Supporting Information

Lanthanide-Doped $GdVO_4$ Upconversion Nanophosphors with Tunable Emissions and Their Applications for Biomedical Imaging

Wenyan Yin[†], Liangjun Zhou[†, #], Zhanjun Gu[†,*], Gan Tian[†, ‡], Shan Jin[†,#], Liang Yan[†], Xiaoxiao Liu[†], Gengmei Xing[†], Wenlu Ren[†], Feng Liu[§], Zhengwei Pan[§], Yuliang Zhao[†,||,*]

[†]Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, P. R.China

[||]Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, National Center for Nanosciences and Technology of China, Beijing, 100190, P. R.China

[#]College of Materials Science and OptoElectronic Technology,Graduate University of Chinese Academy of Sciences, Beijing 100049, P. R.China

[‡]College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China

[§]Faculty of Engineering, Department of Physics and Astronomy, University of Georgia, Athens, Georgia, 30602, USA

[*]Corresponding Authors: zjgu@ ihep.ac.cn, zhaoyuliang@ihep.ac.cn

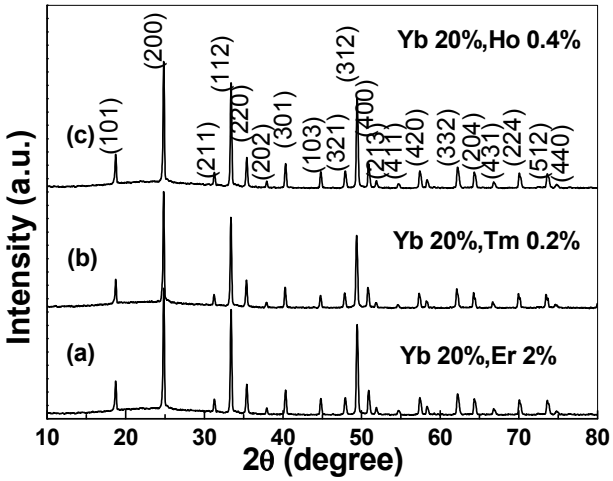

Figure S1 XRD patterns of the lanthanide (Ln) ions (a) Yb 20%, Er 2%, (b) Yb 20%, Tm 0.2% and (c) Yb 20%, Ho 0.4% doped $GdVO_4$ NPs calcined at 700 °C for 2 h in air.

XRD patterns of the samples obtained by calcinations of three $GdVO_4$: Ln at 700 °C for 2 h in air are shown in FigureS1. Strong diffraction lines in all samples can be observed clearly. The XRD results indicated that the as-obtained samples with high crystalline quality match well with tetragonal phase of $GdVO_4$, suggesting their high temperature stability. (Figure S1).

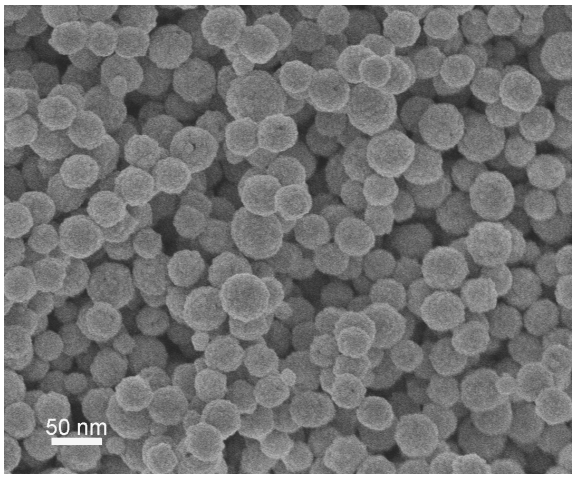

Figure S2. Typical FE-SEM image of $GdVO_4$: Yb, Ho UCNPs after calcinations 700 °C in air for 2 h.

Calcinations of the $GdVO_4$: Yb, Ho sample at 700 °C in air for 2 h resulted in similar morphologies and sizes as those of the $GdVO_4$ before calcinations (Figure S2).

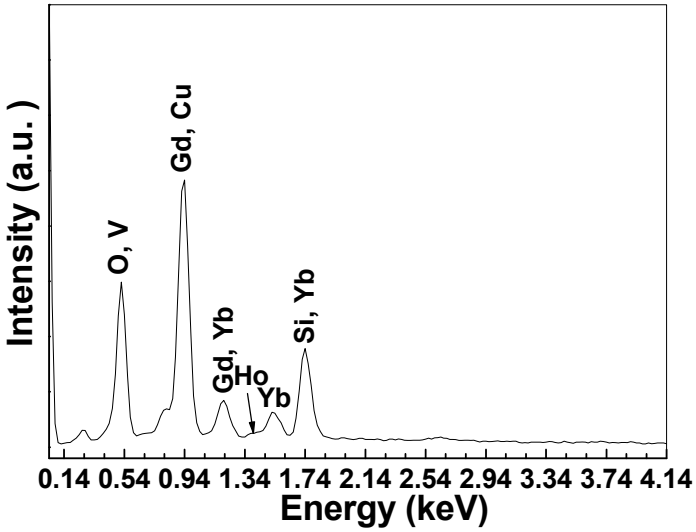

Figure S3. The EDS spectrum obtained from $GdVO_4$: Yb, Ho (20, 0.4 %) UCNPs coated with silica. The Si signal comes from the silica layer and Cu signal comes from the Cu support substrate.

