Ag-SiO$_2$-Er$_2$O$_3$ Nanocomposites: Highly Effective Upconversion Luminescence at High Power Excitation and High Temperature

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Rare Earth (RE) activated upconversion phosphors (UCPs), have demonstrated significant application potentials in some front fields, including solar energy conversion and bio-application. However, some bottleneck problems should be overcome, such as the lower upconversion efficiency, narrower excitation band, concentration-quenching and temperature-quenching. To solve these problems, the Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites were fabricated, in which the upconversion luminescence (UCL) of Er$_2$O$_3$ was white broadband. Through the interaction of Er$_2$O$_3$ with surface plasmon (SP) of silver nanoparticles (SNPs), the threshold power for generating broadbands was suppressed largely in contrast to the Er$_2$O$_3$ nanoparticles (NPs), while the UCL brightness was enhanced remarkably, ranging from several to 10$^4$ times, which strongly depended on the power density of excitation light. At excitation power density of 1.50 W/mm$^2$ of 980 nm light, the UCL intensity of Ag-SiO$_2$-Er$_2$O$_3$ is 40-folds than the well-known NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ commercial powders. And more, it is also interesting to observe that the composites demonstrate two excitation bands extending of 780–980 nm, highly improved UCL with elevated temperature and excitation power density. The UCL mechanism related to UCL enhancement was carefully studied.

UCL, which can convert infrared (IR) radiation into visible light via a two-photon or multi-photon absorption process, has attracted extensive interests because of their potential applications in the field of upconversion lasers, IR quantum counters, three-dimensional (3D) displays, in vivo fluorescence imaging and et al$^{1–5}$. Among various UCP, some RE ions (such as Er$^{3+}$/Yb$^{3+}$ or Tm$^{3+}$/Yb$^{3+}$) co-doped fluoride phosphors are most favorable under 980-nm excitation, because of their sufficient absorption, matching energy levels and low phonon threshold, which lead to relatively efficient UCL$^6$. Yet, these UCL have some disadvantages, which can not satisfy the requirement of various practical applications. First of all, their upconversion efficiency is still low, for instance, bulk NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ in hexagonal phase, which is commonly considered as the most efficient UCP, its efficiency is only 3% under 980-nm excitation. And the strength of corresponding nanosized phosphor (<20 nm) is only one of tenth of the bulk$^{7–8}$. Second, because of the presence of the local thermal effect and saturation effect, the UCL intensity will saturate and even quench at relatively high excitation power density, which vitally influences the brightness of UCL$^9$. Third, the temperature quenching phenomenon usually happens at high temperature, and the concentration quenching occurs as the concentration of activators is too high$^{9,10}$. In addition, for most of RE activated UCPs based on 4f–4f transitions, the excitation band is relatively narrow, which is difficult to satisfy the requirement of various optical devices, especially the requirement of solar spectrum conversion$^{11}$. Until now, it is still a challenge to obtain highly efficient UCPs, especially for applications under extreme conditions, such as high power excitation and high temperature.

Recently, Wang et al. observed that some lanthanide oxides micropowders, such as Yb$_2$O$_3$, Sm$_2$O$_3$, demonstrated efficient UC broadband emissions under the excitation of a 1 W 980-nm laser diode in vacuum, and the upconversion efficiency was estimated to be as high as 10%, and they attributed the broadband emissions to thermal avalanche$^{12}$. Further works were performed to identify the origin of the broadband emissions by Strek et al. and Wang et al$^{13,14}$. Strek attributed the broadband emissions to the charge transfer transition of Yb$^{3+}$. Our group observed that some lanthanide oxides, such as Er$_2$O$_3$, Sm$_2$O$_3$, Nd$_2$O$_3$ and Pr$_2$O$_3$ demonstrated not only...
sufficient UC broadbands, but also sufficient IR broadbands, ranging of 1000–1700 nm under 980-nm excitation. The evolution of upconversion broadband of micro-sized Er\textsubscript{2}O\textsubscript{3} with excitation power were studied, which showed that the broadbands actually came from the contribution of multi-transitions of Er\textsuperscript{3+} ions and spectral broadening of these transitions with elevated temperature\textsuperscript{15}.

