Security Printing of Covert Codes using NIR-to-NIR Upconversion Inks

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Introduction:

Upconversion nanoparticles (UCNPs) of β-phase $NaYF_4$ doped with Yb and Tm exhibit 'upconverted' near-infrared 800 nm emission when excited with 980 nm light. (**Figures 1 and 2**). The intensity of the emission is affected by the concentration of Yb and Tm in the nanoparticles. This so-called NIR-to-NIR luminescence is of interest for security printing because both the NIR excitation and the upconverted NIR emission can pass through selective protective opaque ink or dye layers and cannot be detected by the naked eye. We are working with collaborators at SDSM&T to develop inks that can be used to print NIR-to-NIR upconversion images that can be read using CCD cameras even when covered with visibly opaque protective coatings.

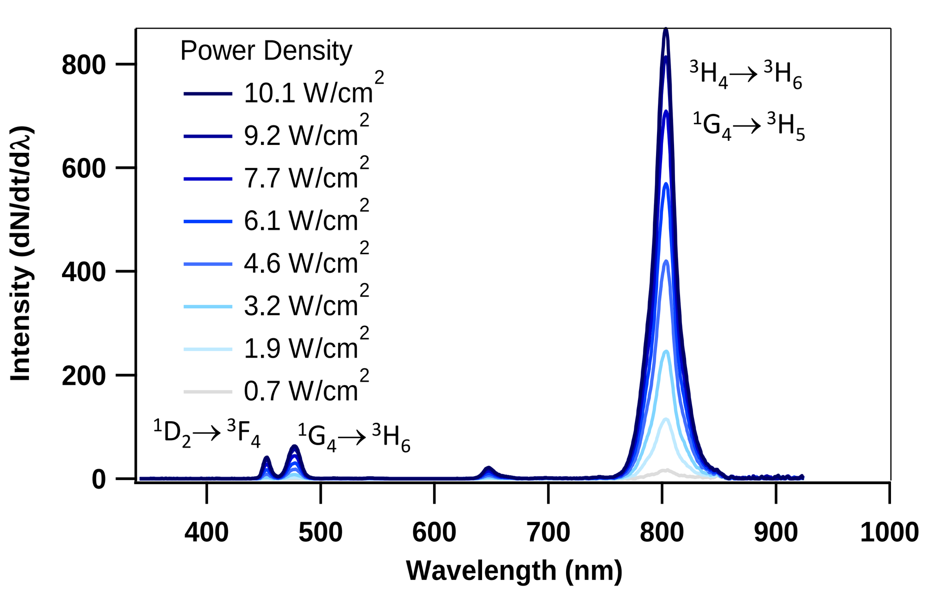

Figure 1: Upconversion emission spectra of $NaYF_4$:Yb/Tm (25/0.3 mol %) excited at 980 nm.

