Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Biomarkerless Targeting and Photothermal Cancer Cell Killing by Surface-Electrically-Charged Superparamagnetic Fe_3O_4 Composite Nanoparticles

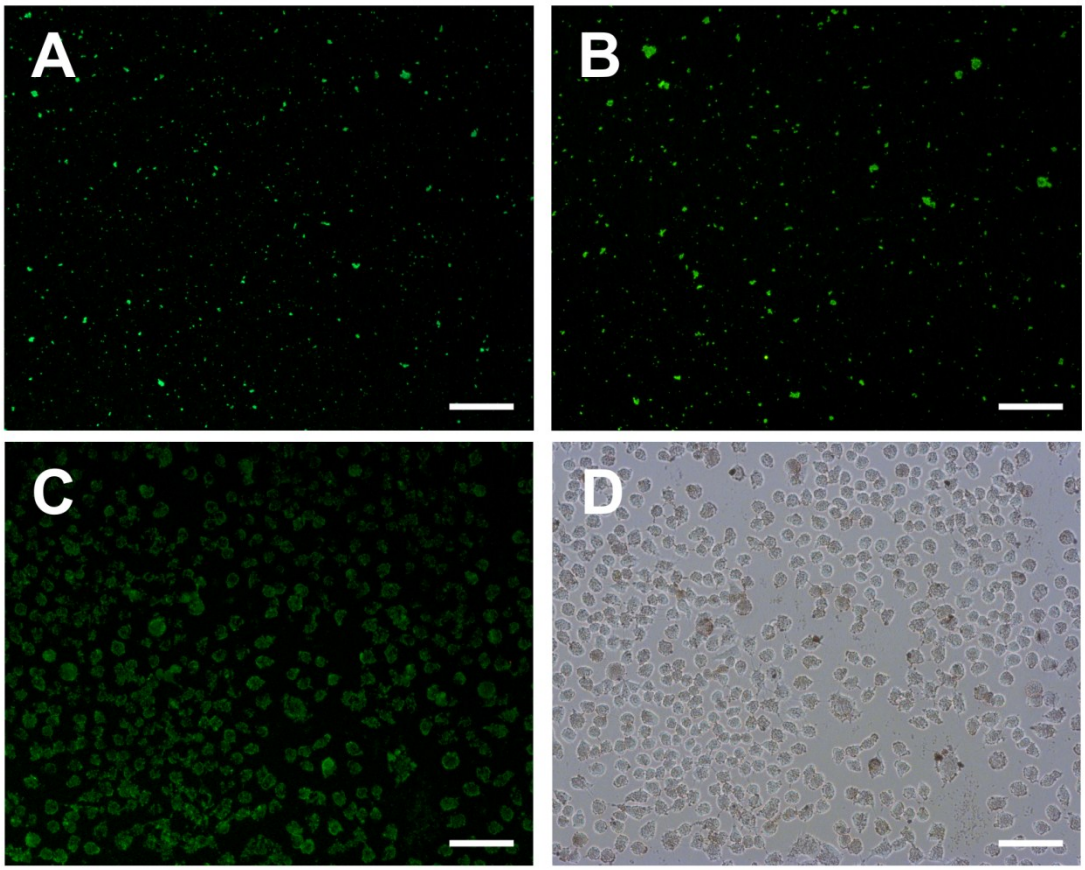

Figure S1. Fluorescent images showing (A) the positively-charged magnetic composites nanoparticles (MNCs); (B) the negatively-charged MNCs; (C) the fluorescent image, and (D) the bright-field image of HeLa cells which are electrostatically bound strongly by the positively-charged MNCs. The scale bars represent 100 μm.

Calculation of the photothermal conversion efficiency

The photothermal conversion efficiency, η, of MNCs was calculated using the formulations developed by Roper et al [36-38]. The photothermal conversion efficiency η can be expressed as (see the Supporting Information for the detailed calculations):

$$\eta = \frac{hS(T_{Max} - T_{Surr}) - Q_s}{I(1 - 10^{-A_{808}})} \quad (1)$$

where the proportionality constant h (mW/(m2·°C) is the heat transfer coefficient; S (m2) is the surface area of the container; the value of hS is obtained from the Figure S2; T_{Max} (°C) is the system maximum temperature; T_{Surr} (°C) is the ambient surrounding temperature; QS (mW) is the energy input by the sample cuvette and the solution, which is measured independently to be 5 mW; I (2 W) is the incident laser power, and A_{808} is the absorbance of the MNCs in the borosilicate glass sample cell at the wavelength of 808 nm, whose value was determined to be 1.2513 in this study.

