We report a new strategy to directly attach Au nanoparticles onto YAG:Ce³⁺ phosphor via a chemical preparation method, which yields efficient and quality conversion of blue to yellow light in the presence of a low amount of phosphor. Photoluminescence intensity and quantum yield of YAG:Ce³⁺ phosphor are significantly enhanced after Au nanoparticle modification, which can be attributed to the strongly enhanced local surface electromagnetic field of Au nanoparticles on the phosphor particle surface. The CIE color coordinates shifted from the blue light (0.23, 0.23) to the white light region (0.30, 0.33) with a CCT value of 6601 K and a good white light CRI value of 78, which indicates that Au nanoparticles greatly improve the conversion efficiency of low amounts of YAG:Ce³⁺ in WLEDs.

The rare-earth doped phosphor crystal YAG (yttrium aluminium garnet) has been widely investigated in the fields of solid-state lighting, lasers, scintillators and refractive coatings, owing to its attractive optical properties, non-toxicity, and its chemical and thermal stability. In particular, cerium doped YAG phosphor (YAG:Ce³⁺), which emits yellow light with a fairly broad spectral power distribution, has become the most commonly used phosphor in commercial white light emitting diodes (WLEDs) for solid-state lighting because of their many advantages, including their long lifetime, easy fabrication, and because they are environmentally friendly and low cost. By incorporating YAG:Ce³⁺ phosphor into the body of a blue light 460 nm InGaN LED, some of the blue light will be converted into yellow light by the phosphor. The remaining blue light, when mixed with the yellow light, results in white light. In this case, the efficiency of WLED is mostly dependent on the performance of the YAG:Ce³⁺ phosphor. However, the main drawback of YAG:Ce³⁺-based WLEDs is their low conversion efficiency. When present in a low amount, the YAG:Ce³⁺ phosphor only weakly emits yellow light due to a low quantum efficiency (QE); this is often not enough to efficiently convert yellow into white light. Given this connection, increasing the amount of YAG:Ce³⁺ phosphor seems to be one of the few options via which more yellow light can be converted into white light; however, using a larger amount of phosphor decreases the efficiency of WLEDs due to stronger re-absorption of light and more substantial backscattering of the emission. Moreover, YAG:Ce³⁺-based WLEDs produce a cool white light due to the fact that YAG:Ce³⁺ is deficient in generating red light. This results in a low colour rendering index (CRI). Enormous research efforts have been undertaken to improve red emission by co-doping with red emitting rare-earth ions such as Cr³⁺, Pr³⁺, Sm³⁺, and Mn²⁺, or by mixing with red emitting phosphors or quantum dots (QDs). However, to date, few environmentally friendly red emitting materials that can be directly excited by blue light are available. One compromise solution is excitation by yellow light from YAG:Ce³⁺ phosphor. Therefore, it is of great importance for a given low amount of YAG:Ce³⁺ phosphor with a high quantum efficiency to obtain a higher conversion efficiency in order to allow the production of phosphor-converted white light to meet industrial needs.