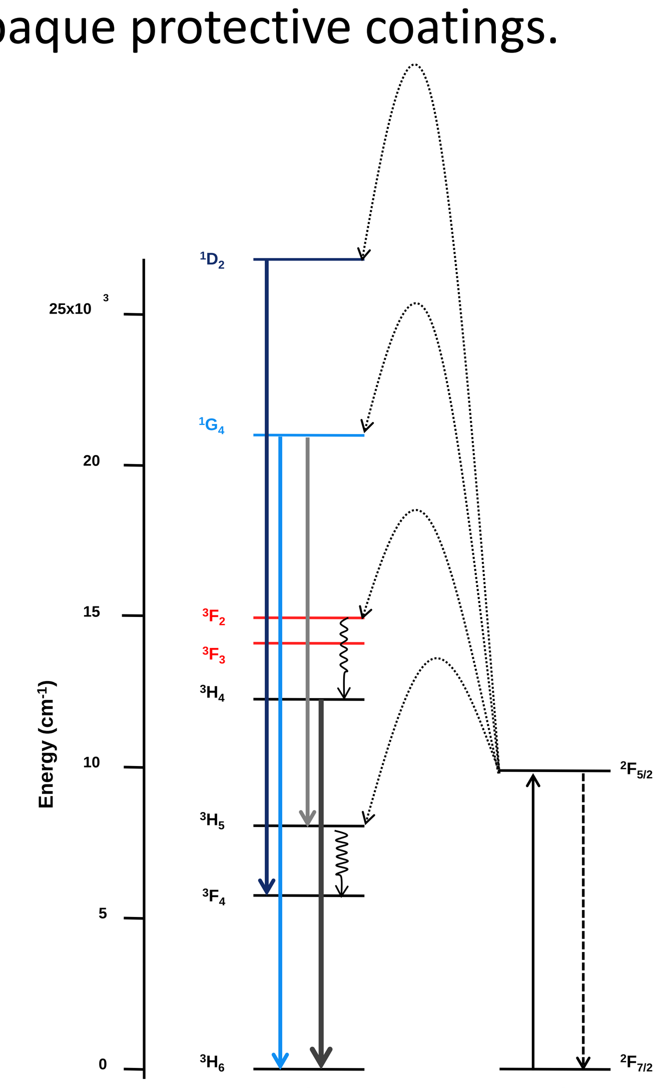

Figure 2 (right) : Energy level diagram illustrating the upconversion of NIR excitation in $NaYF_4$:Yb/Tm

Objectives:

-Optimize dopant concentrations for 800 nm emission

-Select a visibly opaque ink to cover UCNP without blocking 800 nm emission

-Print an upconversion image that can be covered with an opaque coating and read by a CCD camera (**Figure 3**).

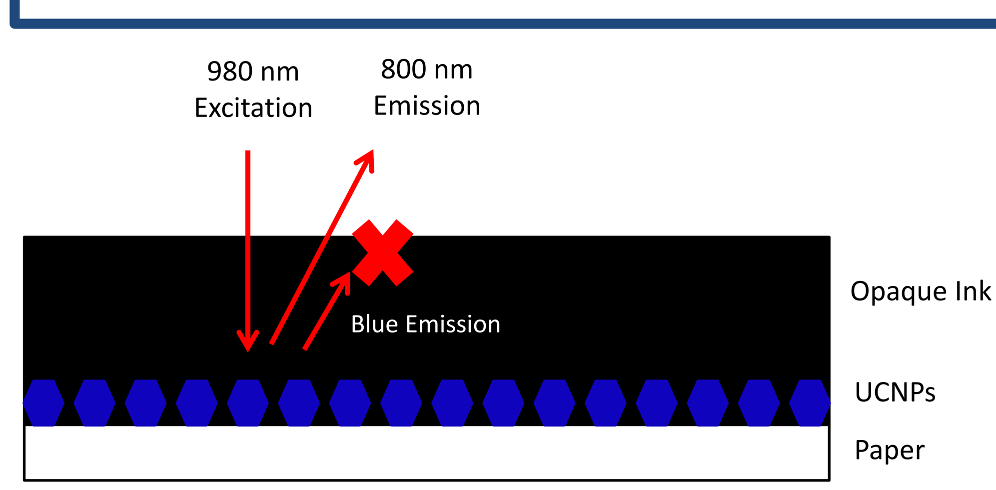

Figure 3: Diagram of NIR-to-NIR security ink concept

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Results:

The absorbance of two opaque ink candidates was measured. Black Hobbicolor inkjet ink transmits nearly 100% of 800 nm light, while black Sharpie ink transmits only about 40% (**Figure 4**). Next, a 3-pass spot of blue UCNP in toluene was spread on white paper and covered by two passes of Hobbicolor Inkjet ink (**Figure 5**). The spot was photographed twice, once with an 850 nm short pass (SP) filter (left) and once with both the 850 nm SP filter and a 750 nm SP filter (right). The transmission spectra of the filters are shown in **Figure 6**. The bright emission of the UCNP is not visible after the 750 nm SP filter is added, suggesting that NIR light can pass through the ink, but visible light cannot.