The value of hS is obtained by the following equation[36]:

$$hS = \frac{\sum_i m_i C_{P,i}}{\tau_s} \quad (2)$$

where m_i and $C_{P,i}$ are respectively the mass and heat capacity of the sample including MNCs suspension and sample cell. τ_s (s) is the sample system time constant which is given by[36]:

$$\tau_s = -\frac{t}{ln\theta} \quad (3)$$

where θ is defined as the ratio of ($T-T_{surr}$) to ($T_{Max}-T_{surr}$), and T (°C) is the solution temperature. ɵ can be expressed as [36]:

$$\theta = \frac{T - T_{Surr}}{T_{Max} - T_{Surr}} \quad (4)$$

where ($T_{Max}-T_{Surr}$) = ΔT and is experimentally determined to be 30 °C in this study. The water mass, m(water) and heat capacity, C(water) are respectively 0.4 g and 4.2 J/g. The ΔT values that indicate the extend of the photothermal effect of the nanoparticles (Figure S2 A) and the time constant, τ_s, that reflects the heat transfer from the system (Figure S2 B) are shown in Supplementary Figure S2. According to Eq. 3, the time constant can be determined by plotting the time, t, in the linear portion of the cooling curve (after 300 s, Figure S2 A) as a function of $-\ln\theta$, as shown Figure S2 B. The slope in Figure S2 B gives the τ_s value of 82.4 s. It is to be noted that t = 0 in Figure S2 B is in fact t = 300 s in Figure S2 A, as the starting point of cooling period. Using Eq. 2, the hS value is calculated to be 20.4 mW/°C. Substituting hS = 20.4 mW/°C into Eq.1

yields η of 31.9%.

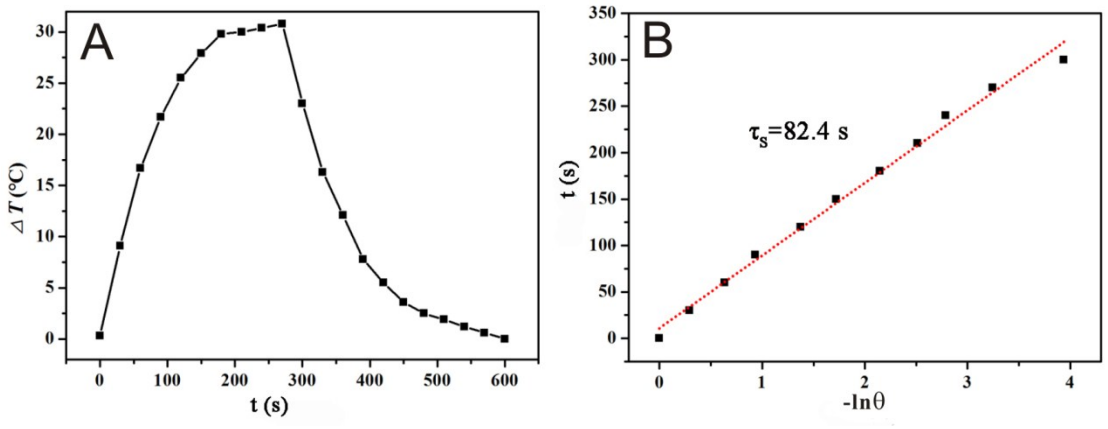

Figure S2 (A) ΔT vs. t (s) for the system studied. ΔT of an aqueous dispersion of MNCs was observed by an 808 nm laser irradiation for the time period indicated. The laser was turned off after irradiation for 300 s, and (B) t (s) vs. - lnθ for the linear portion of the cooling curve (after 300 s, Figure S2 A). τ_s is determined to be 82.4 s by the slope.

