Supporting Information

Enhancing Antitumor Immunity with Stimulus-Responsive Mesoporous Silicon in Combination with Chemotherapy and Photothermal Therapy

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1. Synthesis of thiol functionalized HA (HA-SH)

200 mg HA (0.5 mmol) was dissolved in 30 mL PBS (pH = 7.4). Then, 287.55 mg EDCI (1.5 mmol) and 202.73 mg HOBt (1.5 mmol) were added to react with HA for 4 h to activate the carboxyl, 385.75 mg cystamine dihydrochloride (2.5 mmol) was added and stirred for 24 h at 25 ℃. The above mixture was then dialyzed against deionised water at 25 ℃ for 24 h (MW cutoff: 8000–14000). Subsequently, the above solution's pH value was adjusted to 8-9 with 10 % NaOH (wt %), 385.63 mg DTT (2.5 mmol) was added to the solution, and stirred for 24 h. Then, the pH the resulting solution was adjusted to 3-4 with HCl, and the solution was dialyzed against deionised water at 25 ℃ for 2 days (MW cutoff: 3500). The final product was freeze-dried with lyophiliser at -60 ℃ for 48 h and stored at -20 ℃. Yield: 177 mg (77 %). The chemical structure HA-SH was characterized by FT-IR and ^{1}H NMR (400 MHz).

2. Supplementary figures

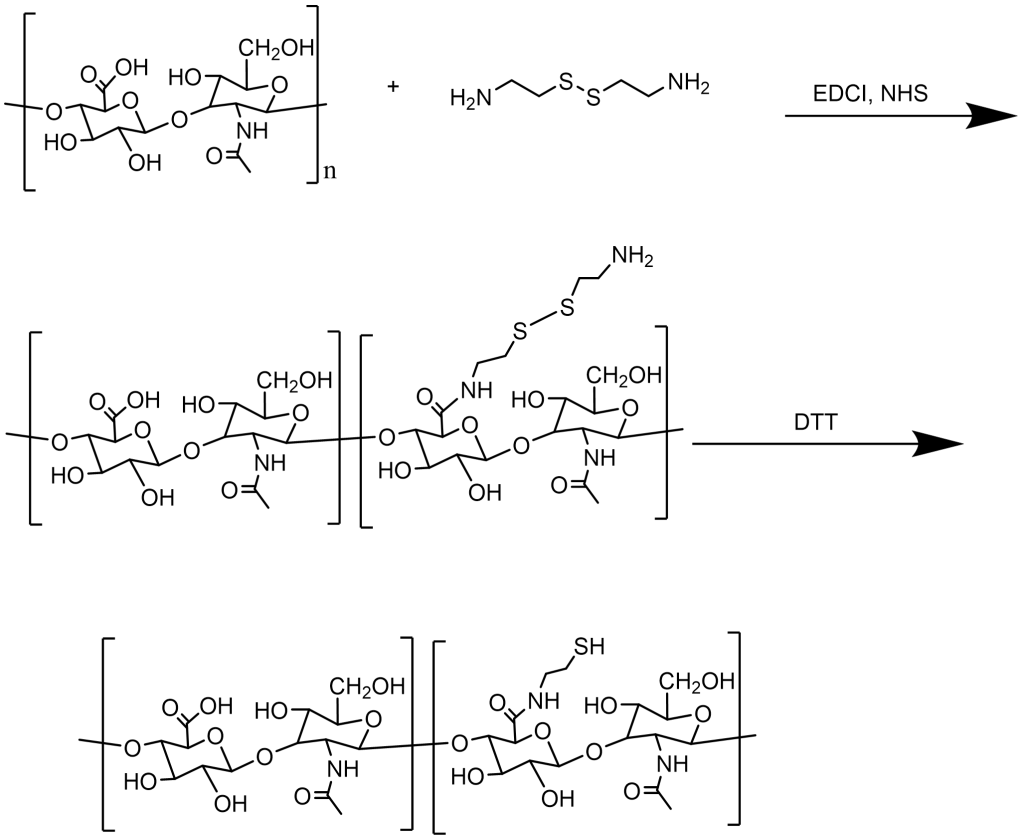

Fig. S1 Synthesis route of HA-HS.

