Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supplementary Information

Magnetic lanthanide sensor with self-ratiometric time-resolved luminescence for accurate detection of epithelial cancerous exosomes

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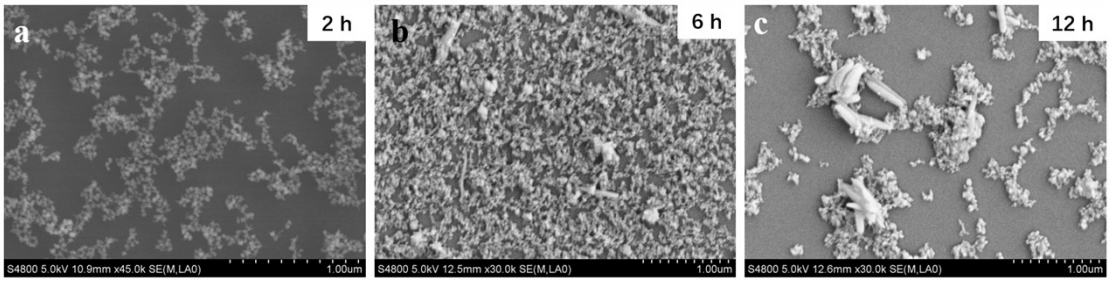

Fig. S1. Different hydrothermal reaction times of $NaYF_4$:Tb@PEI

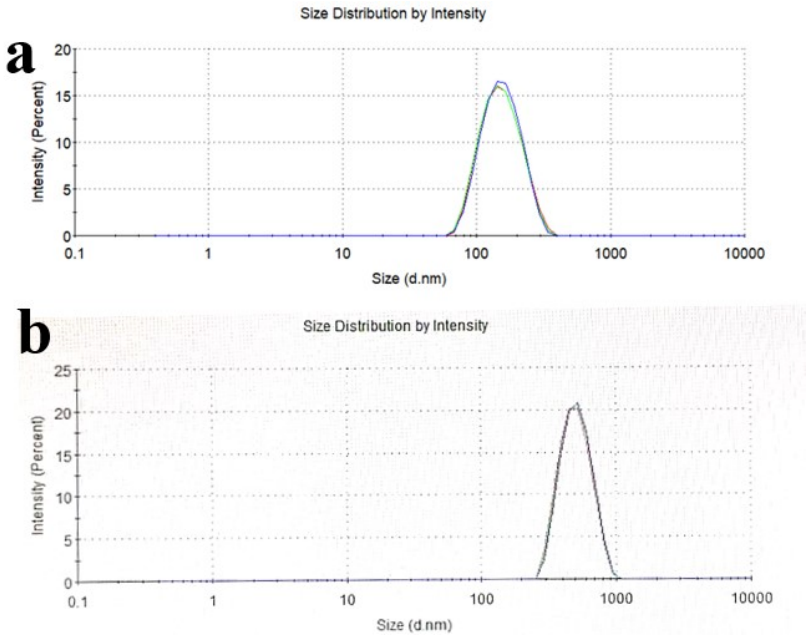

Fig. S2. The hydrodynamic diameter of Fe_3O_4 nanoparticles (a) and Fe_3O_4@$NaYF_4$:Tb nanoparticles (b) measured by DLS.