On the other hand, various methods have been explored to improve the strength/efficiency of UCL of nanophosphors\textsuperscript{16–19}. Surface enhanced fluorescence of emitters on rough noble metal surfaces is a promised way to largely enhance the UCL of RE doped nanophosphors\textsuperscript{20–22}. Recently, UCL enhancement based on the coupling of nanophosphors with noble metals such as gold and silver have been widely observed in UCPs, such as NaYF\textsubscript{4}:Yb\textsuperscript{3+},Er\textsuperscript{3+} and NaYF\textsubscript{4}:Yb\textsuperscript{3+},Tm\textsuperscript{3+}. However, no literatures are related to the UCL enhancement of lanthanide oxides, a novel type of efficient UCP. In this paper, the Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites were prepared to obtain effective enhancement of UCL. It is exciting to observe that in the composites, the UCL was improved an order of 10\textsuperscript{0–10}\textsuperscript{4}, depending of the excitation power density. And the UCL of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} composites was more effective than bulk NaYF\textsubscript{4}:Yb,Er at the high power excitation and the high temperature environment. Furthermore, the UC broadband emission and UCL enhancement mechanism of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites were proposed.

Results and Discussion

Morphology and Structure. First, the morphology of Ag NPs, Ag-SiO\textsubscript{2}, Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites and Er\textsubscript{2}O\textsubscript{3} NPs were examined by HR-TEM images, as shown in Fig. 1 (b–d). Fig. 1(b) shows the TEM image of the Ag NPs, which indicates that the Ag NPs are basically uniform and monodisperse, with an average diameter of \sim 60 nm. From Fig. 1(c), it can be distinguished that after coating with SiO\textsubscript{2}, Ag-SiO\textsubscript{2} composites with core-shell structure are formed and the composites are monodisperse. The thickness of the SiO\textsubscript{2} shell is about 10–15 nm. In Fig. 1(d), it can be seen that after further coating with Er\textsubscript{2}O\textsubscript{3}, the sizes of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} composites grow to 150–200 nm and are sphere-like in shape. Because of large contrast of Er\textsubscript{2}O\textsubscript{3}, the internal structure of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} is unable to identify. The illustration of Fig. 1(d) shows the TEM image of Er\textsubscript{2}O\textsubscript{3} NPs prepared by the same method, which shows that the diameter of Er\textsubscript{2}O\textsubscript{3} NPs is about 150–200 nm, similar to Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} NPs.

In order to further identify the internal structure of the Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites, Fig. 1 (e) shows the EDX mapping to analysis of elements of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} sample. From left to right, they represent silver, silicon, erbium, and oxygen elements, respectively. It can be seen that all of the elements distribute homogeneously in the whole sphere. Layer gradient distribution of elements can not be identified. This suggests that all the elements have been diffused after annealing at 500\textdegree C. In the fringe patterns of the Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites (Fig. 1 (f)), two different fringe spacing was determined to be \sim 0.301 nm and \sim 0.231 nm, which corresponded closely with the spacing of the (222) plane of cubic Er\textsubscript{2}O\textsubscript{3} (0.307 nm) (JCPDS No. 77-0464) and the (111) plane of fcc silver (0.235 nm) (JCPDS No. 87-0717), respectively. From the HR-TEM, we can further deduce the forming of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites.

Fig. 2 shows the XRD patterns of the samples Ag NPs, Ag-SiO\textsubscript{2} composites, Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites. Comparing to the corresponding standard cards, it can be seen that silver and Er\textsubscript{2}O\textsubscript{3} NPs in pure cubic phase are formed. And, after coating with SiO\textsubscript{2} shells, no extra patterns could be identified except Ag NPs, because SiO\textsubscript{2} shells are amorphous in phase. In the Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} composites, both XRD patterns of cubic silver and cubic Er\textsubscript{2}O\textsubscript{3} could be identified, as shown in the figure, implying the formation of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} composites.