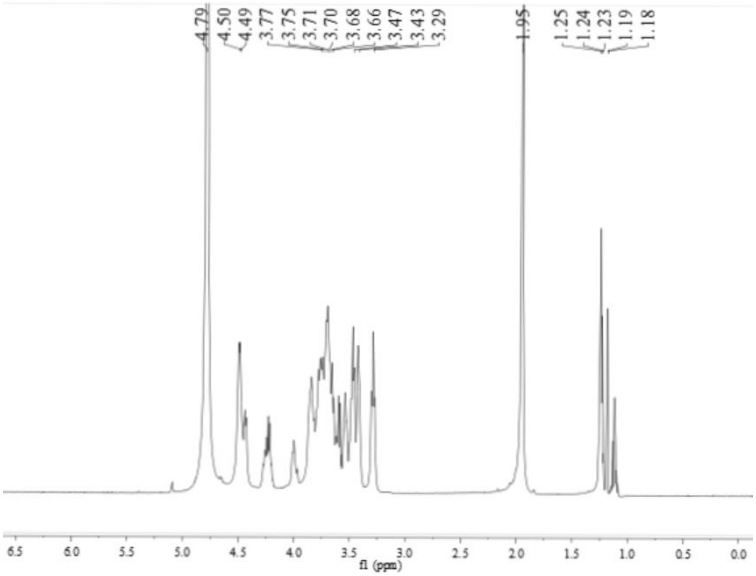

Fig. S2 [1] H NMR spectra of HA.

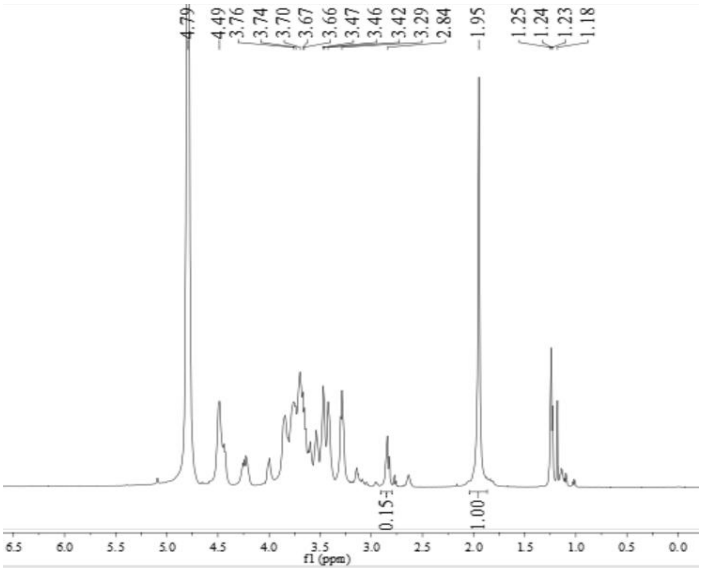

Fig. S3 ^{1}H NMR spectra of HA-SH.

