolution, although more susceptible to aggregation (Fig. 1i,k). Hence, formation of the hydroxycarbonate particles is determined by their solubility in the H_2O/EG mixture, with lower solubility inducing smaller particles.

Figure 2. Time-dependent SAXS profiles of reaction mixtures during formation of (a,d,g,j) $(Y_{0.95}Eu_{0.05})CO_3OH \cdot xH_2O$ particles from homogeneous precursors and (b,e,h,k) $(Y_{0.95}Eu_{0.05})VO_4$ particles from hydroxycarbonates at different H_2O/EG (v.v.) conditions, namely (a-c) 3/2, (d-f) 1/1, (g-i) 1/2, and (j-l) 1/3. The curves were acquired at different reaction times with 5 min intervals. (c), (f), (i), and (l) correspond to the evolution of particle sizes with reaction times for hydroxycarbonates (filled symbols, left) and vanadates (empty symbols, right) obtained from corresponding SAXS profiles. Red dashed lines in (c), (f), (i) and (l) correspond to FWHM values of particle size distributions. Data for hydroxycarbonates and vanadates were acquired in different runs.

Colloidal conversion into $REVO_4$ particles

The variations in number and size of particles in suspension also provides insights upon the conversion of hydroxycarbonate templates into the $REVO_4$ nanoparticles (Fig. 1 and Fig. S10). The results show that variation of H_2O/EG ratio in the one-pot synthesis enables tuning size, shape, and porosity of vanadate nanoparticles. The effect of EG on the morphology of vanadate particles is clearly illustrated by the conversion of conversion of 77 ± 18 nm hydroxycarbonates ($H_2O/EG=3/2$, Fig. 1d). When these particles were isolated and resuspended in water in a two-step process, the final $REVO_4$ particles lost the spherical morphology of the templates and assumed characteristic^{3,4,7} elongated shape (Fig. 1e and Fig. S11). This confirms low size hydroxycarbonates undergo redissolution when dispersed in pure water, and crystallization of the $REVO_4$ phase may occur around the partially dissolved templates. SAXS profiles (Fig. S7) also show only minor changes in scattering over time, which indicates that conversion of amorphous hydroxycarbonates into crystalline vanadate particles take place very fast after few minutes of reaction.

Fittings of SAXS curves are consistent with ellipsoids with minor radii of ~ 48 nm and aspect ratio of 1.8, which is in agreement with DLS (85 ± 20 nm hydrodynamic diameter, Fig. 1e) and TEM sizes (width: 92 ± 10 nm, length: 164 ± 21 nm, Fig. S11). When ~ 77 nm hydroxycarbonates were converted into vanadates by a one-pot process (i.e., in $H_2O/EG=3/2$ conditions), the final particles clearly kept the spherical morphology of the templates, showing slightly larger hydrodynamic diameters

(107 ± 27 nm, Fig. 1b). In this case, the final $REVO_4$ particles displayed hollow morphology, indicating that conversion of hydroxycarbonate templates occurred via the Kirkendall effect (Fig. 1f). Hence, the $REVO_4$ particles were preferentially generated over $RECO_3OH \cdot xH_2O$ templates via unbalanced inward and outward mass transportation across the solid-solid interface formed between these two phases, and $REVO_4$ growth occurred mostly at the solid-liquid interface, thus yielding hollow structures.^{6,36,37} To the best of our knowledge, this is the first demonstration of the possibility of template-effect by Kirkendall-driven formation of low size (~ 100 nm) RE vanadates without application of hydrothermal conditions. SAXS profiles (Fig. 2b) also supported this growth mechanism. The results indicated final $REVO_4$ particles had slightly larger sizes ($\sim 130 \pm 25$ nm diameter) than hydroxycarbonates (Fig. 2c), and number of particles is roughly conserved in terms of orders of magnitude (Fig. 3c). This supports the idea that the majority of the $REVO_4$ particles are generated in a 1:1 conversion from hydroxycarbonate templates to products in this case, although parallel mechanisms, e.g. redissolution, may also take place considering the slight reduction in the estimated number of particles. The small difference in size between template and final particles (radii are the same within FWHM of distributions, Fig. 2c) precludes detailed kinetic evaluation of the $REVO_4$ formation. The increase of EG volume fraction in one-pot conversions led to smaller hydroxycarbonate particles but resulted in the partial loss of the template effect (Fig. 1h,j,l).

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Figure 3. (a) Conductivity (κ) of 1.25 mol L⁻¹ urea solutions in different H₂O/EG mixtures in the absence of rare earth nitrates at 95 °C, and (b) respective normalized rates of change in conductivity against time $[(d\kappa/dt)]$. (c) Number of particles per volume estimated by Eq.(1) for the formation of hydroxycarbonates (left, rose background) and during their conversion into vanadates (right, orange background). (d) Normalized rates of change in the radius $[(dr/dt)]$, solid lines] and in the number of particles $[(dN_p/dt)]$, dotted lines] against the time in the formation of hydroxycarbonates. Colors and symbols in a-d correspond to different H₂O/EG volume ratios, namely 3/2 (40% EG, blue/squares), 1/1 (50% EG, green/circles), 1/2 (67% EG, dark yellow/triangles) and 1/3 (75% EG, dark orange/diamonds).

