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Multifunctional core-shell upconvertion nanoparticles for targeted tumor cells induced by near-infrared light

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Supporting information

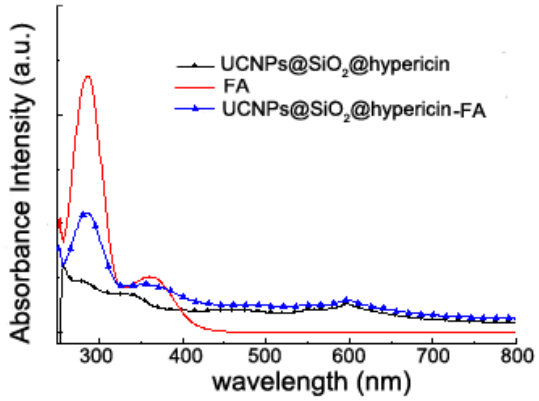

Fig.S1 UV/Vis absorption spectrum of UCNPs@SiO_2@hypericin, FA, UCNPs@SiO_2@hypericin-FA.

As can be seen from Fig.S1, the UV/Vis absorption spectrum shows that FA has a strong peak at 280 nm. Meanwhile, the characteristic peak of FA appears in the UV/Vis absorption spectrum of UCNPs@SiO_2@hypericin-FA compared with the UV/Vis absorption spectrum of UCNPs@SiO_2@hypericin, which prove the success of the functionalization of the nanocomposites with FA.

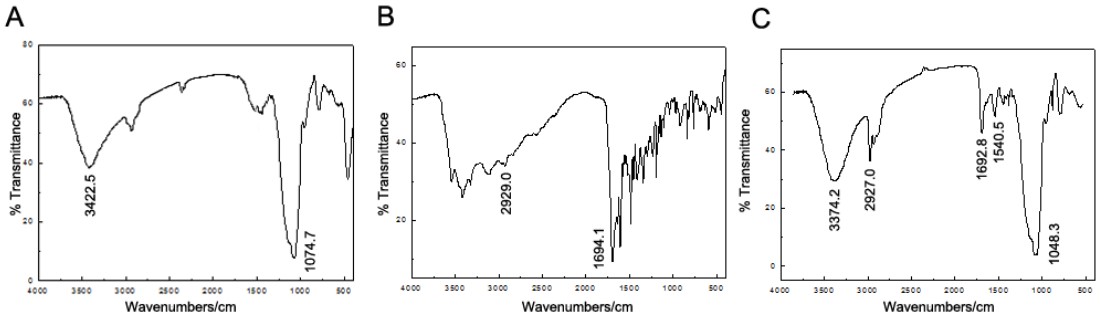

Fig.S2 FTIR spectra of (A) UCNPs@SiO_2@hypericin, (B) FA, and (C) UCNPs@SiO_2@hypericin-FA.

The functionalization of the nanocomposites with folic acid was further investigated by FTIR shown in Fig. S2. In the FTIR spectrum of FA (Fig.S2B), a strong band at 1694.1 cm^{-1} was attributed to the C=O stretching vibrations of carboxyl group. Nevertheless, the feature above shrank remarkably after functionalization with FA, while a band at 1540.5 cm^{-1} showed up, which was characteristic peak of the amido bond. Thus, successful functionalization of the nanocomposites with folic acid was comfirmed based on the above.

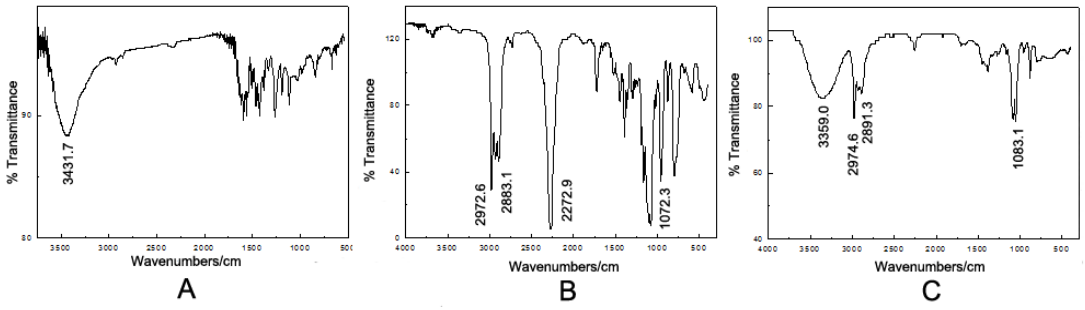

Fig.S3 FTIR spectra of (A) hypericin, (B)TESPIC and (C)TESPIC-hypericin.

The formation of TESPIC-hypericin was investigated by FTIR shown in Fig.S3. In the FTIR spectrum of TESPIC(Fig.S3B), The transmission bands at 2272.9 cm^{-1} were attributed to the –NCO stretching vibrations of isocyanate group. However, the characteristic peak almost disappeared in the FTIR spectrum of TESPIC-hypericin (Fig.S3C), which proved the successful synthesis of TESPIC-hypericin intermediates.

In this paper, loading rate is required by calculating the hypericin concentrations of solutions after the reaction under UV/Vis experiments. The input amount of hypericin in the synthesis of UCNPs@SiO_2@hypericin-FA and UCNPs@SiO_2(hypericin)-FA is the same and quantitative, so we can get the real loading rates. By the calculation, the loading rate of UCNPs@SiO_2@hypericin-FA is 95.0% while the rate of UCNPs@SiO_2(hypericin)-FA is 32.1%. As can be seen from the results, the amount of hypericin loaded in UCNPs@SiO_2@hypericin-FA is higher. At the same time, references[1-4] have reported that organic reagents could easily combine with inorganic layer by covalent bonding with high efficiency.