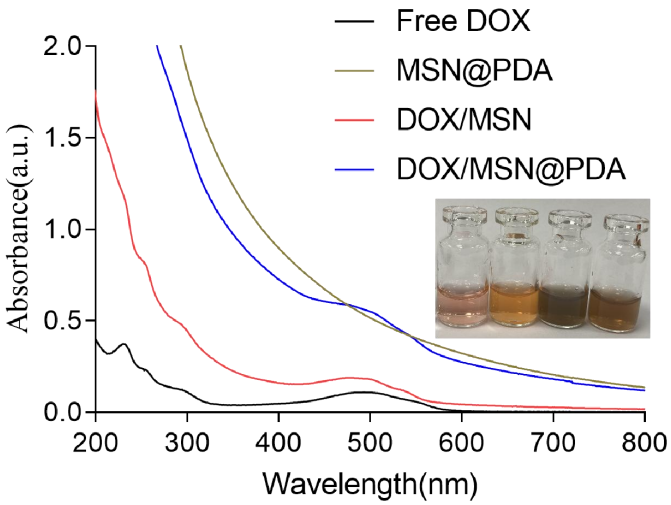

Fig.S4 UV-Vis absorption spectrum of free DOX, MSN@PDA, DOX/MSN and DOX/MSN@PDA.

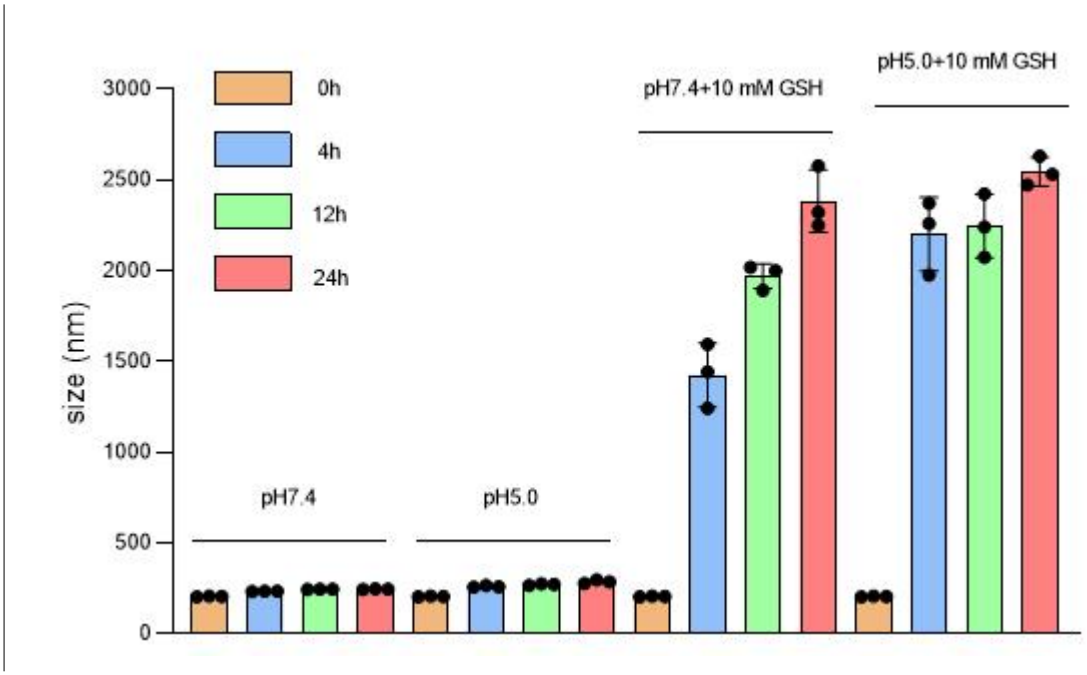

Fig. S5 Changes in Size Responsiveness of MSN@PDA-HA.

