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Graphical Abstract

“A new route through the layered hydroxide form for the synthesis of GdVO₄ dispersible in polar solvents”

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A new strategy is described for the synthesis and the size control of REVO₄ (RE = rare earths) nanoparticles in aqueous solutions at room temperature. In particular, Eu-doped layered gadolinium hydroxychloride was explored as a representative precursor to react with meta-vanadate (VO₃⁻).
A new route through the layered hydroxide form for the synthesis of GdVO$_4$ dispersible in polar solvents

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A new strategy is described for the synthesis and the size control of REVO$_4$ (RE = rare earths) in aqueous solutions at room temperature. In particular, Eu-doped layered gadolinium hydroxochloride was explored as a representative precursor to react with meta-vanadate (VO$_3^-$).

Rare earth orthovanadates (REVO$_4$ where RE = rare earths) are an important family of inorganic materials that have useful catalytic, magnetic, optical, and electronic properties. Because of their excellent luminescence with different colors under ultraviolet (UV), infrared (IR), and cathode-ray excitation, many investigations have also addressed rare earth-doped rare earth vanadates (REVO$_4$:RE). LuVO$_4$:Nd$^{3+}$ and LuVO$_4$:Yb$^{3+}$ were applied as an infrared material for diode pumping and a SiO$_2$/YVO$_4$:Yb$^{3+}$ bilayer film was investigated for increasing photon transmission in c-Si solar cells by the conversion of a UV to two near-infrared (NIR) photons.

In particular, the gadolinium analogs (GdVO$_4$:RE) display bright visible light emission attributed to a strong absorption of UV and successive efficient energy-transfer from VO$_3^-$ to RE$^{3+}$. Therefore, their characteristic high photoluminescence (PL) quantum yields have attracted considerable attention for applications in lamps, X-ray detectors, laser materials, light emitting diodes, and plasma display panels. Due to efficient down-conversion of UV to NIR, GdVO$_4$:Dy$^{3+}$ significantly enhances the spectral response of silicon solar cells, particularly in the range of 200 – 500 nm. The laser emission of GdVO$_4$:Tm$^{3+}$ at ~2 µm is useful for eye-safe related applications. In addition, GdVO$_4$:REs have no significant cytotoxic effects and can be an attractive nanoprobe for dual-modality with biological labeling and magnetic resonance imaging.

However, these particles have been prepared by the solid-state reaction, sol-gel process, and solvothermal methods for which high temperature and/or high pressure conditions are required. Although many advanced techniques such as microemulsion-mediated hydrothermal, complexing agent-assisted, and ultrasonic radiated processes were developed, these methods still need complex procedures and toxic metal-organic precursors or templates. Furthermore, additional surface modification of particles is required to improve their biocompatibility and aqueous colloidal stability. In this context, it would be a great challenge to develop facile and environmentally benign synthetic routes for REVO$_4$ and REVO$_4$:RE that are readily dispersible in polar solvents without any organic or inorganic coating. Here, we describe a new strategy for the synthesis and the size control of REVO$_4$ in aqueous solutions at room temperature (RT).

Layered rare earth hydroxychlorides (LRHs) with the general formula RE$_2$(OH)$_3$Cl$n$H$_2$O (RE = rare earths) have been recently used as a precursor to induce rare earth oxide and oxychloride nanosheets. We previously reported that slurries of this family prepared at RT readily react with transition metal polyoxoanions such as Mo$_6$O$_{19}$$^{4-}$ and [H$_3$W$_4$O$_{12}$]$^{10-}$ to form hierarchical superstructures. In the present work, LRHs were explored as reaction precursors to form REVO$_4$. The framework and polyhedral structure of LRH are illustrated in Fig. 1, where rare earth hydroxoacetate ([RE$_2$(OH)$_3$nH$_2$O]$^{+}$) layers and charge-compensating chloride anion (Cl$^-$) layers are alternately stacked. Because RE(OH)$_3$ with various shapes have been used as self-sacrificing templates to induce REVO$_4$ nanostructures, the main strategy of this work was that meta-vanadate (VO$_3^-$) exchanged for Cl$^-$ anion in the interlayer space of LRH could actively react with [RE$_2$(OH)$_3$nH$_2$O]$^{+}$ hydroxoacetate to form a stable REVO$_4$ even at RT. It is important to note that the size of yielded polyhedra correspond to eight- and nine-coordinated REs linked by intralayer µ$_1$-OH groups, respectively.
particles would be strictly limited by the size of precursor LRH sheets. Furthermore, because no heat treatment is necessary in this procedure, particles induced from rare earth hydroxocations would have a large remnant of hydroxyl groups on their surface so that they could be readily dispersed to form stable aqueous colloidal solutions without any additional surface modification. In the present work, Eu-doped layered gadolinium hydroxide (LGdH:Eu) was selected as a representative example to demonstrate the reaction between hydroxocation nanosheets and VO$_4^{3-}$ anions as well as the optical properties of reaction products.