Directly integrating plasmonic metal nanoparticles into various optoelectronic devices is believed to be a promising approach for enhancing the performance of optoelectronic devices, because plasmonic nanoparticles can generate intense localized electromagnetic fields. By judiciously controlling the size, shape and amount of plasmonic nanoparticle loading, device efficiency can be effectively improved. For instance, the efficiency of InGaN/GaN-based near-ultraviolet,
blue and green LEDs could be enhanced when plasmonic nanoparticles are directly deposited on the surface or embedded into the quantum well layer by physical vapor deposition.\textsuperscript{37–41} Plasmonic nanoparticles can enhance spontaneous emission and recombination of electron–hole pairs in quantum wells.\textsuperscript{42} Plasmon-enhanced phosphor-converted WLEDs with metal nanoparticles have not yet been explored, though plasmon-enhanced photoluminescence (PL) in YAG:Ce\textsuperscript{3+} thin films has already been observed by the physical deposition of silver nano-islands.\textsuperscript{43} However, plasmonic nanopatterned structures prepared by physical vapor deposition are not feasible. For phosphor-converted WLEDs, the most commonly adopted process is to deposit a layer composed of a low amount of phosphor powder and epoxy resin (serving as the encapsulation) on the blue LED chip. Note that there are two undesired consequences arising from incorporation of the plasmonic nanostructures in a such process: first, one may need additional steps to planarize the resin to facilitate the deposition of metallic nano-patterns; second, the presence of metallic structures further degrades the transparency, which is not good for white light emitting purposes.\textsuperscript{45–47} Therefore, one of the most accessible solutions is to chemically attach the plasmonic nanoparticles directly with phosphor microparticles that are then immersed within the encapsulation resin. Since such a step could be a stand-alone process before painting onto blue InGaN chips, it may greatly benefit robust and efficient mass production in the future. Nevertheless, the limited usage of phosphor as pointed out previously imposes a great challenge in producing high-quality white light emission in the phosphor-converted WLED industry, and so in this work we propose and experimentally demonstrate a chemical preparation method to attach Au nanoparticles onto YAG:Ce\textsuperscript{3+} phosphor directly, which yields efficient and quality conversion of blue to yellow light in the presence of a low amount of phosphor. Au nanoparticles directly attached on the surface of YAG:Ce\textsuperscript{3+} nanoparticles strongly enhance the local electromagnetic field of Au nanoparticles on the phosphor particles. This plasmon enhancement effectively improves the conversion efficiency of a low amount YAG:Ce\textsuperscript{3+} in a WLED device through the influence of Au nanoparticles on the radiative and non-radiative energy transfer of the Ce\textsuperscript{3+} 5d level, leading to better white light emission.

In a typical experiment, as sketched in Fig. 1a, 3-aminopropyltriethoxysilane (APTES) is used as the binding molecule for the modification of Au nanoparticles on the surface of YAG:Ce\textsuperscript{3+} phosphors.\textsuperscript{48} APTES covalently attaches to the surface of YAG:Ce\textsuperscript{3+} phosphor and provides uniform and positively charged amine groups on the surface. These groups in turn attract the negatively charged citrate-stabilized Au nanoparticles when adding YAG:Ce\textsuperscript{3+} phosphor into the colloidal Au nanoparticle solution.\textsuperscript{49} Before surface modification with APTES, YAG:Ce\textsuperscript{3+} powder is ground using an alumina mortar and pestle and measured by dynamic light scattering (DLS). Fig. 1b shows that YAG:Ce\textsuperscript{3+} nanoparticles have an average size of 136 nm after grinding. The Au nanoparticles are synthesized by sodium citrate reduction of HAuCl\textsubscript{4} solution and have a uniform size of 21 nm (see ESI, Fig. S1†). The surface morphology of YAG:Ce\textsuperscript{3+} with Au (YAG:Ce\textsuperscript{3+/Au}) nanoparticles confirmed by scanning electron microscope (SEM) images is shown in Fig. 1c. It is found that Au nanoparticles are well attached to the surface of YAG:Ce\textsuperscript{3+} nanoparticles, with both individual particles and small aggregates of Au visible. The material composition analysis of YAG:Ce\textsuperscript{3+/Au} nanoparticles carried out with energy-dispersive X-ray (EDX) spectroscopy also shows the good purity of YAG:Ce\textsuperscript{3+} with Au nanoparticles (Fig. S2†). All the above results confirm unambiguously the successful functionalization of Au nanoparticles onto these YAG:Ce\textsuperscript{3+} nanoparticles.