At H₂O/EG ratios of 1/1, 1/2, and 1/3, a reduction of about 2-3 orders of magnitude in the number of particles is observed during the formation of the vanadate phase (Fig. 3c). This large drop in number reveals that the REVO₄ particles were grown over multiple aggregated RECO₃OH·xH₂O seeds, and partial redissolution of hydroxycarbonates induced by the addition of the vanadate precursors also took place. Hydrodynamic diameters (Fig. 1b) and particle radii calculated by SAXS (Fig. 2f,i,l) also support this conversion mechanism, as particle sizes increased significantly. The one-pot conversion in H₂O/EG=1/1 resulted in 124±30 nm spherical REVO₄ particles (DLS, Fig. 1b), which in general kept a high degree of aggregation (Fig. 1h and Fig. S10). So, even though a small fraction of particles undergoes Kirkendall-driven conversion in H₂O/EG=1/1, the majority of the final REVO₄ particles were formed over aggregates and by template redissolution. The large particle sizes led to discrepancy between hydrodynamic sizes and radii estimated from SAXS curves (Fig. 2e,f). In this case, particle dimensions being close to the limit detectable by SAXS and agglomeration precluded us to model the size of the particles. This is because the only scattering in the evaluated q range from the particles and agglomeration is a Porod slope at low q values (Fig. 2e). The increased scattering at higher q values is probably due to voids between agglomerated particles, which led to apparent radii (~13 nm) that are inconsistent with DLS and TEM observations.

One-pot conversion in higher EG fractions led to smaller REVO₄ particles, with hydrodynamic diameters of 58±13 nm and 34±8 nm for H₂O/EG=1/2 and 1/3, respectively. Hydrodynamic diameters are consistent with sizes obtained from fitting of SAXS curves (Fig. 2h,i,k,l), namely 40 and 25 nm. REVO₄ particles were also formed over aggregated hydroxycarbonates in these conditions, leading to a marked increase in particle sizes in comparison to templates (Fig. 2i,l). However, the one-pot syntheses led to low density and high porosity products in these cases. This is because conversion occurred over large numbers of low size particles (<20 nm diameter) having an increased number of aggregation voids, which resulted in the formation of spheroid REVO₄ particles with high porosity (Fig. 1j,l). Therefore, the results demonstrate that volume fraction of EG can be applied to tune size and morphology of RE vanadate nanoparticles by one-pot conversion of hydroxycarbonates. General effects of the amount of EG on size and ζ potential of final REVO₄ particles are summarized in Fig. 1(c). The RE vanadates obtained herein show characteristic Xenotime tetragonal ($I4_1/amd$) structure (Fig. 4a) in all cases, showing vibrational profiles compatible with orthovanadates containing adsorbed water and residual amounts of carbonates and ethylene glycol [FTIR (Fig. S12): 3300 cm⁻¹ (νOH); 1640 cm⁻¹ (δHOH); 1423+1370 cm⁻¹ (ν₃CO₃²⁻); 1086 cm⁻¹ (ν₁CO₃²⁻, νC-O EG); 1045 cm⁻¹ (νC-O EG); 900-650 cm⁻¹ (ν₃VO₄³⁻)].

Surface, microstructure, and luminescence of (Y,Eu)VO₄ particles

Besides morphological effects described, the amount of EG used in the one-pot conversion of hydroxycarbonates also affects microstructural parameters of the final REVO₄ solids. This highly interesting to tune spectroscopic^{3,4,7-9} and catalytic¹¹⁻¹³ properties, which are strongly dependent on the structure and defect chemistry of RE vanadates. For instance, the size of the templates and the volume fraction of EG showed great impact on the nanocrystallinity of the REVO₄ products (Fig. 4a-c). In all cases, particles are polycrystalline, with crystallite sizes much lower than the dimensions of the particles. However, the larger templates obtained in lower volume fractions of EG resulted in higher crystalline coherence lengths (Fig. 4b). This confirms that the formation of the REVO₄ phase over small, aggregated templates involves multiple crystallization nuclei over hydroxycarbonates, thus resulting in small coherence lengths with a high degree of strain for the smaller particles. By contrast, one-pot conversion of larger templates in lower EG volume fractions involves a greater contribution of Kirkendall-driven conversion, which results in a more homogeneous crystallization step and culminates in larger crystallites. REVO₄ particles prepared in pure water by the two-step process showed intermediate crystallite sizes and low strain, which illustrates how redissolution mechanisms contribute to the formation of multiple crystallization sites over precursor particles inducing higher polycrystallinity.

Figure 4. (a) Powder XRD profiles of (Y_{0.95}Eu_{0.05})VO₄ particles obtained from colloidal conversion of hydroxycarbonates in different solvent mixtures compared to YVO₄ JCPDS standard (17-0341). Experimental data are represented by empty symbols, and profiles calculated from Pawley fits are shown as red lines; residuals are shown as magenta lines. Refined data were used to estimate (b) isotropic crystallite sizes (grey diamonds, left) and strain (red squares, right) and (c) lattice parameters of the *I*4₁/*amd* structure of (Y,Eu)VO₄. (d) N₂ adsorption (filled symbols) and desorption (empty symbols) isotherms of the (Y_{0.95}Eu_{0.05})VO₄ powder particles obtained in different H₂O/EG volume ratios, namely 0% EG (pentagons), 40% EG (squares), 50% EG (circles), 67% EG (triangles) and 75% EG (diamonds). (e) Correlation between BET specific surface areas and BJH pore volumes for (Y_{0.95}Eu_{0.05})VO₄ particles prepared at different H₂O/EG conditions. Insets in (e) show TEM images of particles obtained using different %EG contents. Errors in (b) and (c) were obtained directly from refinements in (a).