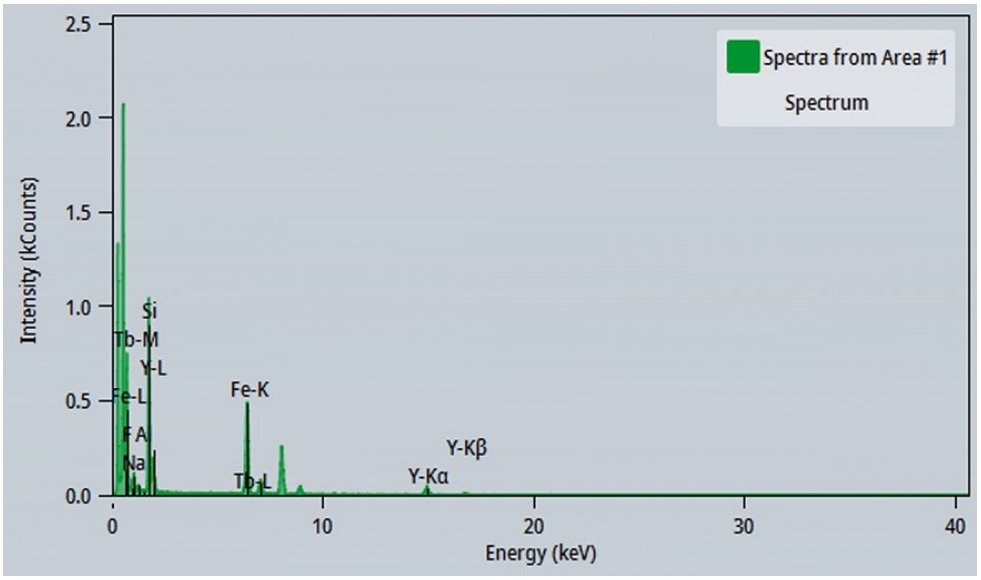

Fig. S3. The EDS analysis for element composition of the Fe_3O_4@SiO_2@$NaYF_4$:Tb.

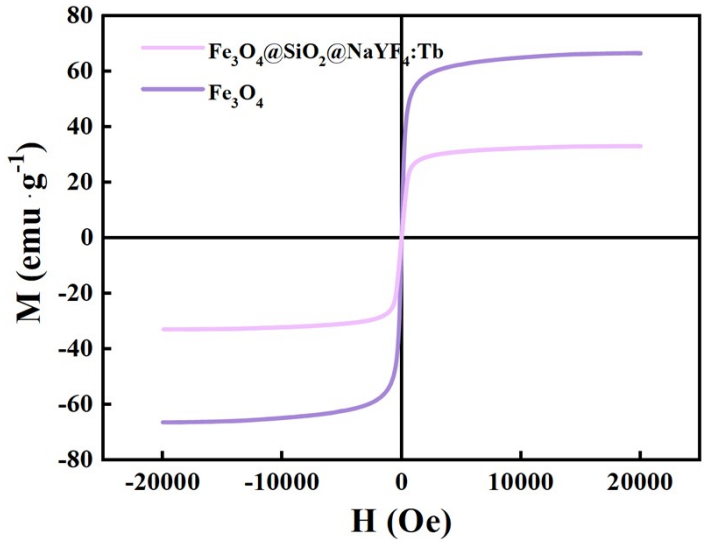

Fig. S4. Magnetic hysteresis loop images of Fe_3O_4 nanoparticles and Fe_3O_4@SiO_2@$NaYF_4$:Tb nanoparticles.

