

## **Supplementary Information**

Fig. S1 Illustration of the relevant processes of energy transfer in UC@SiO<sub>2</sub>@Ag.

UC serve as a light converter to upconvert the NIR light into the visible one, the transition between energy levels in NaYF<sub>4</sub>:Yb,Er under the NIR excitation has been widely acknowledged.<sup>1-3</sup> Under the NIR excitation, the Yb<sup>3+</sup> ions act as sensitizers and are the primary absorbers of the NIR excitation. Then Yb<sup>3+</sup> will transfer the energy absorbed from the NIR excitation to  $Er^{3+}$ , the  $Er^{3+}$  ions are excited from the <sup>4</sup>I<sub>15/2</sub> ground state to the <sup>4</sup>I<sub>11/2</sub> excited state after the Yb<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup> energy transfer. The luminescent states of  $Er^{3+}$  are excited by two consecutive Yb<sup>3+</sup>  $\rightarrow$   $Er^{3+}$  energy transfer events, the first energy transfer is the <sup>4</sup>I<sub>15/2</sub> ground state, and the second energy transfer is the long-lived intermediate excited state (i.e., <sup>4</sup>I<sub>13/2</sub> or <sup>4</sup>I<sub>11/2</sub>). Then the  $Er^{3+}$  ion is excited to the <sup>4</sup>F<sub>7/2</sub> state by a second Yb<sup>3+</sup>  $\rightarrow$   $Er^{3+}$  energy transfer. After that, the  $Er^{3+}$  ion decays nonradiatively to the <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub> and <sup>4</sup>F<sub>9/2</sub> levels, which gives the dominant green luminescence (<sup>2</sup>H<sub>11/2</sub>  $\rightarrow$  <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>S<sub>3/2</sub>  $\rightarrow$  <sup>4</sup>I<sub>15/2</sub>).



Fig. S2 The UV-vis absorbance spectrum of NaYF<sub>4</sub>:Yb,Er@SiO<sub>2</sub>@Ag substrate.

The UV-vis absorbance spectrum of NaYF<sub>4</sub>:Yb,Er@SiO<sub>2</sub>@Ag substrate was shown in Fig. S2. The UV-vis absorbance spectrum showed a broad absorption covered the visible light range. The red shift of the LSPR of Ag NPs may due to the formation of very big clusters and decrease the interparticle gaps when Ag NPs deposited on the NaYF<sub>4</sub>:Yb,Er@SiO<sub>2</sub>.



Fig. S3 The XRD patterns of NaYF<sub>4</sub>:Yb,Er@SiO<sub>2</sub>.

Fig. S3 showed the XRD patterns of SiO<sub>2</sub>-decorated UC microcrystals, due to the amorphous nature, no defined peak from the silica shell is observed except a small uplift on the baseline at the low angle region, which may be caused by the diffraction between irregular molecule layers of amorphous  $SiO_2$ .<sup>4</sup> The detail information of broad diffraction band locating between 20<sup>0</sup> and 30<sup>0</sup> comes from porous  $SiO_2$  can be seen clearly.<sup>5</sup>



Fig. S4 The emission spectrum of NaYF<sub>4</sub>:Yb,Er NCs under 808 nm excitation.

Under the 808 nm excitation, the  $Yb^{3+}$  ions act as sensitizers and are the primary absorbers of the NIR excitation. Then  $Yb^{3+}$  will transfer the energy absorbed from the

NIR excitation to  $Er^{3+}$ , the  $Er^{3+}$  ions are excited from the  ${}^{4}I_{15/2}$  ground state to the  ${}^{4}I_{11/2}$  excited state after the Yb<sup>3+</sup>  $\rightarrow Er^{3+}$  energy transfer. The luminescent states of  $Er^{3+}$  are excited by two consecutive Yb<sup>3+</sup>  $\rightarrow Er^{3+}$  energy transfer events, the first energy transfer is the  ${}^{4}I_{15/2}$  ground state, and the second energy transfer is the long-lived intermediate excited state (i.e.,  ${}^{4}I_{13/2}$  or  ${}^{4}I_{11/2}$ ). Then the  $Er^{3+}$  ion is excited to the  ${}^{4}F_{7/2}$  state by a second Yb<sup>3+</sup>  $\rightarrow Er^{3+}$  energy transfer. After that, the  $Er^{3+}$  ion decays nonradiatively to the  ${}^{2}H_{11/2}$ ,  ${}^{4}S_{3/2}$  and  ${}^{4}F_{9/2}$  levels, which gives the dominant green luminescence ( ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ ,  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ ).



Fig S5 (A) SEM image of Ag NPs, (B) UV-vis diffused reflectance absorption spectra of Ag substrate. (C) The SERS spectra of 10<sup>-6</sup>M PATP under 785 nm on (a) UC@SiO<sub>2</sub>@Ag, (b) Ag substrate; (D) The comparison of enhancement effects at 1434 cm<sup>-1</sup> of the two substrates.