The solvent composition also impacts on the lattice parameters of the REVO₄ solids, which are strongly correlated to size and defect chemistry of the particles. Results indicated that smaller particles, which have shorter crystalline coherence and higher strain, also displayed expanded lattice parameters (Fig. 4c). This implies increased number of dangling bonds on smaller particles, thus resulting in lattice expansion. On the other hand, particles formed from larger templates are richer in Kirkendall voids, resulting in more abundant lattice and surface oxygen and metal vacancies. As those vacant sites such as oxygen defects ($v_{\text{O}}^{\bullet}$) have lower dimensions in comparison to occupied sites, such samples undergo lattice constriction.

To further confirm these observations, we assessed specific surface areas (Fig. 4d,e) and evaluated the behaviour of the particles upon thermal treatment (Fig. 5). The N₂-adsorption/desorption isotherms resulted in BET surface areas (S_{BET}) from ~40 to 220 m² g⁻¹ (Fig. 4d,e, Fig. S13). The surface areas followed the trend in particle sizes, and the smaller particles showed higher BJH cumulative pore volumes. Hence, the higher surface areas of smaller particles showed a strong contribution arising from porosity (Fig. 4e), thus confirming the previous observations from TEM analysis (Fig. 1). This also led to expanded lattice parameters, as discussed above. Samples prepared by the two-step process in water showed lower surface areas and pore volumes (43.9 m² g⁻¹ and 0.197 cm³ g⁻¹) due to rather large particle dimensions and low porosity induced by the template redissolution in water.

Thermal treatment of the (Y,Eu)VO₄ particles in air resulted in the loss of physisorbed water (50–80 °C), and elimination of adsorbed EG, residual carbonates, and OH condensation (330–330 °C, Fig. 5a). The fraction of thermally eliminated material was higher for the smaller particles, both because of the higher

surface areas and because of the higher amounts of EG used in the one pot-syntheses. The (Y,Eu)VO₄ particles lost about 9% to 13% mass when heated up to 500 °C, and volatilization/decomposition of residual species did not result in the formation of new crystalline phases, as shown by diffraction profiles of annealed samples (Fig. S14–S15). Samples obtained by one-pot syntheses showed weight stabilization around 600 °C, but further heating in air resulted in weight increases about 0.28 to 0.51% with respect to the residual mass at 600 °C (Fig. 5a, Table S3). These non-negligible increases in mass could not be observed for TGA runs in N₂ atmosphere (Fig. S16), so they were ascribed to oxidation of oxygen vacancies, which occur in as-prepared particles to compensate V(IV)/V(III) defects or metal vacancies at the bulk [$(v_{\text{O}}^{\bullet})_{\text{lattice}}$] and at the surface [$(v_{\text{O}}^{\bullet})_{\text{surface}}$]. Thermal treatment of bare (Y,Eu)VO₄ particles generates additional $(v_{\text{O}}^{\bullet})_{\text{surface}}$ species due to elimination of H₂O by condensation of surface OH groups (i.e., $2\text{OH}_{\text{O}}^{\bullet} \rightarrow \text{O}_{\text{O}}^{\bullet} + (v_{\text{O}}^{\bullet})_{\text{surface}} + \text{H}_2\text{O}$).⁴⁷ Heating in an oxidizing atmosphere over 600 °C causes oxygen abstraction by the samples and oxidation of bulk and surface vacant sites (i.e., $v_{\text{O}}^{\bullet} + \frac{1}{2}\text{O}_2 \rightarrow \text{O}_{\text{O}}^{\bullet}$). Therefore, O₂ uptakes per mass and per area (considering BET specific surface areas) caused by oxidation of vacancies were estimated from TGA (Fig. 5b,c and Table S3). Uptakes per mass of (Y,Eu)VO₄ showed particles with higher surface area involve abstraction larger amounts of O₂.

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Nanoscale

Figure 5. (a) TGA (left axis) and DTG (right axis) profiles in air of (Y_{0.95}Eu_{0.05})VO₄ particles obtained by hydroxycarbonate conversion in different H₂O/EG v/v. conditions. (b) Variation of O₂ uptakes (μmol O₂ per gram) against specific surface areas. (c) Correlation between O₂ uptakes normalized per surface (10⁻²⁴ mol O₂ per nm²) and cell volumes calculated from XRD. Colors and symbols in a-d correspond to samples prepared with H₂O/EG ratios of 3/2 (40% EG, blue/squares), 1/1 (50% EG, green/circles), 1/2 (67% EG, dark yellow/triangles), and 1/3 (75% EG, dark orange/diamonds)]. Error bars in (b) and (c) were estimated considering that TGA masses are accurate within 1 μg and BET specific surface areas are accurate within 5%.

However, such a correlation is not monotonic, indicating different contribution of bulk vacancies depending on the synthesis conditions (Fig. 5b). Normalizing O₂ uptakes per specific surface areas (*i.e.*, μmol g⁻¹ of O₂ per square meter per gram, so μmol m⁻²) provided an indication of the amount of ($v_{\text{O}}^{\bullet}$)_{lattice} defects (Fig. 5c). Indeed, surface-normalized uptakes correlate well with cell volumes calculated from structural data, showing that smaller particles with expanded unit cells have lower density of ($v_{\text{O}}^{\bullet}$)_{lattice} defects, which led to lower O₂ uptakes per area. Hence, oxygen abstraction by smaller particles arises mainly from generation of ($v_{\text{O}}^{\bullet}$)_{surface} due to OH condensation upon heating. Conversely, particles obtained in H₂O/EG=3/2 showed increased bulk defect density due to Kirkendall voiding, resulting in constricted unit cells which abstract larger amounts of O₂ per area. Finally, even though particles prepared in H₂O/EG=1/1 showed Kirkendall voiding in a lower extent, the low surface area of these solids resulted in the smallest O₂ uptake per mass among the four preparations. In summary, the one-pot conversion of hydroxycarbonate particles can tune not

only the size and morphology of REVO₄ particles, but also the defect density and microstructure of these solids.