Table S1 Summary of the ICP-Ms data on the upconversion nanoparticles obtained under different concentrations of lanthanide ions dopants

Sample	Designed reactants molar ratios (mol)	ICP-Ms results actual molar ratios
1	$GdVO_4$: Yb, Er (20, 2 %)	Gd:Yb: Er = 78.1:19.98:1.897
2	$GdVO_4$: Yb, Ho (20, 0.4 %)	Gd:Yb: Ho = 79.43:20.2:0.327
3	$GdVO_4$: Yb, Tm (20, 0.2 %)	Gd:Yb: Tm = 79.67:20.14:0.194
4	$GdVO_4$: Yb, Er, Tm (20, 0.2, 0.2 %)	Gd:Yb: Er: Tm = 79.4:20.3:0.143:0.122
5	$GdVO_4$: Yb, Er, Tm (20, 0.5, 0.2 %)	Gd:Yb: Er: Tm = 79.4:19.77: 0.479: 0.143
6	$GdVO_4$: Yb, Er, Ho (20, 0.3, 0.4 %)	Gd:Yb: Er: Ho = 79.32:20.1: 0.28: 0. 326

To calculate the actual molar ratios of the as-synthesized lanthanide ions doped $GdVO_4$ nanoparticles, inductively coupled plasma mass spectrometer (ICP-MS, JY Ultima, French) was performed. The results were listed in Table S1. From the ICP-MS data, the actual molar ratios of Gd: Ln (Ln = Yb, Er, Tm, Ho) were measured, which were in good agreement with the designed composition for the six samples with tunable upconversion emission spectra.

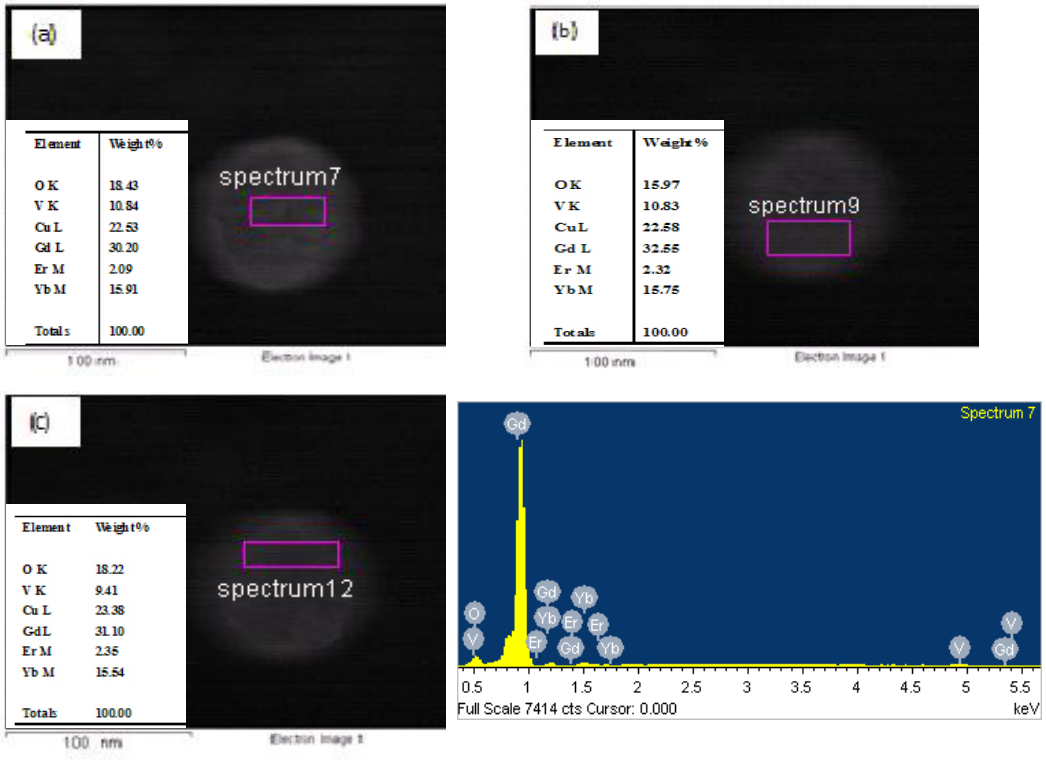

Figure S4 (a-c) SEM images a $GdVO_4$: 20% Yb, 2% Er nanoparticle marked in three different areas with rectangle. (d) EDS spectrum of the $GdVO_4$: 20% Yb, 2% Er nanoparticle in image (a).

The X-ray energy-dispersive spectroscopy (EDS) attached to FE-SEM was used to prove the elements' distribution of the as-synthesized nanoparticles (Figure S4). Taken one typical $GdVO_4$: 20%Yb, 2%Er nanoparticle as an example, the representative EDS spectrum of the nanoparticles confirmed that Gd, V, O, Yb, Er ions have been successfully doped into the nanostructure (spectrum 7 corresponding to the areas in image a). Cu signal comes from the Cu substrate. Three different areas of a $GdVO_4$: 20% Yb, 2% Er nanoparticle were measured and marked in rectangle (Images a, b, and c). Also, the corresponding elements integrating data in the three different areas were summarized and shown in the inset of these images. The content of the elements are similar in the three areas. Therefore, it can be concluded that the elements and their content distribution are uniform and highly dispersed.