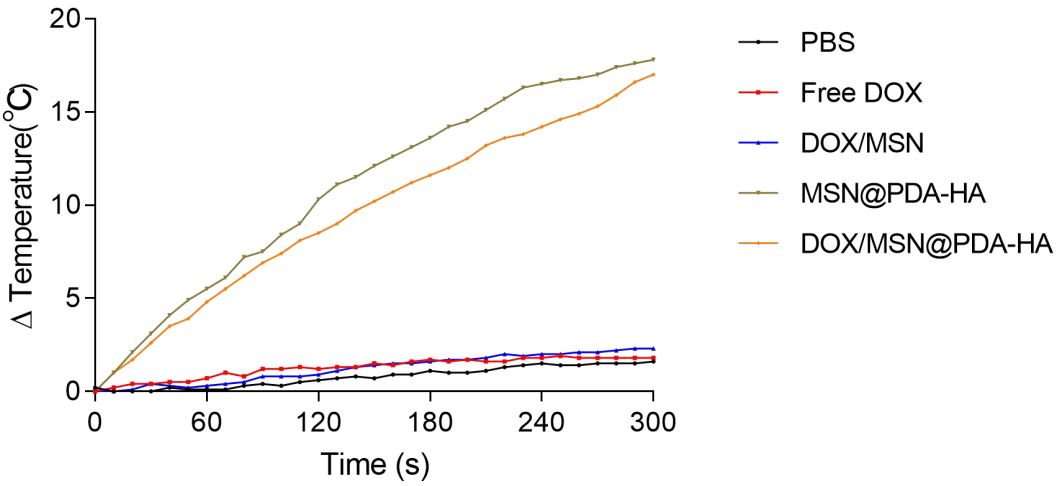

Fig.S6 Real-time temperature growth curves of MSN@PDA-HA and DOX/MSN@PDA-HA at various concentration irradiated with 808 nm laser (2.0 W cm^{-2}).

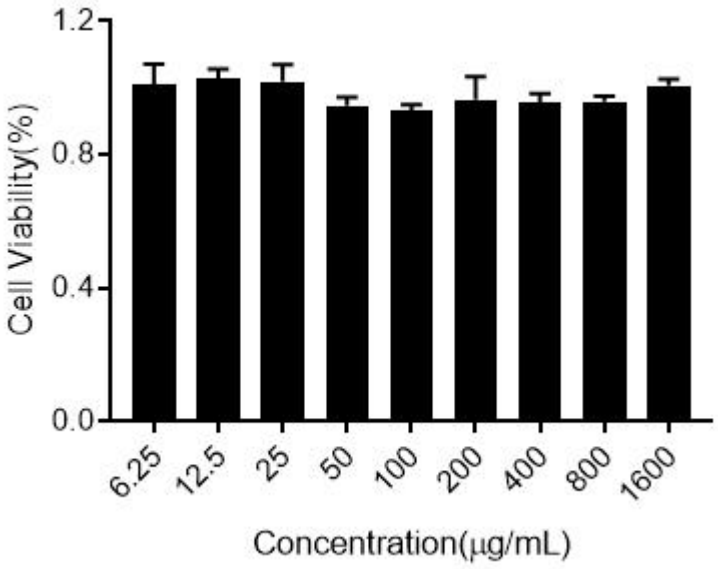

Fig.S7 Cell viability of 4T1 cells measured by CCK-8 assay at 37 ℃.

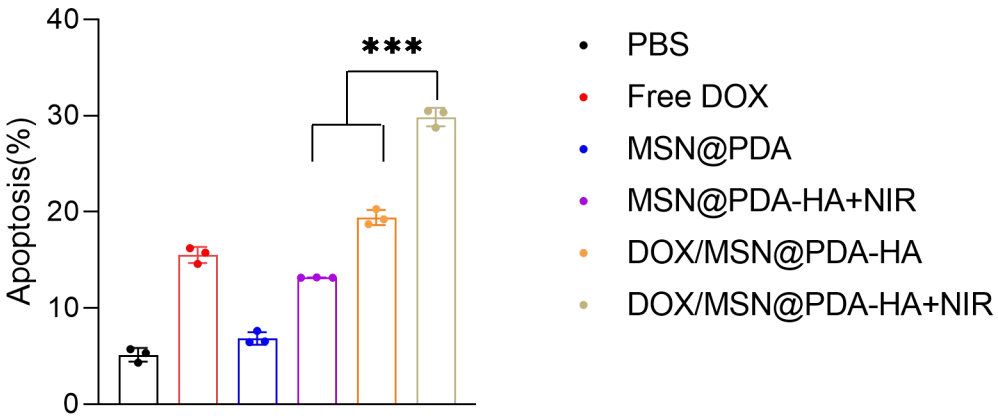

Fig.S8 Quantification of the cell apoptosis induced by indicated formulations after 24 h in 4T1 cells.