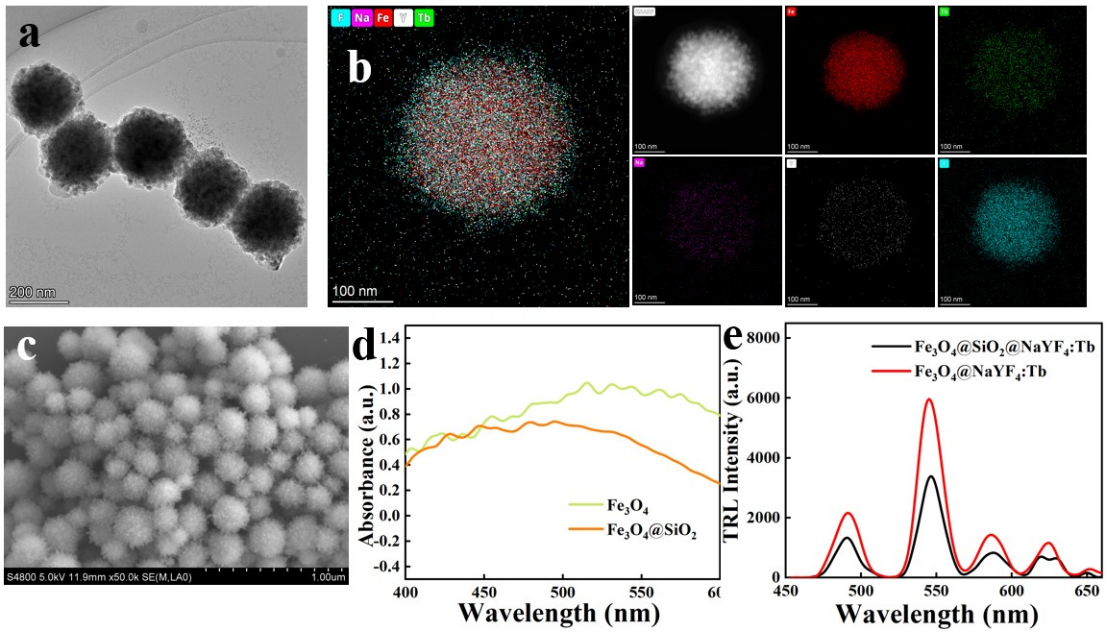

Fig. S5. TEM (a) and SEM (c) images of Fe_3O_4@$NaYF_4$:Tb nanoparticles. (b) EDS analyses of the Fe_3O_4@$NaYF_4$:Tb nanoparticles. (d) UV-vis absorbance spectra of Fe_3O_4 nanoparticles and Fe_3O_4@SiO_2 nanoparticles. (e) The time-resolved luminescence spectrum of Fe_3O_4@ $NaYF_4$:Tb nanoparticles and Fe_3O_4@SiO_2@$NaYF_4$:Tb nanoparticles.

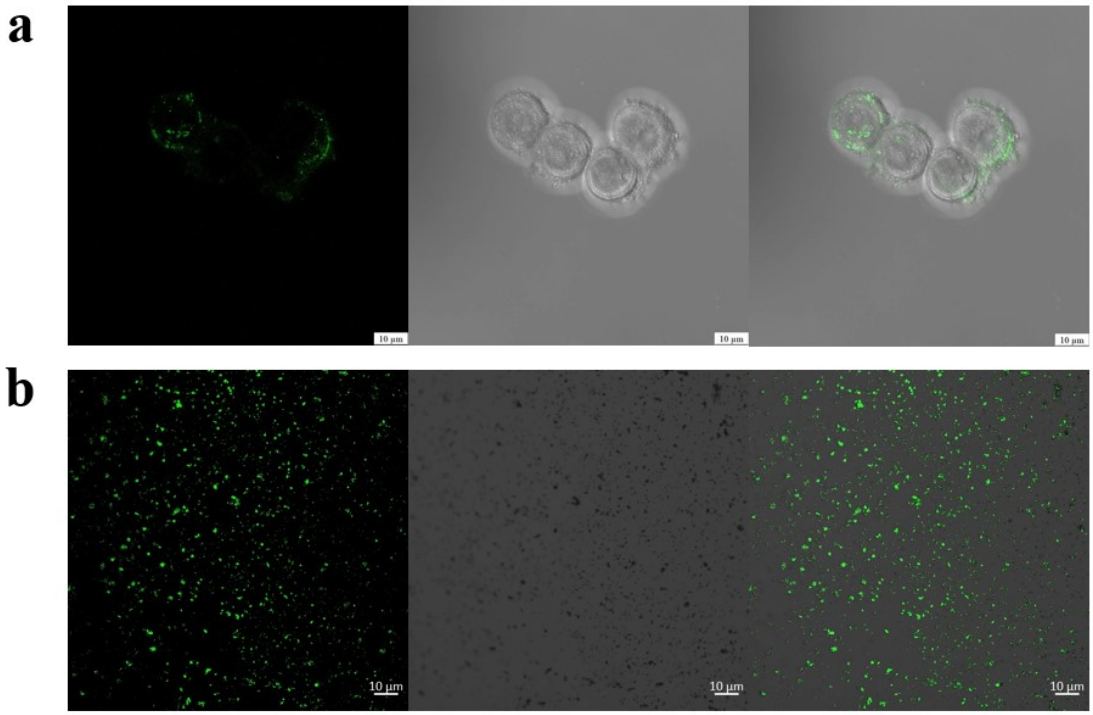

Fig. S6. CLSM images of (a) MCF-7 cells incubated with Apt_{EpCAM}-FAM and (b) MLS@Apt_{EpCAM}-FAM.

