**Why upconversion quenching is observed in Au nanoparticles-doped glass?**

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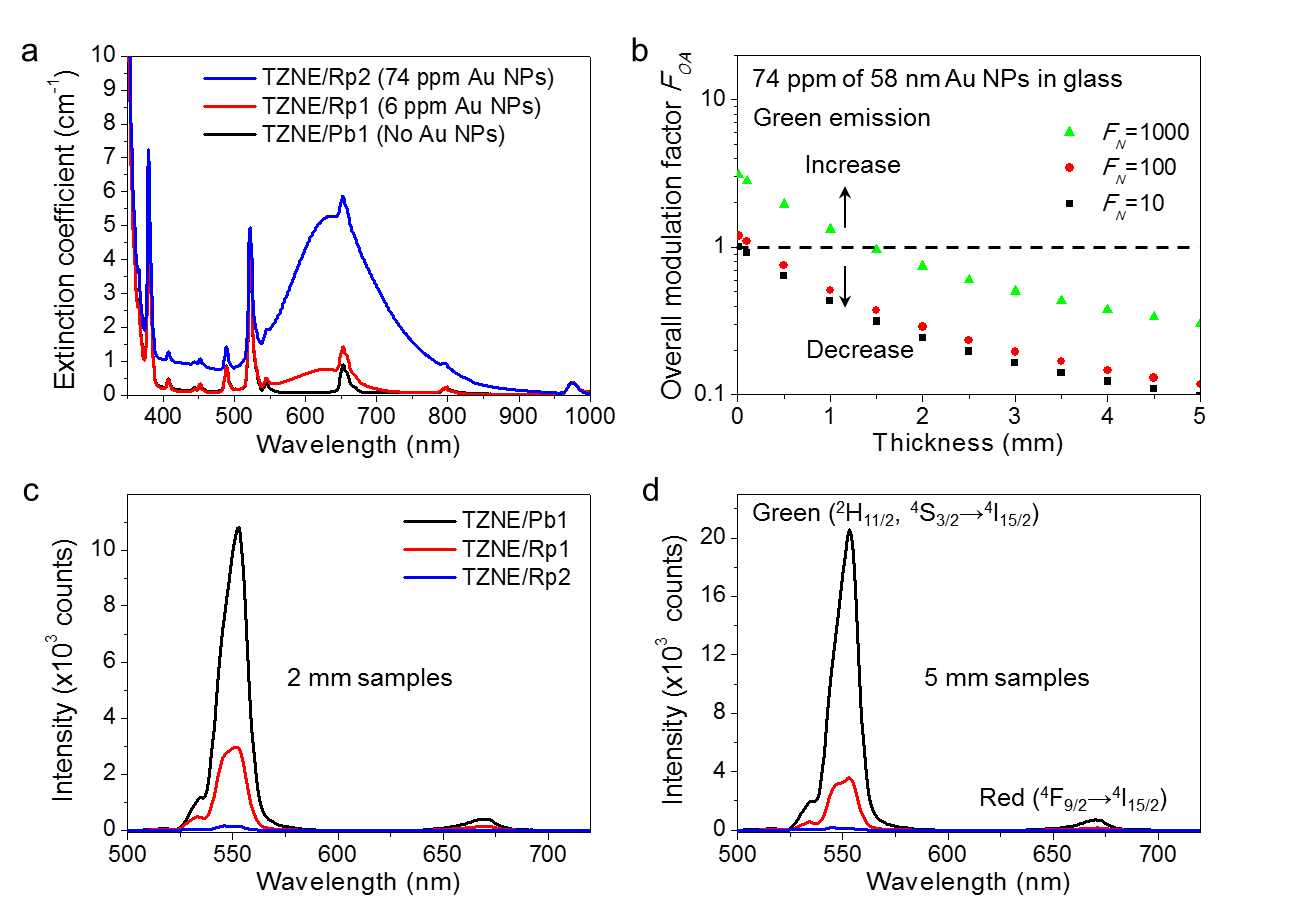
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**Introduction:** Remarkable upconversion emission enhancement has been widely demonstrated via engineering individual upconversion nanoparticles (UCNPs) in the vicinity of plasmonic structures, e.g., Au nanoparticles (Nadort *et al*. 2016). However, this significantly contradicts with the observation of only minor upconversion signal amplification or even drop in Au nanoparticles-doped upconversion glass. Here, using experimental and theoretical investigation, we elucidate this long term puzzle by taking both near-field effects and far-field attenuation into account.

**Methods**: 1 mol% Er3+ (2.2x1019 cm-3) doped tellurite-based glasses (75TeO2-15ZnO-10Na2O, mol%) were prepared, namely TZNE/Rp1 and TZNE/Rp2, which additionally contain 6 and 74 ppm Au NPs (with respective Au ion density of 0.15x1011 cm-3 and 1.9x1011 cm-3), respectively. TZNE/Pb1 parent glass without Au contents was produced as a reference sample.



**Fig.** (a) Extinction coefficient of TZNE/Pb1, TZNE/Rp1 and TZN/Rp2. (b) Modeled overall upconversion emission (550 nm) with 58 nm Au NPs (74 ppm) in TZNE glass, as a function of sample thickness.

**Results and discussions**: In addition to the characteristic 4f-4f transitions of Er3+ in all three glass samples, TZNE/Rp1 and TZNE/Rp2 show the broad localized surface-plasmon resonance (LSPR) band, which is superimposed on the sharp f-f transitions, with peak at ~640 nm (corresponding to Au NPs diameter of about 58 nm) (Fig. a). Under continuous wave 980 nm laser excitation, all three glass samples exhibit upconversion green and red emissions of Er3+, which however shows that: (1) the presence of Au NPs (TZNE/Rp1 and TZNE/Rp2) leads to a decrease of upconversion emissions compared to only Er3+ doped TZNE/Pb1glass, (2) with the same sample thickness, a larger intensity decrease is observed for the glass with stronger LSPR band (TZNE/Rp2 versus TZN/Rp1), and (3) thicker sample thickness leads to more prominent decrease of the upconversion emissions. Since the respective upconversion emissions give the almost same decay lifetimes of all three glass samples, we exclude the energy transfer from Er3+ to Au NPs as the reason for the decrease of upconversion emissions in different glasses. By simulating the combined near-field effects (with different amplification factors) and far-field attenuation (due to Mie scattering), we predict even for the upper bound of 1000× enhancement by near-field effect, upconversion emissions appear to decrease in the presence of 74 ppm Au NPs when the glass sample thickness is larger than 1.1 mm (Fig. b), in good agreement with experimental results.

**Conclusion**: Even tuning the LSPR band to couple with upconversion emissions, we observed a decrease of upconversion emission in Er3+ doped tellurite glasses with in-situ formed Au NPs relative to that of the reference sample without Au contents. We found such intensity decrease is more prominent for the sample containing a larger amount of Au NPs and/or with thicker sample thickness. Based on the simplified physical model, we ascribed the Au NPs-induced emission decrease to the pronounced far-field attenuation that overwhelms the near-field enhancement effects that could exist.

**References**

A Nadort, J Zhao, EM Goldys, Nanoscale **8** (27), 13099-13130.