Fig. 3 shows the UV-Vis-Infrared absorption spectra of Ag NPs, Ag-SiO\textsubscript{2} composites, Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites. Comparing to the corresponding standard cards, it can be seen that silver and Er\textsubscript{2}O\textsubscript{3} NPs in pure cubic phase are formed. And, after coating with SiO\textsubscript{2} shells, no extra patterns could be identified except Ag NPs, because SiO\textsubscript{2} shells are amorphous in phase. In the Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} composites, both XRD patterns of cubic silver and cubic Er\textsubscript{2}O\textsubscript{3} could be identified, as shown in the figure, implying the formation of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} composites.

Fig. 3 shows the UV-Vis-Infrared absorption spectra of Ag NPs, Ag-SiO\textsubscript{2} composites and Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} composites. It can be seen that the silver NPs demonstrate relatively narrow surface plasmon absorption (SPA), peaking around 420 nm. After coating with SiO\textsubscript{2} shell, the SPA of silver shifts toward red side due to the dielectric effect\textsuperscript{23,25}. It’s interesting to observe that the SPA of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} composites demonstrates broadbands, extending from 350–1100 nm.

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**Figure 1** (a) The specific preparing procedure of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites, (b–d) TEM images of the as-prepared Ag NPs, Ag-SiO\textsubscript{2} composites, and Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites, (e) the energy-dispersive X-ray (EDX) mapping of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} sample at the bottom of the figure, (f) the HR-TEM images of Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites.

**Figure 2** XRD patterns of the Ag NPs, Ag-SiO\textsubscript{2} composites, Ag-SiO\textsubscript{2}-Er\textsubscript{2}O\textsubscript{3} nanocomposites samples.
Two bands can be identified, one locates around 450 nm, and the other locates around 700 nm, corresponding to the transverse and longitude SPA of silver, respectively. Furthermore, as a comparison, the absorption spectrum of Er$_2$O$_3$ NPs was given in Fig. 3, it can be seen that there is no obvious peak, and with the decrease of wavelength the absorption increases, attributed to the scattering of the Er$_2$O$_3$ NPs. This suggests that, in the Ag-SiO$_2$-Er$_2$O$_3$ composites, the silver NPs might have been changed into small NPs and these small NPs demonstrate anisotropic, leading to the occurrence of longitude SPA of silver.

UCL Enhancement of Ag-SiO$_2$-Er$_2$O$_3$ Nanocomposites. Fig. 4 (a) and Fig. 4 (b) show the UCL spectra of Er$_2$O$_3$ NPs and Ag-SiO$_2$-Er$_2$O$_3$ composites under the excitation of 0.26–1.41 W/mm$^2$ 980 nm light, respectively. It can be seen that, with relatively low excitation power, the emission spectra of Er$_2$O$_3$ and Ag-SiO$_2$-Er$_2$O$_3$ both have two groups of emission lines. The lines in the green range correspond to the $^4\text{H}_{11/2}/^4\text{S}_{3/2}$ transitions, while those in the red range to the $^4\text{F}_{7/2}/^4\text{I}_{15/2}$ transitions, and the red emissions of $^4\text{F}_{9/2}/^4\text{I}_{15/2}$ are dominant for Er$_2$O$_3$ NPs. This is in consistent with the result of micro-sized Er$_2$O$_3$ and can be mainly attributed to the contribution of cross relaxation channels for Er$^{3+}$ ions$^{15}$. And with increasing the excitation power, a broadband emission ranging of 400–800 nm appears and the intensity ratio of the red to the green emission also decreases with the increasing excitation power. In addition, under the excitation of relatively high excitation power, both Er$_2$O$_3$ and Ag-SiO$_2$-Er$_2$O$_3$ NPs demonstrate broadband emissions, and their central positions both locate around 600 nm (~2 eV), independent of excitation power density. It should be highlighted that in contrast to Er$_2$O$_3$, the threshold power of generating white broadbands in the Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites degraded from 0.65 W/mm$^2$ to 0.26 W/mm$^2$. In our previous work, the UCL of Er$_2$O$_3$ microsized powders was studied, which demonstrated considerable difference comparing to the present Er$_2$O$_3$ NPs and Ag-SiO$_2$-Er$_2$O$_3$ composites. As a comparison, the UCL spectra of bulk Er$_2$O$_3$ were shown in Fig. 4(c)$^{15}$. In the bulk

Figure 3 | The absorption spectra of Ag NPs, Ag-SiO$_2$ composites and the Ag-SiO$_2$-Er$_2$O$_3$ composites.