XPS spectra (Fig. 6) further confirmed the increased defect density in (Y,Eu)VO₄ particles prepared by one-pot conversion at low EG volume fractions. The Y 3d doublet (3d_{5/2}, 158.8 eV and 3d_{3/2}, 160.8 eV, Fig. 6a,e,i,m) showed satellite signals at low binding energies (157.6 and 159.6 eV), which are related to partially reduced Y sites due to oxygen deficiency ($v_{\text{O}}^{\bullet}$).^{48,49} The contribution of these defect-related signals is clearly higher for obtained at H₂O/EG=3/2 and 1/1. The same behaviour was observed for the V 2p doublet (2p_{3/2} and 2p_{1/2}), where signals were better fitted by multiple Voigt peaks arising from V(V), V(IV) and V(III) species, the two last being also a consequence of oxygen vacancies. Because of the presence of reduced vanadium species, the samples as powders show a pale-yellow colour owing to a V(III/IV)-V(V) intervalence absorption in the visible (Fig. S17).²⁶ Deconvolution of XPS signals enabled estimation of surface atomic compositions (Fig. 6d,h,l,p), which clearly demonstrate the higher abundance of partially reduced metal sites in the samples prepared in lower EG volume fractions (Fig. S18). Hence, our results confirm that the difference in the template conversion mechanism effectively controls the density of defects in the final vanadate particles, where one-pot conversion of hydroxycarbonates in lower EG volume fractions induce higher contribution of Kirkendall voiding, thus culminating into higher contribution of partially reduced metal centres. The density of reduced metal sites with respect to the total amount of metal at the surface ($[M]_{\text{defect}}/[M]_{\text{total}}$) calculated from XPS analysis correlated linearly with O₂ uptakes per area (Fig. S18), which confirms the effect of conversion mechanism on the defect chemistry of the final nanoparticles. The C 1s signals in all samples indicate the presence of residual aliphatic carbon and oxidized species (C-O, O-C=O) arising from EG residues and adventitious carbon. However, the contribution of residual CO₃²⁻ to the C 1s envelope is slightly higher for samples produced with lower EG volume fractions. This is a consequence of the lower reactivity of the large hydroxycarbonate templates (H₂O/EG=3/2, and 1/1), which are less readily consumed during the conversion step in comparison to low size templates. The presence of multiple oxidized carbon species and water also yields complex O 1s signals (Fig. 6c,g,k,o), which precludes adequate specification of the contribution of vacant sites in the different samples. However, XPS results also confirm the non-stoichiometry between Y and V contents at the surface of the nanoparticles, showing V-deficient surfaces were produced in all cases (Fig. 6d,h,l,p). This is commonly observed for annealed YVO₄ samples due to vaporization of vanadium oxides,⁴⁸ but the high defect density induced by the colloidal conversion synthesis and the presence of residual CO₃²⁻ and OH⁻ contribute to the non-stoichiometry of the Y/V ratio in the prepared nanoparticles. Eu³⁺ luminescence spectroscopy provided additional insights into the surface and microstructural properties of the (Y,Eu)VO₄ nanoparticles (Figure 7).

Figure 6. XPS spectra and atomic compositions obtained for $(Y_{0.95}Eu_{0.05})VO_4$ particles prepared using different H_2O/EG volume fractions, namely (a-d) 3/2, (e-h) 1/1, (i-l) 1/2, and (m-p) 1/3. Experimental data are shown by empty symbols, and cumulative fits and backgrounds are shown by red and grey lines, respectively. Color legends of Voigt fits are shown in the right for (a,e,i,m) Y 3d, (b,f,j,n) C 1s, (c,g,k,o) V 2p and O 1s signals. Color bars in (d), (h), (l) and (p) show relative atomic compositions obtained from signal deconvolutions (Eu is not shown for clarity). Survey XPS spectra are shown in Fig. S17.

Different Eu^{3+} concentrations, namely 5% 20% and 40% (mol/mol), were evaluated in H_2O and D_2O suspensions of nanoparticles. Excitation spectra (Fig. 7a,d,g) showed characteristic Eu^{3+} f-f absorptions (350–450 nm), and $VO_4^{3-} \rightarrow Eu^{3+}$ energy transfer band due to the symmetry allowed ${}^3T_{1,2} \leftarrow {}^1A_1$ absorption of VO_4^{3-} (250–350 nm). Normalization of excitation spectra on the main Eu^{3+} f-f absorption (${}^5L_6 \leftarrow {}^5D_0$, 395 nm) provided an indication of the efficiency of the $VO_4^{3-} \rightarrow Eu^{3+}$ and energy migration within the YVO_4 lattice for the different samples. At low Eu^{3+} concentrations (5%), the particles with different morphologies and defect densities showed variable $VO_4^{3-} \rightarrow Eu^{3+}$ energy transfer efficiencies. Whilst particles with high surface areas are more prone to non-radiative deactivation by solvent molecules, increased defect densities contribute with more sites to interrupt the energy migration within the lattice. Consequently, the relative intensities of the $VO_4^{3-} \rightarrow Eu^{3+}$ band with respect to the ${}^5L_6 \leftarrow {}^5D_0$ varied with the same general profile of O_2 uptakes (Fig. 5b), where particles with higher surface (e.g. $H_2O/EG=1/3$) and higher defect density ($H_2O/EG=3/2$) showed the lowest energy transfer efficiency. The effect of surface and defects is clearly overcome by the increase of the Eu^{3+} concentration, which induces cross