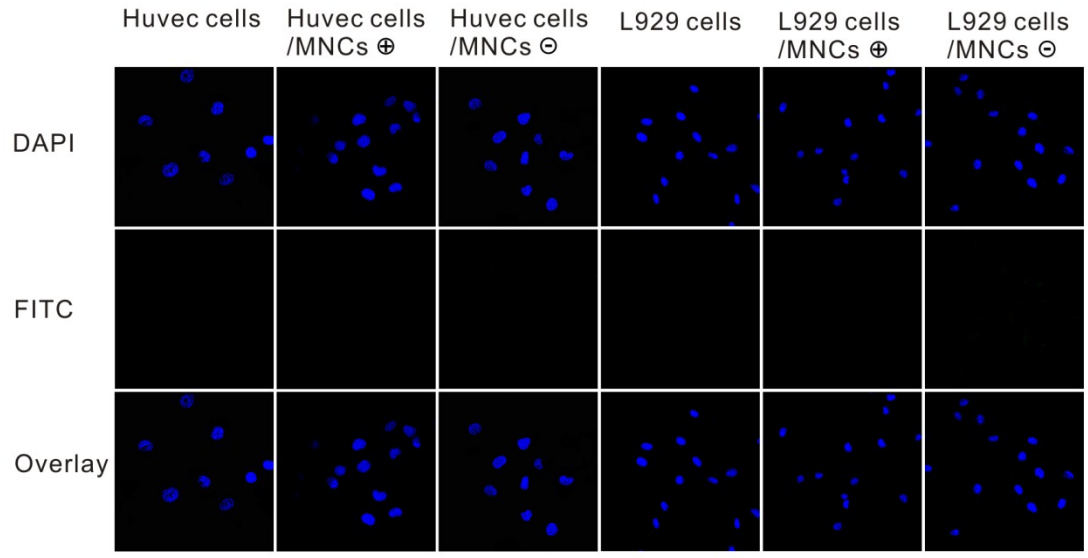

Figure S3. Fluorescence confocal images showing the treated normal cells (Huvec and L929) with magnetic composites nanoparticles of difference charges. DAPI is used to stain the cell nucleus. FITC is labeled on the positively-charged (MNCs⊕) or negatively-charged (MNCs⊖) MNCs.

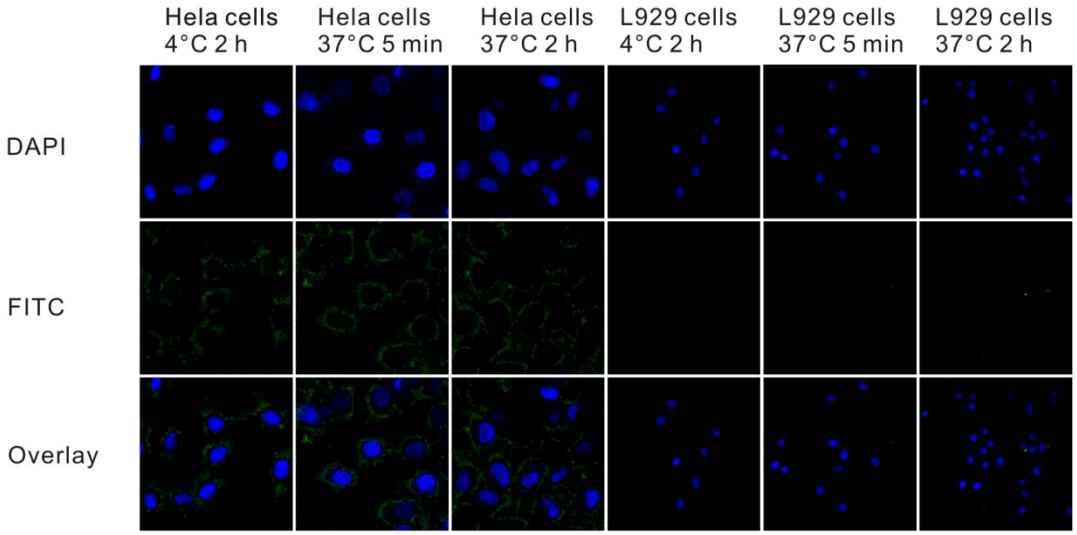

Figure S4. Fluorescence confocal images showing the Hela cells and L929 cells treated with magnetic composites nanoparticles under different conditions (2 h at 4 °C, 5 min at 37 °C, 2 h at 37 °C). DAPI is used to stain the cell nucleus. FITC is labeled on the positively-charged MNCs (MNCs ⊕).