Figure 4 | (a–c) The UCL spectra of Er$_2$O$_3$ NPs, Ag-SiO$_2$-Er$_2$O$_3$ composites, and the UCL spectra of bulk Er$_2$O$_3$ under as a function of 980 nm excitation power density, respectively, (d) the UCL EF as a function of excitation power density.
Er$_2$O$_3$, the UCL of Er$^{3+}$ ions originates from the emissions of Er$^{3+}$ all the time. The generation of broadbands originates from the contribution of different transitions of Er$^{3+}$ ions, $^4\text{H}_{9/2}/^4\text{F}_{5/2}$ and $^4\text{I}_{15/2}$ (three-photons), $^4\text{I}_{15/2}/^4\text{S}_{3/2}$ and $^4\text{I}_{11/2}$ (two-photon) and $^4\text{I}_{15/2}/^4\text{F}_{7/2}$ (three-photon) and their spectral broadening. In the Er$_2$O$_3$ NPs and Ag-SiO$_2$-Er$_2$O$_3$ composites, the broadband locates around 600 nm and is independent of excitation power, which is very similar to our previous result observed in YVO$_4$:Yb,Er$^{3+}$ 600 nm and is independent of excitation power, which is very similar to our previous result observed in YVO$_4$:Yb,Er$^{3+}$ NPs.$^9$ It could be attributed to the UCL of oxygen defects. Actually, the broadband UC emissions in lanthanide oxides are quite complex and their origins have not been clarified, and basically, they could be attributed to charge transfer transitions of rare earths, defect transitions, or electron-hole pairs.$^{13,27,28}$ The mechanism will be discussed later in details.

Fig. 4(d) shows the UCL enhancement factor (EF), which is defined as the ratio of UCL intensity of the Ag-SiO$_2$-Er$_2$O$_3$ composites to that of Er$_2$O$_3$ NPs as a function of excitation power density. It is interesting to see that the enhancement factor (EF) varies significantly with excitation power density, from several times to 10$^4$ times. At relative low excitation power, the UCL intensity of Ag-SiO$_2$-Er$_2$O$_3$ increases from several times to several ten times over that of Er$_2$O$_3$. As the excitation power increases to 0.57 W/mm$^2$, due to the sudden change of UCL (see Fig. 6), the enhancement factor dramatically increases to 9850 times, which shows that the UCL intensity of Ag-SiO$_2$-Er$_2$O$_3$ is about four orders higher than that of Er$_2$O$_3$. As the excitation power density increases further, EF gradually decreases. And at relatively high excitation power density (0.8–1.6 W/mm$^2$), EF gradually decreases to 7 times.