relaxation quenching. For Eu^{3+} concentrations of 20% and 40%, the maxima of the $VO_4^{3-} \rightarrow Eu^{3+}$ energy transfer bands were about 10 times higher than the maxima of the $Eu^{3+} {}^5L_6 \leftarrow {}^5D_0$ absorption regardless of the textural and microstructural properties of the nanoparticles (Fig. 7d,g). The emission profiles under UV excitation ($\lambda_{exc}=280$ nm) (Fig. 7b,e,h) were essentially similar, comprising the characteristic ${}^5D_0 \rightarrow {}^7F_J$ ($J=0-4$) transitions of Eu^{3+} in the YVO_4 host lattice. The effects introduced by morphology and nanocrystallinity on the microenvironment around Eu^{3+} ions could also be detected in the emission spectra of particles with low doping levels. In D_{2d} symmetry sites, the 7F_2 level is composed by four components ($A_1+B_1+B_2+E$), where B_2+E Stark levels are optically active within the ${}^5D_0 \rightarrow {}^7F_2$ transition (Fig. 7 j,k,l,m) in addition to vibronic components. Local distortions on the D_{2d} symmetry affect the broadness and the relative intensity of the ${}^5D_0 \rightarrow {}^7F_2(B_2)$ and ${}^5D_0 \rightarrow {}^7F_2(E)$ components,^{50,51} as also observed by Wu *et al.*⁵² and Wang *et al.*⁵³ in $(Y,Eu)VO_4$ nanophosphors. The relative contribution of B_2 and E components can be evaluated by deconvolution of ${}^5D_0 \rightarrow {}^7F_2$ signals into Lorentzian peaks and comparison of their integrated intensities (Fig. 7j-n).

Figure 7. (a),(d),(g) Excitation ($\lambda_{\text{exc}}=615$ nm) and (b),(e),(h) emission ($\lambda_{\text{exc}}=280$ nm) spectra, and (c),(f),(i) luminescence decay curves (5D_0 level, $\lambda_{\text{exc}}=280$ nm/ $\lambda_{\text{em}}=615$ nm) of $(Y_{1-x}Eu_x)VO_4$ nanoparticles [(a-c) $x=0.05$; (d-f) $x=0.20$; (g-i) $x=0.40$] prepared by one-pot synthesis in different H_2O/EG volume ratios, namely 3/2 (40% EG, blue), 1/1 (50% EG, green), 1/2 (67% EG, dark yellow) and 1/3 (75% EG, dark orange). Excitation spectra in (a), (d) and (g) are normalized by the intensity of the $^5L_6 \leftarrow ^7F_0$ absorption of Eu^{3+} . Emission spectra in (b), (e), and (h) correspond to colloids in H_2O (25 mmol L^{-1}) measured in an integrating sphere. (j-m) Amplification of the $^5D_0 \rightarrow ^7F_2$ emissions of the $(Y_{0.95}Eu_{0.05})VO_4$ colloids under 280 nm excitation showing the deconvolution of the two Stark components (B_2+E) in Lorentzian peaks: $H_2O/EG=$ (j) 3/2, (k) 1/1, (l) 1/2, (m) 1/3; experimental data are shown as points, and fitted peaks correspond to red (B_2) and magenta (E) lines. (n) Correlation between the integrated intensity ratios of B_2 and E Stark components ($I(B_2)/I(E)$) and the fraction of defect metal sites ($[M]_{\text{defects}}/[M]_{\text{total}}$) at the surface of the particles; $I(B_2)/I(E)$ was obtained from the Lorentzian fits in (j-m) and $[M]_{\text{defects}}/[M]_{\text{total}}$ was obtained from XPS analysis (Fig. 6 and Fig. S18).

The relative intensity of B_2 and E peaks is more dependent on the angular distortions in the Eu^{3+} coordination polyhedra rather than long range crystallinity. Reduction of the D_{2d} symmetry enables contribution of optically inactive A_1 components increasing the intensity of the high energy peak.⁵⁰ Hence, particles with increased concentration of reduced metal sites and higher defect densities showed more pronounced distortion on the microsymmetry around Eu^{3+} ions (Fig. 7n), in agreement with the previous discussions. The broadness of the $^5D_0 \rightarrow ^7F_2(B_2)$ and $^5D_0 \rightarrow ^7F_2(E)$ peaks is more related to the long-range crystalline quality and chemical homogeneity of the nanoparticles. The broadness of $^5D_0 \rightarrow ^7F_2$ components was similar for all samples, where particles with higher degree of Y/V non-stoichiometry showed slightly broader signals (Fig. S19). So, Eu^{3+} emission profiles agreed well with the compositional and structural results of the $(Y,Eu)VO_4$ nanoparticles obtained by one-pot conversion of hydroxycarbonates.