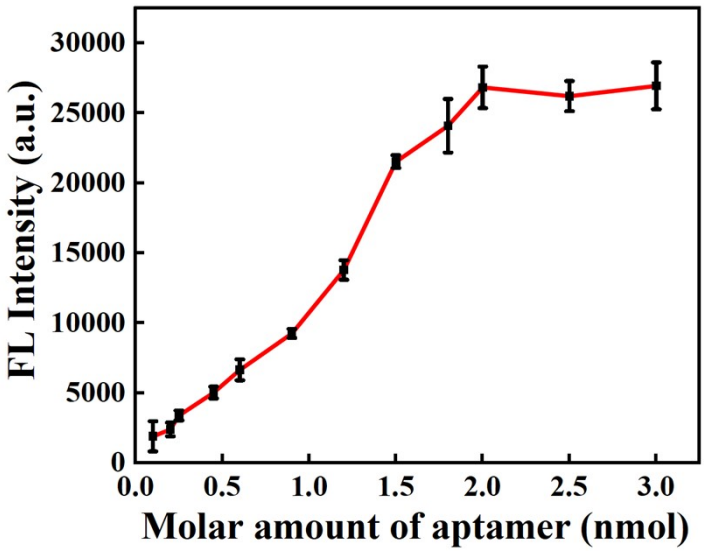

Fig. S7. Optimization of the amount of the Apt_{EpCAM} loaded on Fe_3O_4@SiO_2@$NaYF_4$:Tb nanoparticles.

Magnetic recovery efficiency testing of MLS

First, UV-visible absorption spectra (wavelength scan, slit width 5 nm) of MLS at different concentrations were obtained to establish a standard curve. Then, absorbance

values of the supernatant at different magnetic separation times were recorded and the established standard curve was used to calculate the corresponding concentrations and recovery efficiency of MLS:

$$\frac{concentration\ of\ MLS\ berfore\ magnetic\ separation - initial\ concentration\ of\ MLS}{concentration\ of\ MLS\ berfore\ magnetic\ separation} x\ 100\%$$

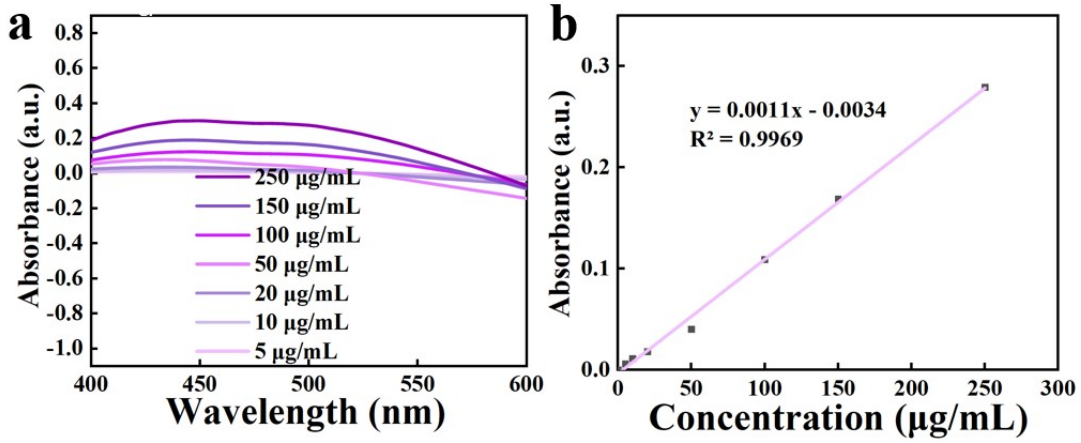

Fig. S8. UV-vis absorbance spectra (a) and (b) corresponding linear relationship of different concentrations of MLS.