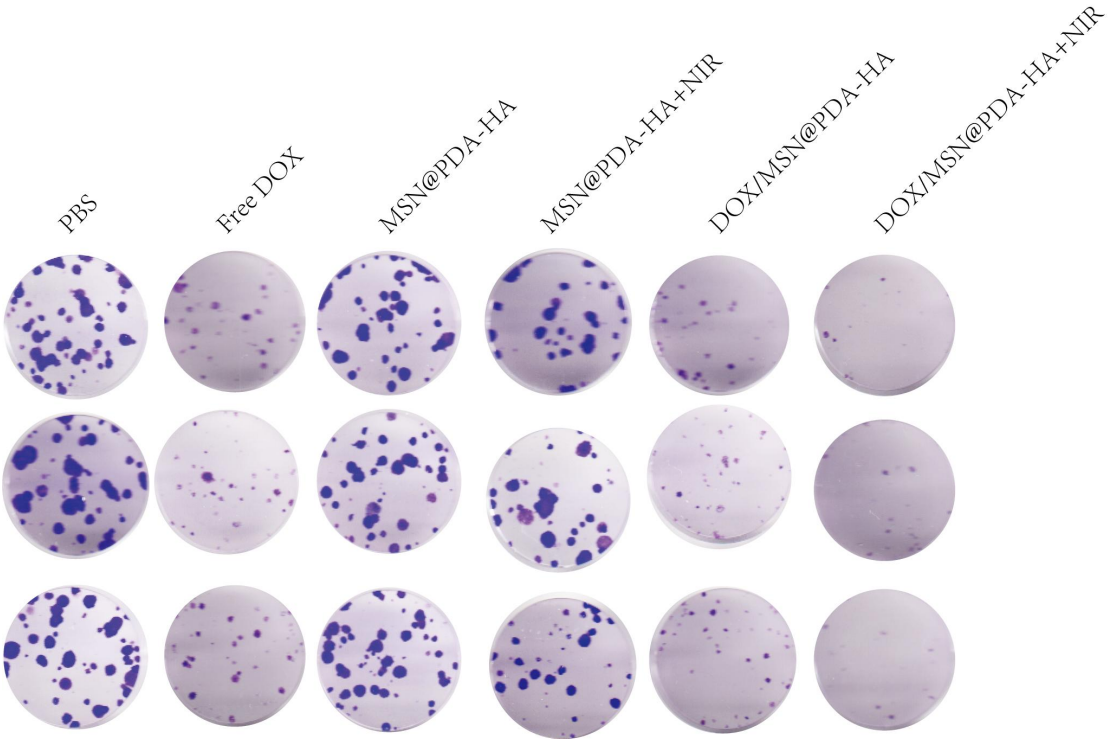

Fig.S9 Representative colony formation of 4T1 after different treatments.