The particles containing 20% of Eu^{3+} showed the highest absolute emission intensities among the activator concentrations evaluated. The effects of morphology and microstructure resulted in different absolute intensities for

each set of particles of a given Eu^{3+} concentration. The emission intensities depend on a complex balance between particle concentration, scattering, absorptivity, local refractive index, local crystal field, and nonradiative deactivation pathways for each system. Hence, we described the luminescence of the different $(Y_{1-x}Eu_x)VO_4$ nanoparticles in terms of radiative and nonradiative probabilities within the 5D_0 level, as calculated from emission spectra and luminescence lifetimes. The 5D_0 decay kinetics (Fig. 7c,f,i) corresponded to a superposition of decays from multiple sites in all cases. The experimental profiles fitted well for tri-exponential decay functions (Fig. S20-S22), where an average lifetime (τ_{av}) was calculated from Eq. (4):

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3} \quad (4)$$

In which τ_1 , τ_2 and τ_3 correspond to the individual lifetimes for each type of site, and A_1 , A_2 and A_3 are the respective amplitudes. Even though Eu^{3+} should occupy equivalent D_{2d} sites in tetragonal YVO_4 , for nanosized solids one may expect significant contribution of surface and defect-distorted sites, giving rise to multiple decays.

Figure 8. Results of fittings of ${}^5\text{D}_0$ decays ($\lambda_{\text{exc}}=280$ nm) by tri-exponential functions (Eq.(4)) for $(\text{Y}_{1-x}\text{Eu}_x)\text{VO}_4$ nanoparticles prepared at different by at different $\text{H}_2\text{O}/\text{EG}$ conditions: (a,b,e,f,i,j) Luminescence lifetimes in (a,e,i) H_2O and (b,f,j) D_2O , (c,g,i), amplitude factors, and (d,h,m) $|\tau_{\text{H}_2\text{O}}^{-1}-\tau_{\text{D}_2\text{O}}^{-1}|$ differences against specific surface areas of the different nanoparticles. Figures on top (a-d), middle (e-h), and bottom (i-m) refer to τ_1 , τ_2 , and τ_3 respectively. (n) illustrates the nature of sites (in red) giving rise to τ_1 , τ_2 , and τ_3 decays on $(\text{Y}_{1-x}\text{Eu}_x)\text{VO}_4$ nanoparticle. Colors in (a-m) refer to different Eu^{3+} concentrations, namely 5% (green/triangles), 20% (brown/spheres), and 40% (purple/X marks).

The shortest lifetimes observed in our case (τ_1 , 0.04-0.15 ms) depended both on the concentration of Eu^{3+} ions and dispersing medium ($\text{H}_2\text{O}/\text{D}_2\text{O}$, Fig. 8). Contributions from VO_4^{3-} emission are negligible at the detected wavelengths and should yield much faster decays (< 1 μs), so these short τ_1 lifetimes may be related to surface sites strongly influenced by solvent and ions at the Stern layer. Amplitudes associated with τ_1 sites were higher for larger Eu^{3+} concentrations (Fig. 8c) indicating higher proportions of Eu^{3+} occupying positions at the surface in such cases (Fig. 8c). The difference $|\tau_{\text{H}_2\text{O}}^{-1}-\tau_{\text{D}_2\text{O}}^{-1}|$ is an indication of how excited state decays are affected by the exchange of OH by OD oscillators for the considered sites.^{54,55} Sites associated to τ_1 lifetimes showed $|\tau_{\text{H}_2\text{O}}^{-1}-\tau_{\text{D}_2\text{O}}^{-1}|$ differences varying from ~ 0 to 14 ms^{-1} , confirming that both specific surface areas and solvent strongly affect the excited state decay of Eu^{3+} at such positions. Eu^{3+} sites linked to the τ_2 lifetimes showed intermediate decay constants (0.10-0.65 ms) with amplitudes practically independent of the particle surface areas and of Eu^{3+} concentrations (Fig. 8g). Such sites also showed intermediate $|\tau_{\text{H}_2\text{O}}^{-1}-\tau_{\text{D}_2\text{O}}^{-1}|$ differences, which therefore suggests that Eu^{3+} occupies positions at the vicinity of the particle surfaces and defects, because they have long lived excited states but are affected by non-radiative decays induced by the solvent. Finally, τ_3 lifetimes should correspond to bulk sites, which must be the least affected by the exchange of OH by OD oscillators and by specific surface areas (Fig. 8m). These sites comprised the longest components of the lifetimes (0.25-1.35 ms) with amplitudes decreasing with higher Eu^{3+} concentrations (Fig. 8l), suggesting that the Eu^{3+} impurities tend indeed to concentrate preferentially at the surface of the particles.^{26,47,56}

We also accessed radiative (A_{RAD}) and nonradiative (A_{NRAD}) decay rates to compare internal quantum yields (η) of the Eu^{3+} ${}^5\text{D}_0$ levels in the different particles. Internal quantum yields

(also named quantum efficiencies) are defined as the ratio between radiative and total decay rates (Eq. (5)):

$$\eta = \frac{A_{\text{RAD}}}{A_{\text{RAD}} + A_{\text{NRAD}}} = A_{\text{RAD}}\tau_{\text{av}}^{-1}. \quad (5)$$

Radiative decay rates were calculated from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ emissions considering the magnetic dipole-allowed ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition as a reference by (Eq.(6)):

$$A_{\text{RAD}} = A_{\text{MD}}n_{\text{ef}}^3 \frac{I_{0-j}}{I_{\text{MD}}}, \quad (6)$$

where A_{MD} is the probability of spontaneous emission for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition in vacuum ($A_{\text{MD}}=14.65$ ms^{-1}),^{56,57} I_{0-j} is the sum of the integrated intensities of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ transitions, and I_{MD} corresponds to the integrated intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition. The effective refractive index (n_{ef}) was calculated by (Eq. (7)):

$$n_{\text{ef}} = \varphi n_p + (1 - \varphi)n_{\text{med}}, \quad (7)$$

where φ is the concentration of particles expressed as volume fractions, and n_p and n_{med} are the refractive indices of the particles and of the dispersing medium, respectively (n_p was assumed to be 1.99,⁵⁸ and n_{med} was considered as 1.33 for both D_2O and H_2O).⁵⁹