The procedure to prepare an aqueous colloidal suspension of GdVO$_3$:Eu via the formation of intermediate LGdH:Eu nanosheets is schematically represented in Fig. 1.

$$\text{Gd}_{1.90}\text{Eu}_{0.10}(\text{OH})_2\text{Cl}n\text{H}_2\text{O} \quad (\text{LGdH:Eu})$$

was prepared at room temperature (ESI†). Fig. S1 shows X-ray diffraction (XRD) patterns of LGdH:Eu and powders recovered after reaction in 10 – 50 mM aqueous VO$_4^{3-}$ solutions for 12 h at RT. The XRD pattern of the dried LGdH:Eu slurry is similar to that of Gd$_2$(OH)$_3$Cl$n$H$_2$O, confirming the formation of the typical layered structure. The interlayer water content ($n$) determined by thermogravimetric (TG) analysis was close to 1.5. Compared with relative intensities of GdVO$_3$, diffraction patterns of powders obtained after reactions indicated that the transformation of LGdH:Eu to Gd$_2$(OH)$_3$Cl$n$H$_2$O (LGdH:Eu) was complete in 25 and 50 mM VO$_4^{3-}$ solutions. Thus, the essential formation reaction of GdVO$_3$:Eu in this work was characterized by the equation:

$$\text{Gd}_{1.90}\text{Eu}_{0.10}(\text{OH})_2\text{Cl}n\text{H}_2\text{O} + 2\text{VO}_4^{3-} \rightarrow 2\text{Gd}_{0.95}\text{Eu}_{0.05}\text{VO}_4 + \text{OH}^- + \text{Cl}^- + (2 + n)\text{H}_2\text{O} \quad (1)$$

Scanning electron microscopy (SEM) images showed that the precursor slurry is composed of 100 to 200 nm lateral-sized nanosheets, whereas GdVO$_3$:Eu particles have a rice-like shape (Fig. S2). It was also demonstrated that, because the particle size is restricted by the size of precursor nanosheets, the reaction of LGdH:Eu with VO$_4^{3-}$ ions yielded GdVO$_3$:Eu with a uniform size.

In XRD patterns measured as a function of reaction time (Fig. S3) after adding LGdH:Eu in 50 mM aqueous VO$_4^{3-}$ solution at RT, the disappearance of (00l) reflections from the LGdH:Eu phase was accompanied by the enhancement of reflections associated with GdVO$_3$, resulting in the complete formation of GdVO$_3$:Eu within 2 h at RT. These XRD patterns were consistent with corresponding SEM images (Fig. S4), where no sheet-like particle (i.e. LGdH:Eu) was observed after reaction for longer than 2 h. The reaction between LGdH:Eu and VO$_4^{3-}$ was also characterized by a significant change in PL. Although LGdH:Eu did not show any distinguishable excitation when monitored at 618 nm, the formation of GdVO$_3$:Eu led to a dramatic increase in photoexcitation intensity even after reaction for just 5 min at RT (Fig. S5), suggesting the triggering of conversion at the surface. This strong and broad excitation band centered at around 314 nm is ascribed to charge-transfer (CT) from the oxygen ligands to the central vanadium atom within the VO$_5^{3-}$ group ions, indicating the energy-transfer from CT band to the excited states of Eu$^{3+}$ ions in the GdVO$_3$ matrix. The most efficient charge transfer was observed with GdVO$_3$:Eu obtained after reactions for 1 – 2 h.

Their emission spectra showed typical strong $^5D_{0} \rightarrow ^7F_2$ and weak $^5D_{0} \rightarrow ^7F_1$ transitions of Eu$^{3+}$ (4f$^0$) ions at 618 and 590 nm, respectively.