It is interesting to observe that, in the Er$_2$O$_3$ NPs, the UCL of the broadband was obtained not only under the excitation of 980 nm, corresponding to the excitation of $^4\text{I}_{15/2}-^4\text{I}_{11/2}$ transition of Er$^{3+}$ ions, but also under the excitation of 780–860 nm laser, corresponding to the excitation of $^4\text{I}_{15/2}-^4\text{F}_{9/2}$ transition of Er$^{3+}$ ions, as shown in Fig. 5. The UCL spectra of Ag-SiO$_2$-Er$_2$O$_3$ under the excitation of 808 nm light were recorded in Fig. S1, which showed that the UC emission bands extended of 400–750 nm, and the central emissions located at around 660 nm, corresponding to the $^4\text{I}_{15/2}-^4\text{I}_{11/2}$ transitions of Er$^{3+}$ ions and the other transitions of Er$^{3+}$ ions, $^4\text{I}_{15/2}/^4\text{I}_{11/2}$ and $^4\text{I}_{15/2}/^4\text{F}_{7/2}$ could also be identified. From the absorption spectra of Er$^{3+}$ ions in Fig. 5, it’s known that the absorption value of 808 nm is significantly lower than 980 nm, the achievement of UC broad band emission under 808 nm excitation should have higher excitation power density than that under 980 nm excitation. And the excitation power density of 808 excitation (0.29–0.37 W/mm$^2$) in Fig S1 is lower than that with the 980 nm excitation, leading to the weaker UC broad band emission. Because the intrinsic transition of Er$^{3+}$ ($^4\text{I}_{9/2}-^4\text{I}_{11/2}$) is the main emission, leads to red-shift of the central emissions to 660 nm, so the broad band for 808 nm excitation is different from that for 980 nm excitation. In fact, we measured the UC broad band emission under 808 nm excitation (with excitation power density $\sim$6 W/mm$^2$, at the excitation spectra measurement), the broad band emission is exactly in accordance with those under 980 nm excitation. Furthermore, the UC excitation spectra in the range of 780–860 nm in Er$_2$O$_3$ NPs and Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites were measured and compared (the excitation power density $\sim$6 W/mm$^2$), as shown in Fig. 5. It should be noted that the UC broadband emission spectra are exactly in accordance with those under 980 nm excitation. With the excitation range of 780–860 nm, the obvious excitation bands were identified, centering around 790 nm, for both Er$_2$O$_3$ NPs and Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites, which were in accordance with the $^4\text{I}_{15/2}-^4\text{I}_{9/2}$ excitation transition of Er$^{3+}$ ions. In Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites, the UCL enhancement of several times was observed in the whole range from 780 nm to 860 nm. The UCL enhancement in Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites could be due to three reasons: First, under 780–980 nm excitation, corresponding to the longitude SPA of Ag NPs, ET from Ag NPs to Er$_2$O$_3$ happened effectively, leading to UCL enhancement in Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites; Second, the excitation and emission strength enhanced due to the field enhancement effect; Third, the thermal effect happened with the surface plasmon excitation of Ag NPs, leading to the thermal avalanche enhancement effect;
In order to further confirm the mechanism of UCL enhancement, the Ag-SiO2-Y2O3:10%Yb,1%Er nanocomposites on excitation power density of 980 nm light in logarithmic coordinate. It can be seen that basically the power density dependence can be divided into three periods. For Er3+ NPs, the overall UCL intensity first decreases slowly with the increasing excitation power before the generation of UC broadband. As the UC broadband appears, the UCL intensity increases dramatically with the increasing excitation power, with a power law of 1 ~ P^n and the slope n is as high as 18.1. Then, as the excitation power continuously increases, the slope n drops to 3.8. For the Ag-SiO2-Er2O3 composites, the UCL intensity increases with a slope of n = 2.27 before generation of the broadband. Then, a sudden increase occurs, accompanying the generation of UC broadband, and after that, the UCL intensity increases with a slope of n = 9.3. Finally, the slope drops to n = 1.07. Presently, the super-strong and complex power dependence of the UCL intensity has not been completely understood. It is suggested that during the UC process, photon avalanche or thermal avalanche probably happens. For comparison, the excitation power density dependence of integral UCL intensity (including H1/2/6, S3/2, F9/2-4I15/2 transitions) of the bulk NaYF4:Yb, Er were given in Fig. 6. The value of slope n was about 1.1, which was much smaller than the required photon number (n = 2, 3) populating to the corresponding levels. This can be attributed to the saturation effect as well as the local thermal effect induced by the laser exposure. And with further increasing the excitation power, the UCL intensity has a decrease in NaYF4:Yb, Er. Fig. 6(b) shows the UCL enhancement factor (EF1), which is defined as the ratio of UCL intensity of Er2O3 and Ag-SiO2-Er2O3 NPs to that of the NaYF4:Yb, Er powders, respectively, as a function of excitation power density. From Fig. 6(b), it’s observed that at lower excitation power density, the traditional UCL material such as NaYF4:Yb, Er has great advantage because of the lower excitation threshold, however with higher power excitation, Er2O3 and Ag-SiO2-Er2O3 nanocomposites have higher UCL intensity, because of the high saturation effect and the local thermal effect in NaYF4:Yb, Er samples. In Fig. 6(a), it can be seen that the enhancement of Ag-SiO2-Er2O3 nanocomposites has higher UCL intensity than that of Er2O3 NPs, which is beneficial for the generation of broadband emission.