WLEDs were fabricated by combining surface-mounting InGaN-based blue emitting LEDs (\(\lambda_{\text{em}} = 460 \text{ nm}\)) with the same amount of pure YAG:Ce\textsuperscript{3+} or YAG:Ce\textsuperscript{3+/Au} nanoparticles embedded with epoxy resin (Fig. 2a). Fig. 2b shows the electroluminescence (EL) spectra of pure YAG:Ce\textsuperscript{3+} (black coloured curve) and YAG:Ce\textsuperscript{3+/Au} nanoparticle-based (red coloured curve) WLEDs. The performance of the YAG:Ce\textsuperscript{3+}-converted WLED depends on the maximum energy conversion from the pumped blue light to the phosphor. In Fig. 2b, we normalize the EL spectra of the LED with YAG:Ce\textsuperscript{3+/Au} nanoparticles at 460 nm: the peak ratio (Peak 550 nm/Peak 460 nm) is much higher than that of the LED with pure YAG:Ce\textsuperscript{3+}. This indicates that the energy conversion from the pumped blue light to YAG:Ce\textsuperscript{3+} improves, which can be attributed to the plasmonic effect of Au nanoparticles. With a low amount of pure YAG:Ce\textsuperscript{3+} (3.36 mg cm\textsuperscript{−2}), the Commission Internationale de l’Eclairage (CIE) coordinates of (0.23, 0.23) show that the device still emits blue light due to the low conversion efficiency of YAG:Ce\textsuperscript{3+}. After Au nanoparticle modification, the CIE color coordinates move to the white light region (0.30, 0.33), which indicates that the Au nanoparticles effectively improve the
conversion efficiency of a low amount of YAG:Ce$^{3+}$ in WLEDs. It exhibits a Correlated Colour Temperature (CCT) value of 6601 K and a good white light CRI value of 78. We further increase the amount of pure YAG:Ce$^{3+}$ nanoparticles to 5.18 mg cm$^{-2}$ to emit more yellow light, which can also achieve white light with similar CIE colour coordinates. Therefore, we can reduce a 35% amount of YAG:Ce$^{3+}$ nanoparticles in WLEDs.

To clarify the plasmonic effect of Au nanoparticles for YAG:Ce$^{3+}$ phosphor, a further study is conducted by UV-visible spectroscopy (Fig. 3a). The absorption band peak at 468 nm is a contribution from YAG:Ce$^{3+}$. The additional peak of the YAG:Ce$^{3+}$/Au nanoparticle composite (weight ratio = 100 : 5.5) at 536 nm is caused by surface plasmon resonance of the Au nanoparticles. Indeed, theoretically calculated optical properties of YAG:Ce$^{3+}$/Au nanoparticles using the finite-difference time-domain (FDTD) method (Lumerical Solutions, Inc.) confirm the presence of the two major bands of the YAG:Ce$^{3+}$/Au nanoparticles (Fig. 3b). The experimental and simulation results agree with each other. Fig. 3c and S3† depict the simulation of the electric field profile of the YAG:Ce$^{3+}$/Au nanoparticles with and without Au nanoparticles at the 536 nm Au absorption peak. The coupling of the Au nanoparticles at the surface is expected to strongly affect the local surface electromagnetic field profile of the phosphor nanoparticles structure. The plasmonic effect of the Au nanoparticles is clearly seen in the contrast of the electric field profiles shown in Fig. S4,† where the change in the electric field profiles with and without Au nanoparticles is depicted. It is observed that the enhanced plasmonic near fields caused by Au nanoparticles alter the local surrounding fields near the phosphor surface. Further, PL emission and time-resolved spectroscopy measurements of PL from YAG:Ce$^{3+}$ phosphor without and with Au nanoparticles are investigated to verify the plasmonic effect of Au nanoparticles in Fig. 4. It is found that the PL emission intensity of YAG:Ce$^{3+}$ phosphor is significantly enhanced with Au nanoparticle modification (Fig. 4a). The absolute internal PL quantum yield (QYint) of YAG:Ce$^{3+}$ phosphor is found to be 41%. The absorption ratio and external QY (QYext) are 35% and 14%, respectively. After Au nanoparticle modification, the QYint of YAG:Ce$^{3+}$/Au nanoparticles reached up to 66%. The absorption ratio and external QY (QYext) are 44% and 29%, respectively. In addition, the measurements show that the addition of Au nanoparticles reduces the decay time of the YAG:Ce$^{3+}$ from 70.7 to 68.2 ns (Fig. 4b). As the Au nanoparticle plasmon resonance around 536 nm overlaps well with the YAG:Ce$^{3+}$ phosphor luminescence band, the radiative rate can be enhanced. The radiative rate was proportional to the QY, indicating that the increase of the radiative recombination rate by the surface plasmon resonance is the main reason.
for the enhancement of the PL of YAG:Ce3+ phosphor after Au nanoparticle modification.58–60 The temporal stability of WLEDs based on the same amount of YAG:Ce3+ nanoparticles with and without Au nanoparticles are investigated with increasing operating time (Fig. 4c). After the first 30 hours, the luminance of YAG:Ce3+ nanoparticles without Au nanoparticles starts to decline due to thermal quenching and non-radiative losses. After modification with Au nanoparticles, the luminance of WLED shows good stability, which is attributed to improvement of the radiative recombination rate of YAG:Ce3+ under the plasmonic effect of Au nanoparticles.