According to Equation (1), the transformation reaction from LGdH:Eu to GdVO$_3$:Eu is accompanied by the liberation of OH$^-$ and Cl$^-$. Therefore, it was expected that the concentration of OH$^-$ and/or Cl$^-$ in the aqueous solution system could significantly affect the reaction rate. The pH after mixing LGdH:Eu suspension and VO$_4^{3-}$ solution was around 7. To confirm such influences, the solution pH was adjusted to 8, 9, and 10. The Cl$^-$ concentration in the mixture was also increased to 100 mM and 1.0 M at pH ~ 7. Fig. 2A compares XRD patterns of powders recovered after reacting LGdH:Eu with VO$_4^{3-}$ at different pHs, Cl$^-$ concentrations, and reaction times. Although the formation of GdVO$_3$:Eu is practically complete after 1 h at pH ~ 7, a considerable amount of LGdH:Eu remained after 1 h, 2 h, and 3 h at pH ~ 8, 9, and 10, respectively. Similarly, in contrast to the completion after 1 h in 100 mM NaCl solution, the same reaction was not complete after 1 h in 1.0 M NaCl solution. Based on SEM images of GdVO$_3$:Eu particles obtained after complete transformation through prolonged reactions at various conditions (Fig. 2C and Figs. S6 and S7), the particle size is controllable, with higher OH$^-$ and Cl$^-$ concentration resulting in smaller size, while longer reaction time led to larger particle size. Thus, it is clearly demonstrated that the increase in OH$^-$ and/or Cl$^-$
concentration retards the reaction between LGdH:Eu and VO$^{4-}$, and consequently leads to a decrease in size of yielded GdVO$_4$:Eu particles. For instance, when GdVO$_4$:Eu was prepared by the single-step without intermittent separation of LGdH:Eu powder, the high Cl$^-$ concentration in the aqueous solution induced much smaller particle size. In addition, the reduced particle size enhances the photoemission intensity, probably due to the enlarged surface area (Fig. 2B).

The conversion of LGdH:Eu to GdVO$_4$:Eu could also be confirmed by FT-IR spectroscopy (Fig. S8). The librational mode of water ($\sim$640 cm$^{-1}$) and Gd–O stretching vibration ($\sim$550 cm$^{-1}$) in the [Gd$_2$(OH)$_3$]$^-$ layers$^{17}$ were not observed after reaction with VO$^{4-}$. Instead, the vibration of V–O bonds of the VO$_3^-$ group was observed at $\sim$813 cm$^{-1}$. The most interesting feature was that a broad and intense band centered at $\sim$3400 cm$^{-1}$, attributed to the stretching vibration of the hydroxyl group, was still observed after formation of GdVO$_4$:Eu phase. Furthermore, when GdVO$_4$:Eu obtained at different pHs and NaCl concentrations were heated to 500 °C, the weight loss in the range of 9.3 – 10.5% was observed without structural change (Fig. S9). These amounts of weight loss were surprisingly similar to those observed after surface functionalization of GdVO$_4$:Eu nanoparticles with polyacrylic acid ($\sim$9 %) and amino-dextran ($\sim$10 %).$^{11b}$ Thus, it can be proposed that many hydroxyl groups remain on the particle surface because the hydroxocation precursor was converted to GdVO$_4$:Eu phase in an aqueous solution at RT.

Because the surface O–H groups can form hydrogen bonds with polar solvents, the particles functionalized by O–H groups are generally well dispersed in polar solvents.$^{10b}$ In this respect, GdVO$_4$:Eu particles with a great number of surface hydroxyl groups were expected to form a stable colloidal suspension in water without additional surface functionalization. A vigorous shaking of the aqueous solution containing our GdVO$_4$:Eu (10 – 100 mg/L) actually led to translucent suspensions that were stable for more than a week, and these suspensions were readily dispersed in PVA solutions to form transparent GdVO$_4$:Eu/PVA composite films (Fig. 3). The fact that surface modification is not necessary to disperse in polar solvents provides another advantage of our strategy for the synthesis of GdVO$_4$:Eu. Despite the luminescence quenching effect, wherein surface hydroxyl groups significantly reduce the PL efficiency, the colloidal solutions and composite films of GdVO$_4$:Eu in the present work showed sufficiently strong emission. When a commercial 254 nm UV lamp was used, the bright emission from GdVO$_4$:Eu was both visually and spectroscopically confirmed (Fig. S10).