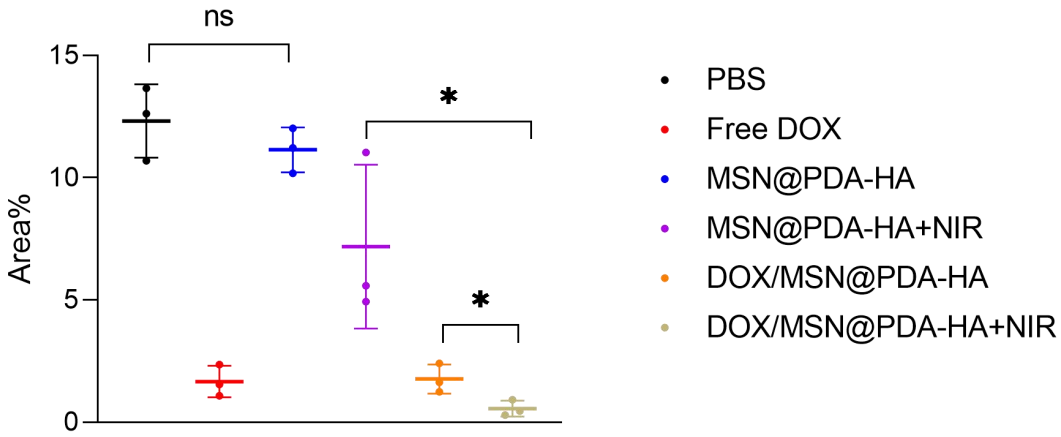

Fig.S10 Quantification of colony formation of 4T1 after different treatments. Data are shown as mean ± SD (n = 3, one-way ANOVA).

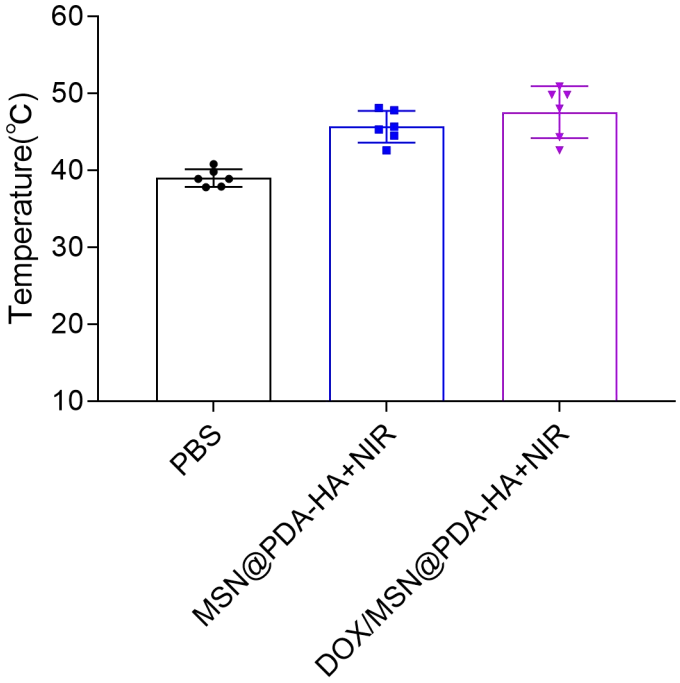

Fig.S11 Real-time temperature of the tumor after 12 hours of different treatments with 808nm laser irradiation for 3 minutes.

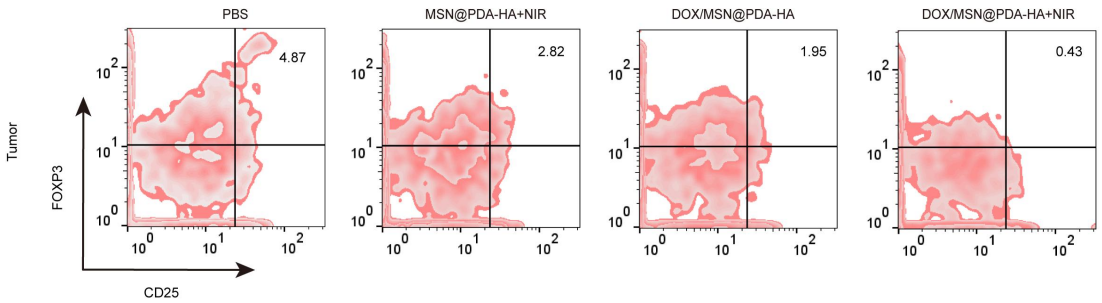

Fig.S12 Flow cytometry plots showing different groups of Treg cells in tumor (gated on $CD4^+$ cells).