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As is known, the concentration quenching phenomenon would happen especially in UCL material as the concentration of activators is too high because of cross relaxation, which limits the UC strength of the RE activated UCP. Recently, Jin et al. reported that high excitation irradiance could alleviate concentration quenching in UCL when combined with high activator concentration. In Er2O3 and Ag-SiO2-Er2O3 NPs, which the concentration of activator was 100% in molar ratio, the similar phenomenon was also observed. As the excitation power density was lower, the concentration quenching happened seriously, which was confirmed by the much lower UCL intensity of Er2O3 in comparison to that of Y2O3:Yb, Er. However, at sufficient excitation power, the effective UCL was generated for both nanosized and bulk Er2O3 (See Fig. 6), and Ag-SiO2-Er2O3, implying the concentration quenching was perfectly suppressed (In the bulk Er2O3, the luminescent centers were contributed by Er3+ ions all the time, and in the nanosized samples, the generation of broadband originated from the excitation of Er3+ ions).

Furthermore, the temperature dependence of the UCL integral intensity (normalized at 300 K) of Er2O3 NPs, Ag-SiO2-Er2O3 composites, and bulk NaYF4:Yb, Er on 980 nm light excitation.

The origin of UC Broadband Emission. In order to better understand the origin of the UCL process, the temperature and photocurrent, as a function of excitation power density in the Er2O3 NPs and Ag-SiO2-Er2O3 nanocomposites with the increasing temperature. From the results, we can deduce that it’s difficult to realize effective UCL in traditional materials (such as NaYF4:Yb, Er) at high power excitation, high concentration activator and high temperature conditions. While for Ag-SiO2-Er2O3 composite, it overcomes these problems, which has great significance in extreme conditions.
was shown in Fig. 8b. The photocurrent increases with the excitation power density, which is along with generating the UC broadband. And the photocurrent has higher value in Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites. It's interesting to observe that the integral intensity of UC broadband in Er$_2$O$_3$ and Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites satisfies with the linear dependencies with the photocurrent increasing (Fig. 8c–d). From Fig. S3, the photocurrent increases dramatically with the increasing excitation power, with a power law of $I_c \propto P^n$ and the slope $n$ is 6.9 and 3.8 in Er$_2$O$_3$ and Ag-SiO$_2$-Er$_2$O$_3$ nanocomposites, respectively. The high slope $n$ of UC broadband ($I_c \propto P^n$) would be attributed to the high slope $n$ of photocurrent ($I_c \propto P^n$). Furthermore, the temperature dependent photocurrent of Er$_2$O$_3$ and Ag-SiO$_2$-Er$_2$O$_3$ composites was shown in Fig. 9. According to the Boltzmann distribution, the relationship between the electrical conductivity $\sigma$ and the temperature $T$ can be written as, $\sigma = \sigma_0 e^{-\Delta E/k_0 T}$, where $k_0$ is Boltzmann’s constant, $\Delta E$ is the energy difference between the valence band maximum of Er$_2$O$_3$ and the unknown confined state in the bandgap (Most of RE$_2$O$_3$ compounds were p-type semiconductors[31]). According to Figure Fig. 9, $\Delta E$ was deduced to be 1.11 eV and 1.21 eV. As to the origin of the unknown state, has not been clarified. Here, we suggest that the excited state of Er$^{3+}$ (4I$_{13/2}$) is the possible candidate of the confined state (its ground state locates above the valance band maximum).