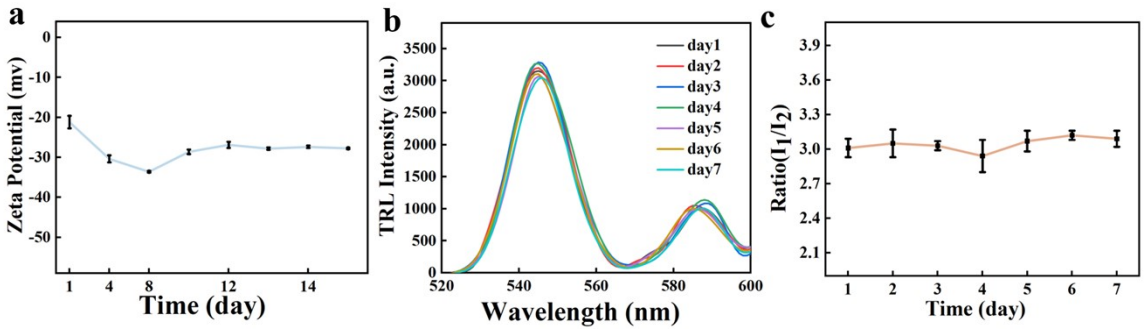

Fig. S9. Storage stability curve of MLS. (a) Zeta potential stability and (b-c) TRL stability.

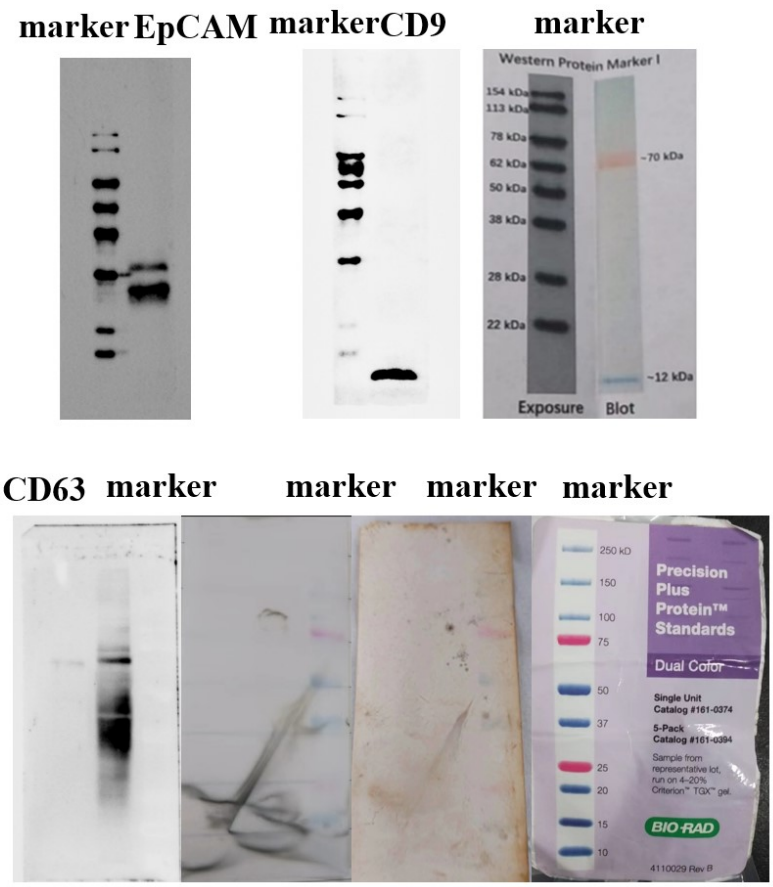

Fig. S10. The raw data of western blotting experiments for demonstrating the two exosomal proteins and one epithelial cancer-associated protein on MCF-7 exosomes.