Radiative decay rates (A_{RAD}) are nearly constant within $<10\%$ for all preparations (460 ± 30 s^{-1} , Fig. 9a) for suspensions in both H_2O and D_2O . This confirms morphology, nanocrystallinity, and surface area have minor effects on the radiative probability of the 4f-4f centered emissions of Eu^{3+} as expected, provided local refractive indices are kept constant. Conversely, non-radiative decay rates were strongly affected by Eu^{3+} concentration and OH/OD exchange (Fig. 9b), thus being the determinant parameter with respect to internal quantum yields. The A_{NRAD} values ranged from ~ 400 s^{-1} (5% Eu^{3+} in D_2O) to ~ 8200 s^{-1} (40% Eu^{3+} in H_2O), also varying with the specific surface area of the particle.

Figure 9. Dependence of (a, left column) Non-radiative (A_{NRAD}) and (b, right column) radiative (A_{RAD}) $^5\text{D}_0$ decay rates of $(\text{Y}_{1-x}\text{Eu}_x)\text{VO}_4$ nanoparticles on specific surface areas [(i) $x=0.05$, (ii) $x=0.20$, and (iii) $x=0.40$]. (c,d) Correlation between internal quantum yields divided by particle diameters (η/D_H) and specific surface areas for particles dispersed in (c) D_2O and (d) H_2O . (e) Correlation between overall quantum yields divided per particle diameters (q_{exp}/D_H) and specific surface areas. Symbols and colors in (a–e) refer to different Eu^{3+} concentrations, namely 5% (green triangles), 20% (brown hexagons), and 40% (purple stars); empty symbols refer to measurements in H_2O , filled symbols refer to particles dispersed in D_2O .

The effect of the surface on luminescence stems from distortion of coordination sites and interactions with defects and solvent. Non-radiative decay rates of particles with different Eu^{3+} concentrations and specific surface areas confirmed that solvent interactions can account up to $\sim 50\%$ of the non-radiative events at high surface areas (Fig. 9b(i–iii)), even though Eu^{3+} concentration is still the determinant factor for deactivation of $^5\text{D}_0$ excited state. In H_2O , the internal quantum yields reached maximum values about $\sim 35\%$, 22% , and 8% for Eu^{3+} concentrations of 5%, 20, and 40%, respectively. These values are moderate even considering the low Eu^{3+} concentration (5%) and account for the high surface areas, oxygen defects, as well as the presence of residual carbon species, as previously discussed. In this sense, for example, it is known that significant enhancement of luminescence intensities can be achieved, for instance, by surface passivation with YF_3 layers in core@shell particles.⁶⁰ In our case, the

replacement of OH by OD oscillators resulted in significant increase in internal and overall quantum yields (Table S3).

Concerning the pronounced effect of solvent on luminescence parameters, we initially expected that the difference on non-radiative decay rates of particles in H_2O and in D_2O ($A_{\text{NRAD}}^{\text{H}_2\text{O}} - A_{\text{NRAD}}^{\text{D}_2\text{O}}$) should provide an indirect measurement of the specific surface area of the particles. However, crystallinity and defect density also contribute strongly to non-radiative depletion of excited states. Such effects cannot be isolated and are not constant within the set of particles synthesized at different conditions, so we could not find direct correlation between S_{BET} and $A_{\text{NRAD}}^{\text{H}_2\text{O}} - A_{\text{NRAD}}^{\text{D}_2\text{O}}$ or internal quantum yield values (Table S4). We found, however, that the fluctuations on the values of $^5\text{D}_0$ internal quantum yields with respect to specific surface areas were compensated by dividing η by experimental mean particle diameters (D_H , Fig. 1). The inverse of experimental particle diameters is directly proportional to the surface-to-volume ratio of the nanoparticles, so the proposed experimental correlation may comprise contributions of both surface area and structural parameters (e.g. density and cell volumes). These last are ultimately related to the defect densities. Plotting η/D_H against S_{BET} yielded approximately linear correlations for the three studied Eu^{3+} concentrations in the $(\text{Y}_{1-x}\text{Eu}_x)\text{VO}_4$ nanoparticles suspended in D_2O or H_2O (Fig. 9c,d). Intercepts were nearly 0 in all cases, whilst slopes were higher for low Eu^{3+} concentrations and for suspensions in D_2O , suggesting slopes are inversely proportional to non-radiative decay rates. Given the upper limit of 1 for internal quantum yields, this linear correlation is probably held only for the limited range of specific surface areas and diameters studied. However, such results suggest that measuring particle sizes and internal quantum yields should enable estimation of specific surface area for particles in suspension, provided additional information on solvent/activator interactions and defect chemistry is accessible. This would be highly useful to access surface areas via very simple measurements for particles difficult to isolate, such as those generated *in situ* or of very small sizes.