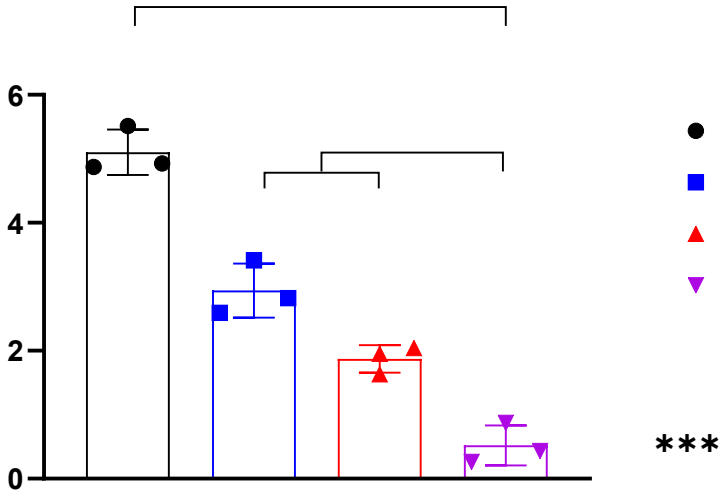

Fig.S13 Quantitative analysis of Treg cells in tumor after the mice received different treatments.

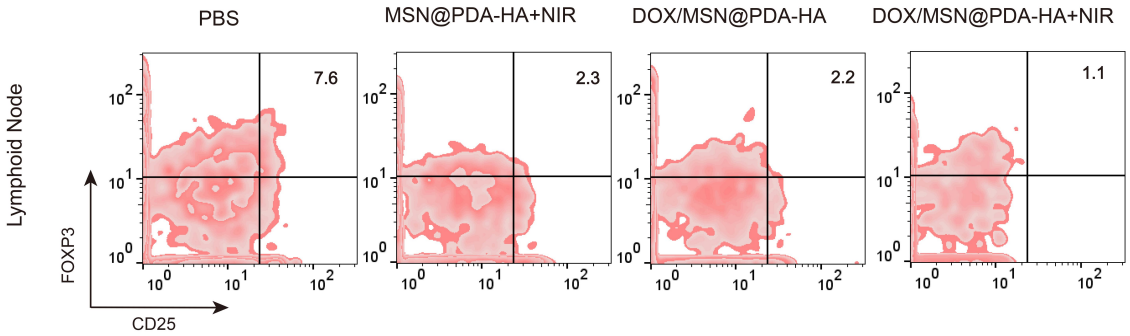

Fig.S14 Flow cytometry plots showing different groups of Treg cells in lymphoid nodes (gated on $CD4^+$ cells).