Fig. 2c shows EL spectra of WLEDs fabricated with increasing amounts of YAG:Ce3+/Au nanoparticles from 1.39 mg cm−2 to 5.18 mg cm−2. It is found that the absorption of blue (460 nm) excitation light increases with increasing particle amount, which results in the enhancement of the PL intensity of YAG:Ce3+ due to the plasmonic effect of Au nanoparticles. Table S1† summarizes the parameters of YAG:Ce3+/Au nanoparticle-based WLEDs for different particle amounts. The CIE coordinates, CRI, CCT and luminous efficiency (LE) values of the WLEDs are improved when increasing the particle amount to 4.43 mg cm−2. These results suggest that Au nanoparticles can improve the conversion efficiency of YAG:Ce3+ by increasing the amount of YAG:Ce3+/Au nanoparticles. However, the PL intensity of YAG:Ce3+ does not increase further, and a decrease in performance of the WLEDs was observed at higher amount of particles (5.18 mg cm−2), because non-radiative recombination occurs when Au nanoparticles are in close proximity to each other due to the resulting destructive interference of the surface plasmons.61

It is known that the blue excitation light (460 nm), used to excite YAG:Ce3+ in Ce4+ doped YAG converted WLED system, can cause Ce3+: 2F5/2 (or 2F7/2) to Ce3+: 2D3/2 transitions.62 The electrons at the 2D3/2 excited level are unstable and non-radiatively decay to 2D5/2 due to an electron–phonon interaction.62 Consequently, the yellow luminescence is associated with Ce3+: 2D3/2 to 2F7/2 or 2F5/2 transitions. Fig. 4d shows the X-ray photoelectron spectrum (XPS) of YAG:Ce3+ phosphor and Au nanoparticles before and after modification. The binding energies of 893.0 eV and 909.8 eV represent Ce3+ 3d3/2 and 3d5/2 states, respectively.63 After modification by Au nanoparticles, the binding energies of Ce3+: 3d3/2 and 3d5/2 significantly shift to higher energy, which is attributed to the plasmonic effect of Au nanoparticles on the 5d level of Ce3+. This further confirms the influence of Au nanoparticles on the radiative and non-radiative energy transfer from the 5d level, which results in the improvement of the QY of YAG:Ce3+. Moreover, the binding energies at 84.30 eV and 87.90 eV correspond to the 4f7/2 and 4f5/2 states of the Au nanoparticles (Fig. S5†). After attachment to the surface of the YAG:Ce3+ nanoparticles, the binding energies of Au 4f7/2 and 4f5/2 shift to higher values, demonstrating the strong interaction between Au nanoparticles and YAG: Ce3+.64 Based on the above discussions, the energy level diagram for the Ce3+ in YAG affected by Au nanoparticles is represented in Fig. 4e.31,65,66