Results in Fig. 9c,d suggest an apparent positive effect of porosity on internal quantum yields for a given activator concentration. This is because the experimental correlation implies that, for a constant particle diameter, higher values of η would be achieved at higher specific surface areas. In our set of nanoparticles, lower surface areas are associated to particles with increased Kirkendall voiding and more oxygen defects contributing to increase non-radiative decay rates. Even though higher surface areas result in stronger non-radiative interactions with the solvent, the small particles obtained in this work ($\text{H}_2\text{O}/\text{EG}=1/2$ and $1/3$) showed lower amounts of defects (Fig. 5 and 6) to deplete non-radiatively the excited states. Both higher surface areas and higher defect densities may contribute to distortions in Eu^{3+} sites, increasing radiative probabilities by mixing with opposite parity states and by dynamic coupling interactions.⁶¹ However, our results demonstrate these contributions are overcome by the increase of non-radiative

probabilities by both parameters. In our set of (Y,Eu)VO₄ nanoparticles, these effects appear to be interbalanced and can be correlated to surface-to-volume ratios and specific surface areas, which opens room for improved theoretical detailing of the effects of textural and microstructural parameters on the luminescence of Ln³⁺ ions in colloidal oxide nanoparticles.

We observed the same trend considering overall quantum yields (q_{EXP}) related to particle diameters and specific surface areas. Overall quantum yields are defined as the ratio between emitted photons and absorbed photons at a given excitation wavelength. In our case, overall quantum yields were determined in an integrating sphere using 2-aminopyridine in sulfuric acid solution as standard⁴⁴ applying Eq.(8):

$$q_{\text{EXP}} = q_{\text{ST}} \left[\frac{(I_{\text{em}}^{\text{X}} - I_{\text{em}}^{\text{O}})(I_{\text{exc}}^{\text{O}} - I_{\text{exc}}^{\text{ST}})}{(I_{\text{em}}^{\text{ST}} - I_{\text{em}}^{\text{O}})(I_{\text{exc}}^{\text{O}} - I_{\text{exc}}^{\text{X}})} \right], \quad (8)$$

where q_{ST} is the quantum yield of the standard (0.60), I_{em} are integrated intensities at the emission wavelengths and I_{exc} are integrated intensities at the excitation peak ($\lambda_{\text{exc}}=280$ nm) ["X", "O", and "ST" superscripts refer to sample, blank, and standard, respectively; pure water was used as blank]. As measurements were performed in aqueous colloids with relatively low concentrations (25 mmol L⁻¹), absolute luminescence intensities were essentially low. Consequently, samples containing 5% and 40% Eu³⁺ gave <1% quantum yields and therefore could not be compared. Samples doped with 20% Eu³⁺ showed the highest intensities, which resulted in q_{EXP} values suitable for significant comparison (Table S4). In this case, overall quantum yields showed the same linear dependence upon particle diameters and specific surface areas (Fig. 9e), demonstrating the correlation calculated from ⁵D₀ decay rates is also kept for absolute luminescence intensities. Again, a reduced contribution of non-radiative parameters resulted in a higher slope, showing the derivative of $q_{\text{EXP}}/D_{\text{H}}$ with respect to S_{BET} is inversely proportional to A_{NRAD} . The q_{EXP} measurements provided additional evidence for the positive effect of porosity on luminescence intensities, suggesting low defect densities may compensate non-radiative interactions with solvent molecules for (Y,Eu)VO₄ nanoparticles in suspension.

Conclusions

We hereby demonstrated the possibility of tuning morphology, surface area and microstructure of YVO₄ nanoparticles by a one-pot sacrificial template approach based on the conversion of hydroxycarbonates in water/ethylene glycol mixtures at 1 atm and 95 °C. The H₂O/EG volume ratios affected both size and aggregation of hydroxycarbonates, which further determined the mechanisms of colloidal conversion. Low EG volume fractions favoured Kirkendall-type conversion of larger templates, yielding particles with higher defect densities. Higher EG volume fractions contributed to the conversion of small and aggregated templates, producing small YVO₄ nanoparticles with increased porosity. The effects and consequences of surface areas and defect densities were discussed in terms of multiple characterization techniques and

correlated in detail with Eu³⁺ spectroscopic parameters. We found an interesting correlation between surface areas, particle sizes and internal or overall quantum yields, which points towards a positive effect of porosity on the luminescence efficiency of the nanoparticles in suspension. Further investigation comprising particles with comparable defect composition and sizes and variable porosity is the necessary. Also, the results suggest specific surface areas may be accessed by luminescence measurements provided activator concentration and non-radiative contribution of solvents and defects are known. These measurements would obviously vary with pH, ion strength and adsorbates, but they may consist in potential simple tools to estimate active surfaces of luminescent colloidal nanoparticles, also being a highly interesting topic for theoretical modelling of Ln³⁺ luminescence in oxide nanocrystals.

Author Contributions

PCdSF conceived the idea of the work along with GG, who performed most of the synthesis and characterisation experiments with help of the other co-authors. PCdSF and RIW wrote the manuscript with contributions from all co-authors. SH and MW contributed towards SAXS and XPS acquisition and data processing, respectively, under supervision of RIW. All authors reviewed and have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank FAPESP (São Paulo State Research Foundation, Brazil) for grants number 2017/11764-2 (AP-R, PCdSF) and 2018/08334-9 (SPRINT FAPESP-University of Warwick, PCdSF/RIW). We thank the Brazilian agencies CAPES, CNPq, and FAEPEX (Unicamp) for financial support and scholarships. The authors are also grateful to Laboratory of Structural Characterization (LCE/DEMa/UFSCar) for TEM analysis, and to professors O.L. Alves (LQES/Unicamp) and F. Galembeck (Unicamp/inct-INOMAT) for the use of N₂-adsorption and TEM instrumentation. Some of the equipment used in this work was provided by the University of Warwick's Research Technology Platforms.

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