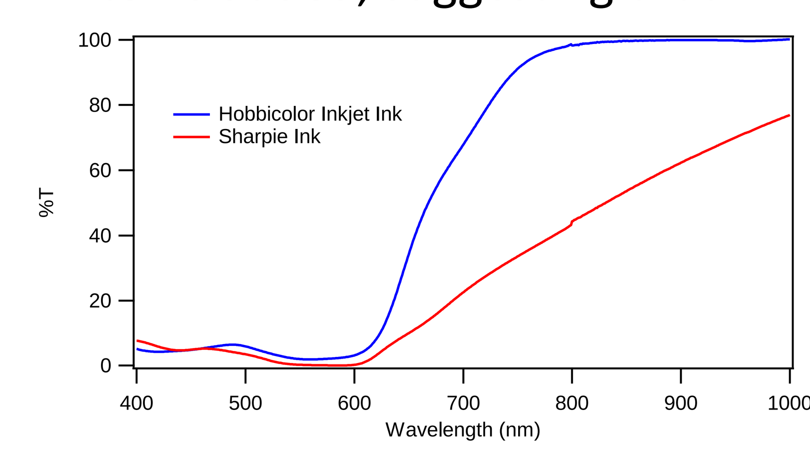

Figure 4: Transmission spectra of Hobbicolor Ink-jet ink and Sharpie ink

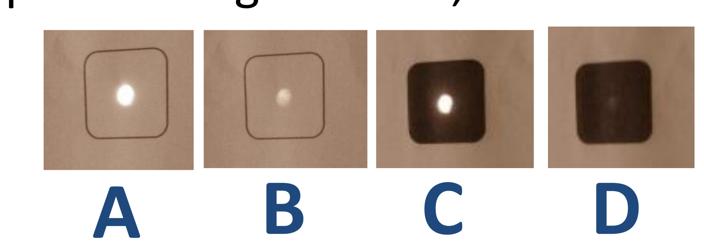

Figure 5: Printed spots of UCNPs excited by 980 nm and photographed using modified digital camera with 850 nm SP filter (A,C) and 750 nm SP filter (B,D). In photos C and D, UCNP spot is covered by 2-pass layer of black Hobbicolor Inkjet ink.

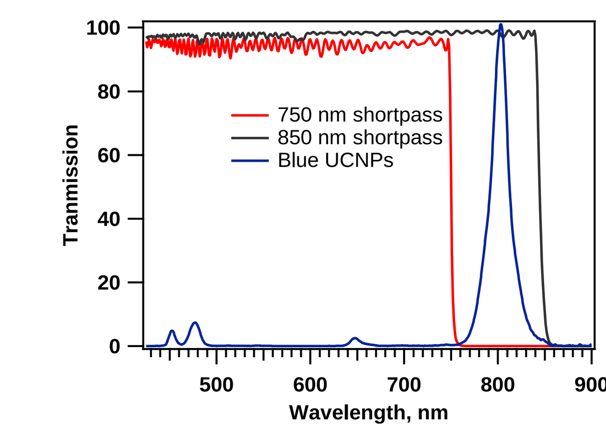

Figure 6: Transmission spectra of 850 nm SP and 750 nm SP filters and emission spectrum of UCNPs

UNCPs with a variety of dopant concentrations were synthesized. A precise mass of UCNPs was dispersed in a precise volume of toluene, and the emission spectrum of the solution was measured at 7 different excitation power levels. All dopant concentrations produced strong 800 nm emission, but UCNPs with higher Tm concentrations produced little to no visible emission (**Figures 7**). Absorbance measurements were used to calculate the corrected relative intensity, or relative intensity per nanoparticle, of the 800 nm emission. UNCPs with 46.3% Yb and 3.7% Tm produced the greatest per particle intensity of 800 nm light (**Figures 8, 9, and 10**).

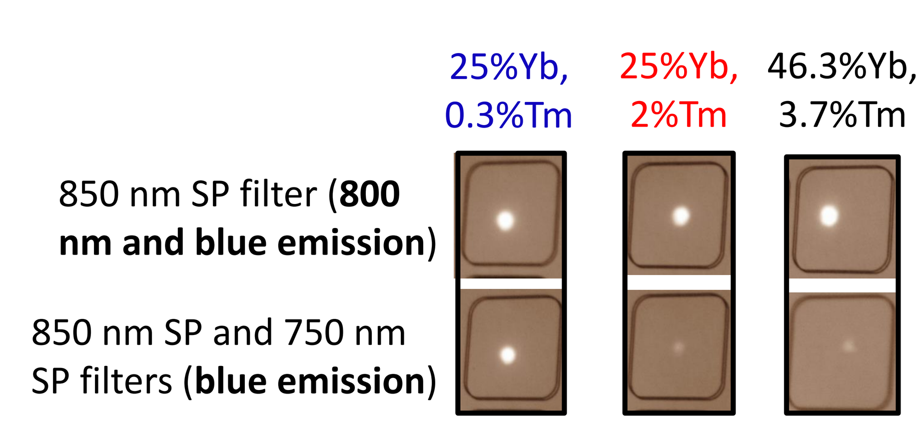

Figure 8: Printed spots of UCNPs with varied dopant concentrations excited by 980 nm light and photographed using modified digital camera with 850 nm SP filter (top row) and 750 nm SP filter (bottom row).