Experimental section

The YAG:Ce3+ (Ce0.06Y2.94Al5O12) powder sample was synthesized by a conventional high temperature solid state reaction method. The 99.99% pure mixture of Al2O3, Y2O3 and CeO2 was ground for 1 h, followed by a heating process at 900 °C for 3 h. After cooling to room temperature, the powders were reground to improve the mixture. The powders were then moved into the furnace at 1660 °C for 10 h. During the 10 h heating process, a gas mixture of H2 and N2 was introduced to prevent the formation of Ce4+ ions, which are not readily excited by the UV/blue photons. Finally, we obtained a particle size distribution of D50 = 15 μm. In order to reduce the particle size to the order of nanometers, we took the 0.05 g YAG:Ce3+ nanoparticles in the mortar and manually ground it by using a pestle for 6 hours. The color of phosphor powder changed from yellow to off-white or milky. The YAG:Ce3+ nanoparticles were functionalized by APTES purchased from J&K Scientific Ltd, 0.01 g of powdered YAG:Ce3+ nanoparticles were mixed with 450 ml absolute ethanol and 0.5 ml APTES, and stirred at room temperature. After 90 minutes, the sample was centrifuged and rinsed in DI water. We then dispersed them into a 2 ml solution of Au nanoparticles (21 nm, 0.275 mg ml−1)
and kept shaking at room temperature for 24 hours. The YAG:Ce\(^{3+}\)/Au weight ratio was around 100:5.5 (i.e. 55 mg of Au nanoparticles per g of YAG:Ce\(^{3+}\) phosphor). The average size of the Ce-doped phosphor material particle distribution was analysed using the dynamic light scattering (DLS) method (Malvern Instruments, Model ZEN3690). The material composition and morphology were examined using a scanning electron microscope (Carel Zeiss Microscopy) that also included an energy dispersive X-ray spectrometer (Oxford Instruments, Model 51-XMX1004). The PL spectra were measured using a fluorescence spectrometer “Fluoromax-4” with a Xe lamp under an excitation wavelength of 450 nm and a PL decay time determined by a NanoLED-455 nm laser with a pulse duration of 1.4 ns (HORIBA JobinYvon). Absolute quantum yields were measured using a quanta-phi integrated sphere module equipped in a Fluoromax-4 spectrophotometer. The absorption spectra were recorded by a UV/visible spectrometer (Lambda 750 PerkinElmer). The binding energy of Ce\(^{3+}\) in YAG:Ce\(^{3+}\) and YAG:Ce\(^{3+}\)/Au nanoparticles was measured by X-ray photoelectron spectroscopy (Kratos Analytical Shimadzu Group Company).

The WLED formed of YAG:Ce\(^{3+}\) and YAG:Ce\(^{3+}\)/Au nanoparticles embedded with epoxy resin was fabricated and pumped by a 460 nm InGaN blue LED in a remote configuration. The LED chip was coated with different amounts of YAG:Ce\(^{3+}\)/Au nanoparticles (0.062 mg, 0.089 mg, 0.150 mg, 0.198 mg, and 0.231 mg) mixed with epoxy resin (1 mg) using a dispensing method. The LED optical properties were measured by a spectrometer (Photo Research Inc. Model PR-655) connected with a Keithley 2400s source meter. All the mentioned measurements were performed at room temperature. The interaction between the localized plasmons from the Au nanoparticles and the YAG:Ce\(^{3+}\) was numerically calculated by using a commercial FDTD solver (Lumerical FDTD Solutions). The YAG:Ce\(^{3+}\) and Au optical properties were modelled according to our UV/visible optical measurements and also from established experimental sources.\(^{5,6}\) In order to closely model the experimental setup, the YAG:Ce\(^{3+}\)/Au nanoparticle system was modelled as a periodic structure with a unit cell of 250 by 250 nm consisting of a spherical YAG:Ce\(^{3+}\) particle with a radius of 68 nm coupled with an Au nanoparticle with a radius of 10.5 nm. The sizes of the YAG:Ce\(^{3+}\) and Au nanoparticles were selected based on DLS measurements. In order to uniformly excite the structure, a circularly polarized light source was used. The total absorption in the structure was calculated in the visible spectra range.

### Conclusions

In summary, we present an approach for using a low amount of YAG:Ce\(^{3+}\) to convert white light by direct chemical modification of Au nanoparticles on the surface of YAG:Ce\(^{3+}\) nanoparticles. PL intensity and QY of YAG:Ce\(^{3+}\) phosphor in WLEDs are significantly enhanced after Au nanoparticle modification due to the improvement of energy conversion from the pumped blue light to YAG:Ce\(^{3+}\), which can be attributed to the strongly enhanced local surface electromagnetic field of Au nanoparticles on the phosphor particle surface. The FDTD simulation, time-resolved spectroscopy, and XPS data unanimously verify the plasmonic effect of Au nanoparticles on the YAG:Ce\(^{3+}\) phosphor. Radiative and non-radiative energy transfer from Ce\(^{3+}\) 5d level is directly affected by the surface plasmon of the Au NPs, resulting in the improvement of the CIE coordinates, CCT and CRI of the YAG:Ce\(^{3+}\)/Au nanoparticles-based WLED. Our work not only demonstrates that employing plasmonic nanoparticles can improve the conversion efficiency of phosphor, but also provides a very promising way to develop high efficiency phosphor-converted WLEDs as solid-state light sources. The Au nanoparticle modification route should be applicable to various converting materials, and will facilitate the formation of many converters/Au composites leading to new and intriguing properties and applications.

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### Notes and references