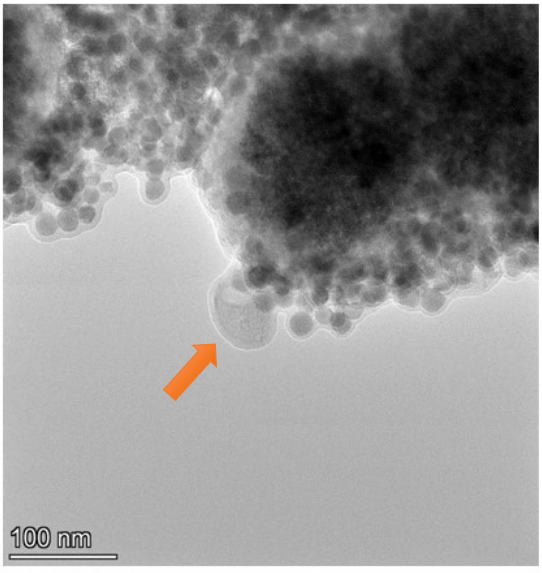

Fig. S11. TEM image of the MLS@exo, and one captured exosome was pointed out by an arrow.

Tab. S1 The TRL intensity experimental results in model samples.

Number of Exosomes	Peak value at 543 nm (I_1) (repeated 3 times)	Peak value at 583 nm (I_2) (repeated 3 times)	Ratio (I_1/I_2)	Average Ratio	STDEV	RSD (%)
2.3×10^2	3495	1129	3.096	3.162	0.0605	1.91
	3515	1116	3.150			
	3589	1107	3.242			
2.3×10^3	3748	1113	3.367	3.369	0.0371	1.10
	3727	1121	3.325			
	3781	1107	3.415			
2.3×10^4	4040	1132	3.569	3.541	0.0512	1.44
	4038	1164	3.469			
	4047	1129	3.584			
2.3×10^5	4462	1188	3.756	3.746	0.0325	0.87
	4441	1175	3.779			
	4446	1201	3.702			
2.3×10^6	4651	1216	3.825	3.822	0.0187	0.49
	4666	1214	3.843			
	4660	1227	3.798			
2.3×10^7	4941	1252	3.947	3.993	0.0332	0.83
	4993	1241	4.023			
	5002	1248	4.008			
2.3×10^9	5373	1271	4.227	4.202	0.0178	0.42
	5368	1281	4.190			
	5391	1287	4.189			

** STDEV: Standard Deviation, RSD: relative standard deviation.*

Tab. S2 Information of clinical samples.

Sample	Type	Gender	Age
H1	Health	Male	31
H2	Health	Male	34
H3	Health	Female	45
H4	Health	Female	28
H5	Health	Female	36
B1	Breast Cancer	Female	48
B2	Breast Cancer	Female	85
B3	Breast Cancer	Female	67
B4	Breast Cancer	Female	50
B5	Breast Cancer	Female	69
L1	Liver Cancer	Female	50
L2	Liver Cancer	Female	58
L3	Liver Cancer	Female	49
L4	Liver Cancer	Male	70
L5	Liver Cancer	Male	50

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Tab. S3 The TRL experimental results in real samples.

Samples		Peak value at 543 nm (I_1)	Peak value at 583 nm (I_2)	Ratio (I_1/I_2)	Average Ratio	STDEV	RSD (%)
Health	**H1**	4480	1320	3.394	3.427	0.155	4.522
	H2	4073	1297	3.140			
	H3	4342	1218	3.565			
	H4	4134	1184	3.491			
	H5	4334	1223	3.544			
Breast cancer	**B1**	4455	1133	3.932	3.977	0.101	2.554
	B2	4753	1165	4.080			
	B3	4327	1134	3.816			
	B4	4929	1205	4.090			
	B5	5105	1287	3.966			
Liver cancer	**L1**	4820	1165	4.137	4.253	0.095	2.228
	L2	5196	1235	4.207			
	L3	5272	1205	4.375			
	L4	5334	1273	4.190			
	L5	5031	1155	4.356			
RSD between the health and breast cancer (%)							7.429
RSD between the health and liver cancer (%)							10.758
RSD between breast cancer and liver cancer (%)							4.120

** STDEV: Standard Deviation, RSD: relative standard deviation.*