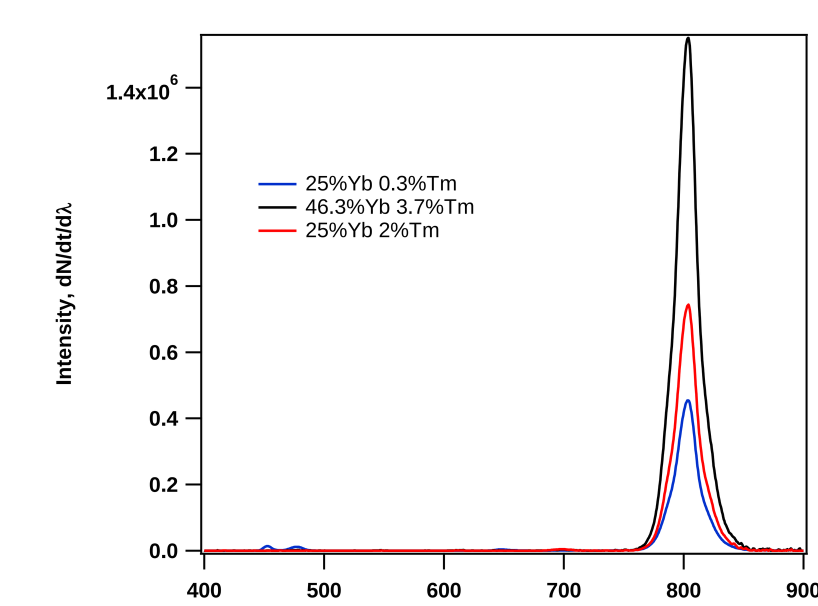

Figure 9: Relative per-particle intensity of UCNP emissions

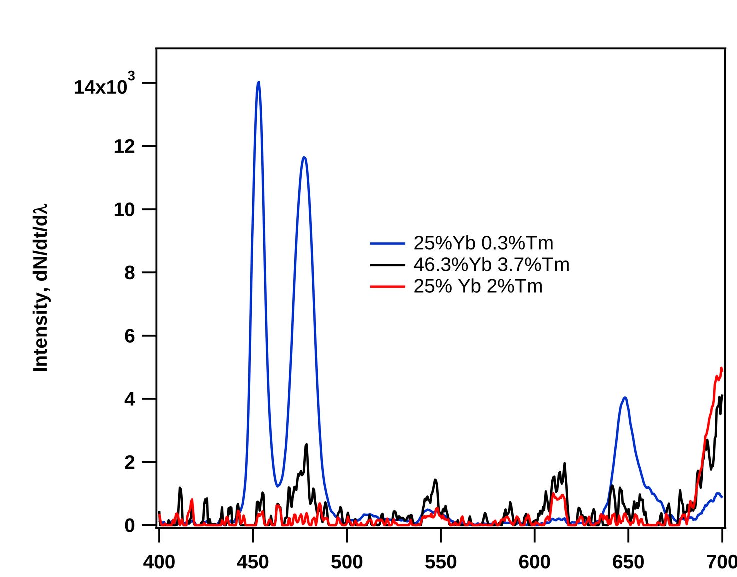

Figure 10 (left) : Intensity of UCNP emissions vs. excitation power (visible region only)

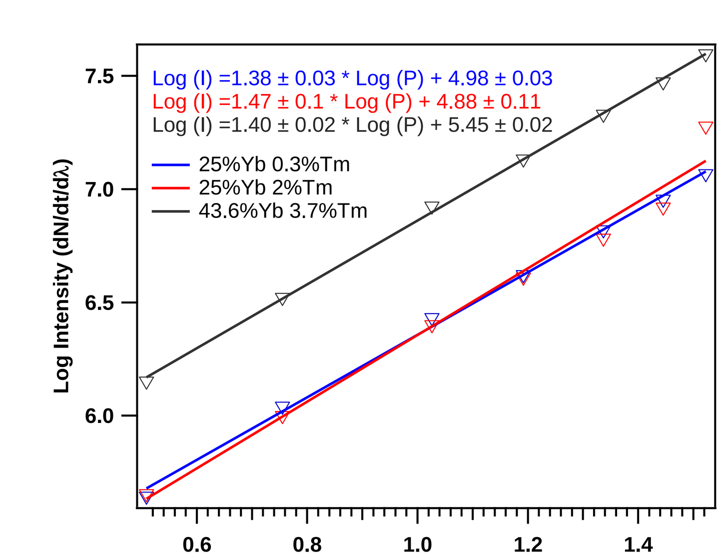

Figure 11 (left): Log of intensity of UCNP emissions vs. Log of excitation power

Conclusions:

Initial experiments prove that the 800 nm emission of $NaYF_4$:Yb/Tm can be detected by a CCD camera even when the nanoparticles are buried under a layer of opaque ink. By increasing the concentrations of Yb and Tm in the nanoparticles, the intensity of the 800 nm emission can be increased, and the blue emission can be eliminated, making the nanoparticles an even more promising candidate for NIR-to-NIR security printing.