Recently, Strek et al. have also observed UC broadband in LiYbPO$_4$O$_{12}$ and its origin was attributed to the radiative charge transfer transitions of Yb$^{3+}$ or Yb$^{2+}$[32]. According to the literatures, the charge transfer (CT) emissions of Yb$^{3+}$ and Yb$^{2+}$ located at around 560 nm (~2.2 eV) and 650 nm (~1.9 eV) in oxide compounds, respectively, which was different from the present result at 600 nm (~2.0 eV). In our previous work, in YVO$_4$:Yb, Ln$^{3+}$ (Er$^{3+}$, Tm$^{3+}$,
The schematic of the possible mechanism of UC broadband emission in Er₂O₃ NPs and UCL enhancement in Ag-SiO₂-Er₂O₃ nanocomposites.

Figure 11

**Conclusions**

In this paper, Ag-SiO₂-Er₂O₃ nanocomposites were prepared by a wet-chemical method and characterized by XRD patterns, TEM images, EDX mapping, and UV-vis absorption spectra. The results show that the anisotropic small Ag NPs distribute randomly and have strong SPA in the range of 400–1000 nm in the composites. In the composites the UCL intensity was improved greatly over that of Er₂O₃, depending strongly on excitation power of 980-nm laser diode. The enhancement factor changed from several times until to ~10⁴, and under the excitation of 1.5 W/mm², the UCL intensity of Ag-SiO₂-Er₂O₃ improved 40 times over the well known NaYF₄:Yb³⁺,Er³⁺ commercial powders. And more, it should be noted that the UCL of the broadband in Ag-SiO₂-Er₂O₃ as well as Er₂O₃ demonstrated favorable two excitation bands, could effectively avoid concentration quenching and temperature quenching. The mechanism of the broadband UCL in Er₂O₃ and Ag-SiO₂-Er₂O₃ was attributed to the electron-hole combination and the UCL enhancement in Ag-SiO₂-Er₂O₃ was mainly attributed to thermal effect, which dramatically increased the density of holes on the valence band. Overall, the Ag-SiO₂-Er₂O₃ composite is a novel favorable UCP with super intense UCL and is promised to work at extreme conditions such as at high pumping power and at high temperature.

**Methods**

**Sample preparation.** The specific preparing procedure was as follows, shown in Fig. 1(a). Firstly, the 60-nm silver was prepared through ethylene glycol reduction method. In a typical synthesis process, 3.3 g PVP-K40 was first dissolved in EG at the room temperature, after that 0.14 g AgNO₃ was added and stirred for ten minutes. The mixture was heated to 120 °C for an hour, then allowed to cool naturally. The whole process had the protection of nitrogen. The Ag nanoparticles (NPs) were isolated by centrifugation and washed several times with acetone and deionized water. Then, Ag-SiO₂ composites were prepared by the modified STOBER method. The
as-prepared Ag NPs and a small amount of ammonia and TEOS were dissolved in ethanol and stirred for 24 hours at room temperature. Then, the precipitates were collected and washed three times with alcohol. After that, the precipitates (Ag-SiO₂) were dissolved in deionized water, added into Er(NO₃)₃·H₂O and urea, heated at 90°C for an hour and cleaned with alcohol three times. Then, the obtained sample was annealed at 500°C for 3 hours. At last, the Ag-SiO₂:Er₂O₃ composites were collected. For comparison, Er₂O₃ NPs were synthesized by a similar method.

Characterization. The morphology of the products was recorded on a Hitachi H-81001 transmission electron microscope (TEM) under an acceleration voltage of 200 kV. The energy-dispersive X-ray (EDX) elemental mapping images were recorded on a FEI Tecnai G2 S-Twin microscope under a working voltage of 200 kV. Raman spectra and the phase structure and purity of the as-prepared samples were characterized by X-ray powder diffraction (XRD) with a Rigaku D/max 2550 X-ray diffractometer, using a monochromatized Cu target radiation (λ = 1.54 Å). UV/Vis–NIR absorption spectra were measured with a Shimadzu UV-1800PC UV/Vis–NIR scanning spectrophotometer in the range from 300 to 1100 nm. In the measurements of power-dependent UCL spectra, a continuous 980 nm was used to pump the samples. A visible photomultiplier (350–850 nm) was combined with a double-grating monochromator to collect the UCL signals. A continuous 980 nm was used to pump the samples. A visible photomultiplier (350–850 nm) was combined with a double-grating monochromator to collect the UCL signals.

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