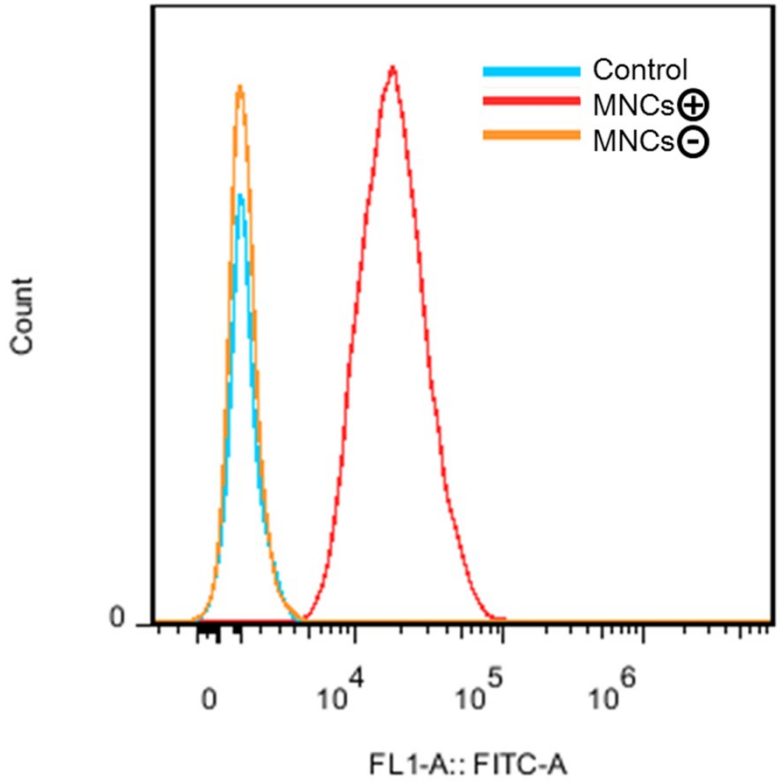

Figure S5. Fluorescent spectra of Hela cells treated with the magnetic composites nanoparticles (MNCs) of different charges as indicated, obtained by flow cytometry. Red line: incubated with the positively-charged MNCs (MNCs⊕), orange line: with the negatively-charged MNCs (MNCs⊖), blue line: blank cell control.

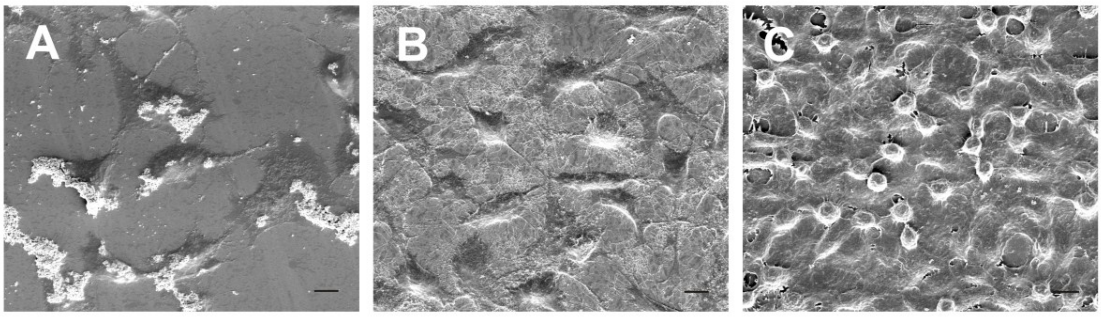

Figure S6. SEM images showing the treated cancer cells (A: HeLa) and normal cells (B: Huvec and C: L929) with the positively-charged MNCs at high resolution. The scale bars are 10 μm.

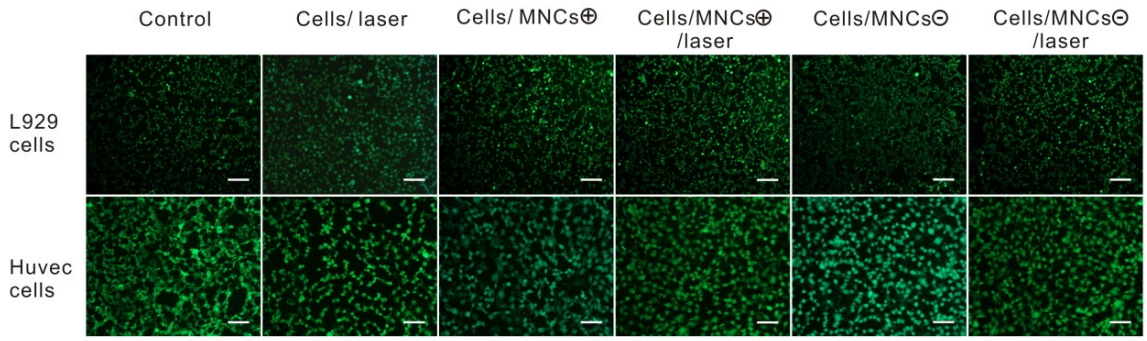

Figure S7. Fluorescent confocal images showing the live-dead staining of two normal cells (L929 and Huvec cells) treated with the charged MNCs under the same condition as in Figure 7. The scale bars are 100 μm. MNCs⊕ refers to the positively-charged MNCs, and MNCsΘ refers to the negatively-charged MNCs.