Title: Mechanistic Investigations on the Dramatic Thermally-Induced Luminescence Enhancement in Upconversion Nanocrystals and Anticounterfeiting Applications

Abstract: Luminescent bulk materials generally suffer from the thermal quenching, while upconversion nanocrystals (UCNCs) have recently been found to show the dramatic emission increase at elevated temperatures. A deep understanding on this quite different light-heat interaction at the nanoscale is important both scientifically and technologically. Herein, temperature-dependent upconversion luminescence (UCL) is investigated for UCNCs with various sizes, activators (Ho^{3+}, Tm^{3+}, Er^{3+}) and core/shell structures. An anomalous UCL enhancement with increasing temperature is found for UCNCs with larger surface/volume ratios (SVRs). Moreover, this UCL increase shows a pronounced dependence on the SVRs, activators, emitting levels and measuring environments. Substantial evidence confirms that the thermally-induced UCL increase is primarily due to the temperature-dependent quenching effect of surface-adsorbed H_2O molecules, instead of the previously proposed surface phonon-assisted mechanism. Temperature-dependent spectral investigations also show that the energy-loss process of Yb^{3+}-sensitized UCNCs is largely due to the deactivation of Yb^{3+} ions caused by surface quenchers, rather than the direct quenching to activators.[1] UCNCs with an active-shell (doped with Yb^{3+}) exhibit the similar thermally-

induced UCL increase, due to energy migration to the surface over the Yb-Yb internet. Utilizing opposite luminescent temperature-dependences between active-core@inert-shell (thermal quenching) and active-core@active-shell (thermally-induced enhancement) UCNCs, the hybrids of them are obtained by a simple mixing method and show obvious color changes under 975 nm excitation with increasing temperature. Various color-shifting pathways (from white to green, blue to green, etc.) are achieved by adjusting the core/shell NC combinations in the hybrids. Moreover, color changes of the printed patterns using the hybrid NC inks can be realized simply by the hairdryer heating, increasing the laser power or prolonging the irradiation time. The results indicate the great potential of these core/shell NC hybrids for anticounterfeiting applications with multilevel security and convenient authentication methods.[2]

Keywords: upconversion, luminescence, anticounterfeiting, temperature-dependent, hybrid

References

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