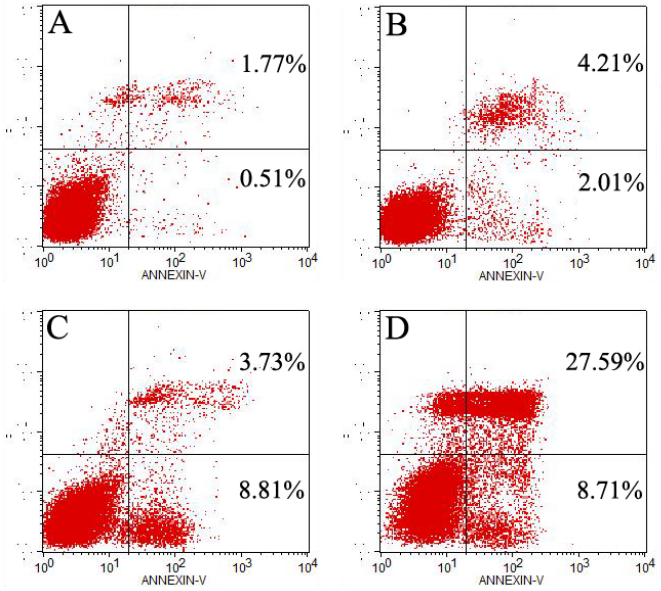

Fig. S4 Flow cytometry of apoptosis of Hela cells stained with Annexin V-FITC/PI induced by different loading rates of photosensitizer-bonded UCNPs@SiO_2@hypericin-FA. The different loading rates are A) 19.6%, B) 38.2%, C) 63.1%, D) 95.0% respectively.

To prove the loading capacity affects the PDT efficiency, flow cytometry of apoptosis of Hela cells induced by different loading rates of photosensitizer-bonded UCNPs@SiO_2@hypericin-FA was carried on. The changes of apoptosis rate in the presence of different loading rates of photosensitizer-bonded UCNPs@SiO_2@hypericin-FA were directly compared as shown in Fig.S4. The corresponding apoptosis rates were 2.28%, 6.22%, 12.54% and 36.30%, as expected, which indicated high loading rate of hypericin-bonded UCNPs@SiO_2@hypericin-FA was more effective than the low loading rate of hypericin in the the PDT efficiency.

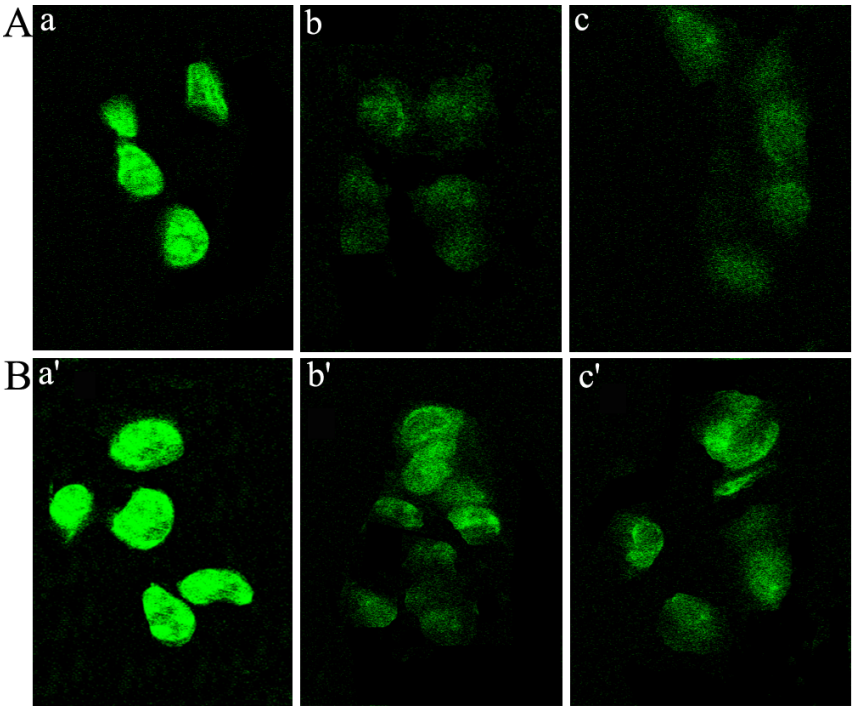

Fig. S5 Confocal luminescence images of FR(+) Hela cells and FR(-)293T cells incubated with UCNPs@SiO_2@hypericin-FA or UCNPs@SiO_2@hypericin under different concentrations, (A) 50 μg·mL^{-1}, (B) 200 μg·mL^{-1}.
(a, a') FR(+) Hela cells incubated with UCNPs@SiO_2@hypericin-FA.
(b, b') FR(-)293T cells incubated with UCNPs@SiO_2@hypericin-FA.
(c, c') FR(+) Hela cells incubated with UCNPs@SiO_2@hypericin.

The cell uptake studies were carried out under conditions of different concentrations of UCNPs@SiO_2@hypericin-FA or UCNPs@SiO_2@hypericin. As is shown in Fig. S5A, srong green upconversion luminescence was observed when Hela cells were incubated with UCNPs@SiO_2@hypericin-FA(Fig. 5S-a), however, there is much lower luminescence from 293T cells which were incubated with UCNPs@SiO_2@hypericin-FA (Fig. 5S-b) and Hela cells which were incubated with UCNPs@SiO_2@hypericin (Fig. 5S-c). The same phenomenon appeared when the concentrations of UCNPs@SiO_2@hypericin-FA or UCNPs@SiO_2@hypericin were 200 μg·mL^{-1} (Fig. 5SB). All the above results showed that UCNPs@SiO_2@hypericin-FA could selectively accumulated in the Hela cells.

References

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