As a reference, the Ag nanoparticle sols were prepared according to the classical citrate reduction method. 5  $\mu$ L of the 100-fold concentrated Ag sols dried in air on the surface of silicon wafer can form the multilayers of Ag NPs, which were used as the reference substrate. The interparticle gap among Ag substrate was less than 5 nm (Fig. S4A) that can maximize the localized electric field and greatly amplify the Raman signals of target molecules. The UV-vis diffused reflectance absorption spectra of dry Ag substrate showed two peaks located at 411 and 538 nm (Fig. S4B). The red shift of the LSPR of Ag may due to the formation of very big clusters and decrease the interparticle gaps when the substrate is dried. Fig. S4C showed the SERS spectra of 10<sup>-6</sup>M PATP under 785 nm on (a) UC@SiO<sub>2</sub>@Ag, (b) Ag substrate. The intensity of

the 1434cm<sup>-1</sup> peak is only about 595 cnts produced by the SiO<sub>2</sub>@Ag. The corresponding SERS intensity of the 1434cm<sup>-1</sup> peak of PATP adsorbed on UC@SiO<sub>2</sub>@Ag is about 3150 cnts, which is about 5.3 times larger than that obtained on Ag substrate. The shape, LSPR and size of the Ag NPs decorated on NaYF<sub>4</sub>:Yb,Er@SiO<sub>2</sub> were similar to that of the pure Ag NPs. More importantly, the interparticle gaps among the Ag NPs decorated on NaYF<sub>4</sub>:Yb,Er were larger than that of Ag substrate and the density is lower than that of Ag substrate, which will reduce the coupling of the Ag NPs. Therefore, it should be the presence of UC materials that contributed to the greatly improved SERS performance of UC@SiO<sub>2</sub>@Ag as shown in scheme 1.



Fig S6 The SERS spectra of 10<sup>-5</sup>M CV on Ag substrate (black line) and UC@SiO<sub>2</sub>@Ag (red line) under (A) 785 nm, (C) 633 nm and (D) 532 nm; (B) The comparison of enhancement effects at 1172 cm<sup>-1</sup> of the two substrates under 785 nm.

To further verify the improved SERS performance of UC@SiO<sub>2</sub>@Ag, a resonant dye molecule 'crystal violet', also a widely-used SERS reporter, was used to examine these differences. Fig. S5A showed the SERS spectra of 10<sup>-6</sup>M CV on Ag substrate (black line) and UC@SiO<sub>2</sub>@Ag (red line) under 785 nm. The intensity of the 1172 cm<sup>-1</sup> peak is only about 360 cnts produced by Ag substrate. The corresponding SERS intensity of the 1172 cm<sup>-1</sup> peak of CV adsorbed on UC@SiO<sub>2</sub>@Ag is about 2400 cnts as shown in Fig. S5B, which are about 6.7 times larger than that obtained on Ag substrate. As the longitudinal comparison of a same sample, another two different

monochrome laser lines (532 nm and 633 nm) were employed to carry out SERS experiments, which further demonstrate the key role of UC cores in SERS performance under NIR excitation. Fig. S5C showed the SERS spectra of 10<sup>-6</sup>M CV on Ag substrate (black line) and UC@SiO2@Ag (red line) under 633 nm. The intensity of the 1172 cm<sup>-1</sup> peak is about 2100 cnts produced by Ag substrate. The corresponding SERS intensity of the 1172 cm<sup>-1</sup> peak of CV adsorbed on UC@SiO<sub>2</sub>@Ag is about 1700 cnts. The intensity of the 1172 cm<sup>-1</sup> peak produced by Ag substrate and UC@SiO<sub>2</sub>@Ag under 532 nm are 5900 and 4300 cnts, respectively, as shown in Fig. S5D. Under 633 and 532 nm excitation, the intensity of the 1172 cm<sup>-</sup> <sup>1</sup> peak produced by Ag substrate is stronger than that obtained on UC@SiO<sub>2</sub>@Ag. The probable reason is that the UC cannot efficiently convert the lasers of 532 nm and 633 nm into visible light to improved SERS performance. Moreover, the interparticle gaps among the Ag NPs decorated on NaYF4:Yb,Er were larger than that of Ag substrate and the density is lower than that of Ag substrate (Fig.2A), which will reduce the coupling of the Ag NPs. Therefore, it should be the presence of UC materials that contributed to the greatly improved SERS performance of UC@SiO2@Ag.



Fig. S7 The UV-vis absorbance spectrum of SiO<sub>2</sub>@Ag substrate.



Fig. S8 The normal Raman spectrum of MAMP powder.

## References

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