In conclusion, we developed an aqueous solution route for the synthesis of GdVO$_4$:Eu using layered gadolinium hydroxochloride as a precursor. No heating process is required in this procedure but the particle size is controllable by adjusting solution pH or salt concentration. The large quantities of hydroxyl groups remaining on the surface make GdVO$_4$:Eu particles prepared by this route homogeneously dispersible in polar solvents without any further surface modification. Our room temperature aqueous solution route can be exploited for the large scale synthesis of monodisperse REVO$_4$:RE particles for the whole rare earth series.

**Experimental**

Eu-doped layered gadolinium hydroxochloride,

Gd$_{1.95}$Eu$_{0.05}$(OH)$_3$Cl·nH$_2$O (LGdH:Eu) was prepared in aqueous solution at room temperature. Typically, stoichiometric amounts of GdCl$_3$·6H$_2$O and EuCl$_3$·6H$_2$O were dissolved in distilled water to prepare aqueous solutions (0.05 M). After a clear solution was formed, an aqueous KOH solution (0.10 M) was added drop-wise (molar ratio; Gd$^{3+}$/OH$^-\sim1/2$, solution pH $\sim$ 6.8) with uniform stirring. The resulting mixture was kept for 2 h with stirring at room temperature. The precipitate (LGdH:Eu) was centrifuged and washed with water several times.

Aqueous meta-vanadate (VO$^{4-}$) solutions (10, 25, and 50 mM) were prepared by dissolving desired amounts of NaVO$_3$ in distilled water. The obtained LGdH:Eu precursor slurry (10 g/L) was then reacted in VO$^{4-}$ solutions of different concentrations for 5 min – 12 h with vigorous stirring at room temperature. To control the reaction rate and/or the particle size, the reaction of LGdH:Eu in 50 mM VO$^{4-}$ solution was performed at pH = 7, 8, 9, and 10, and NaCl concentrations of 0, 100 mM, and 1.0 M. The precipitate Gd$_{1.95}$Eu$_{0.05}$VO$_3$ (GdVO$_4$:Eu) was centrifuged, washed with water several times, and dried at 60 °C. (Although they were dried at 60 °C to avoid uncertainty of water content, all products can be used without extensive drying.)

For the synthesis of aqueous colloidal suspensions, GdVO$_4$:Eu obtained by the reaction of LGdH:Eu in 50 mM VO$^{4-}$ solution for 2 h were vigorously stirred in deionized water (10, 50, and 100 mg/L). GdVO$_4$:Eu particles were readily dispersed to produce translucent suspensions within 5 min. Single-step synthesis of an aqueous colloidal solution containing GdVO$_4$:Eu particles was accomplished by the consecutive process without intermittent recovery of LGdH:Eu powder; 12 h after drop-wise addition of the KOH solution (0.10 M, 20 mL) into the GdCl$_3$·6H$_2$O and EuCl$_3$·6H$_2$O solution (0.05 M, 30 mL), the NaVO$_3$ solution (molar ratio; LGdH:Eu/VO$^{4-}$ $\sim 1/2$, solution pH $\sim$ 7) was added and the mixture was kept for 2 h with vigorous stirring at room temperature. The final mixture was ultrasonicated to obtain a stable colloidal solution.

GdVO$_4$:Eu/PVA (RE = Eu and Tb) composite films were prepared by the solution casting method. PVA (Mw = 85,000–124,000, 99+% hydrolyzed, 2.0 wt%) was dissolved in water without additional surface functionalization. A vigorous shaking of the aqueous solution containing our GdVO$_4$:Eu (10 – 100 mg/L) actually led to translucent suspensions that were stable for more than a week, and these suspensions were readily dispersed in PVA solutions to form transparent GdVO$_4$:Eu/PVA composite films (Fig. 3). The fact that surface modification is not necessary to disperse in polar solvents provides another advantage of our strategy for the synthesis of GdVO$_4$:Eu. Despite the luminescence quenching effect, wherein surface hydroxyl groups significantly reduce the PL efficiency, the colloidal solutions and composite films of GdVO$_4$:Eu in the present work showed sufficiently strong emission. When a commercial 254 nm UV lamp was used, the bright emission from GdVO$_4$:Eu was both visually and spectroscopically confirmed (Fig. S10).

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diameter) and allowing the water to evaporate at 50 °C. After drying, the film was readily removed from the plate.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Powder XRD patterns, SEM images, PL spectra, TG curves, and FT-IR spectra of GdVO₄:Eu obtained after reactions at various conditions. See DOI: 10.1039/b000000x/

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