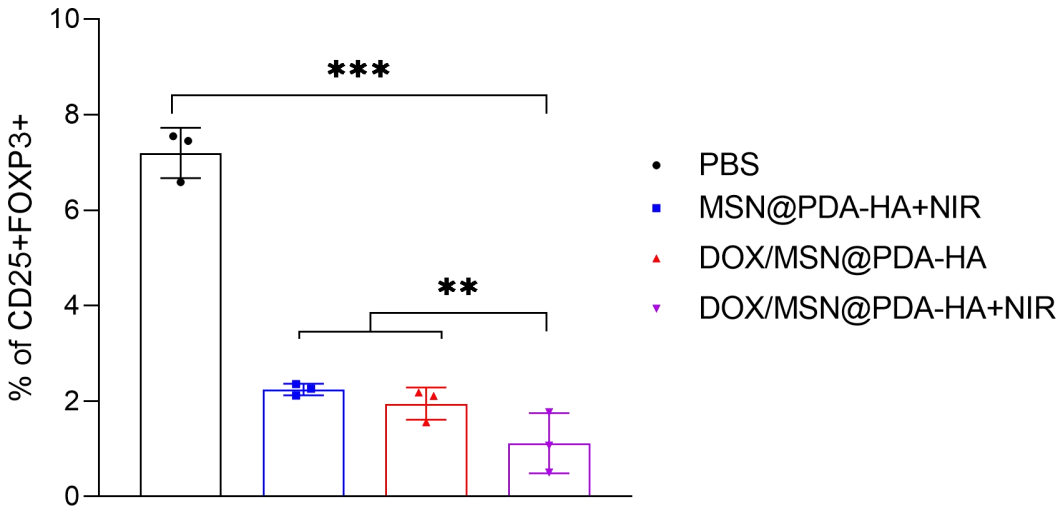

Fig.S15 Quantitative analysis of Treg cells after the mice received different treatments.

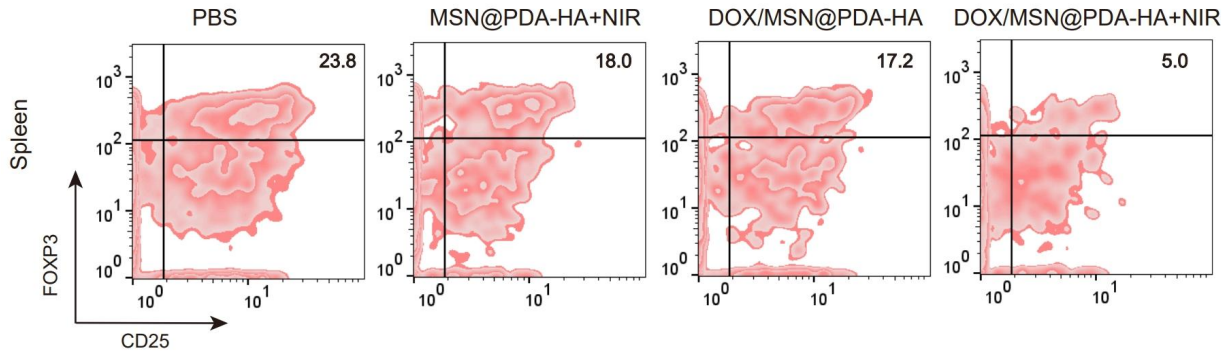

Fig.S16 Evaluation of the percentages of Treg cells in spleen (gated on $CD4^+$ cells).

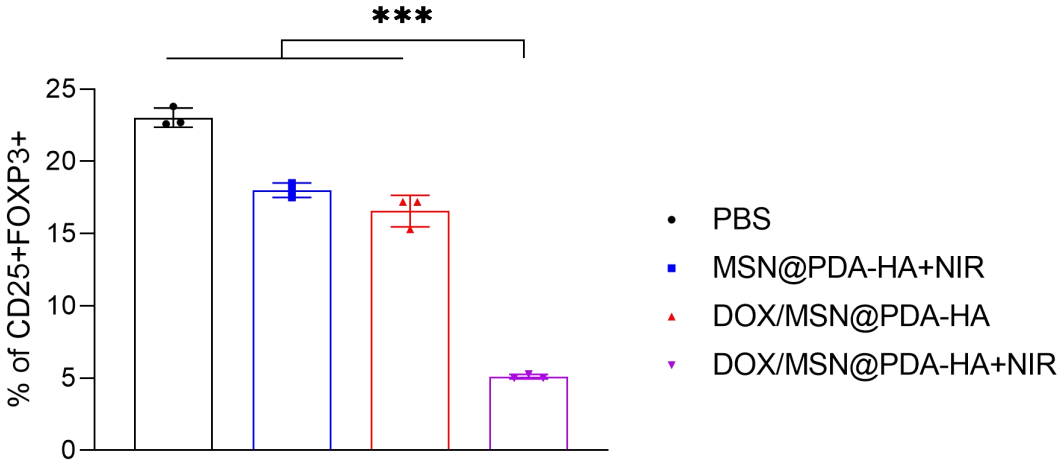

Fig.S17 Quantitative analysis of Treg cells after the mice received different treatments.

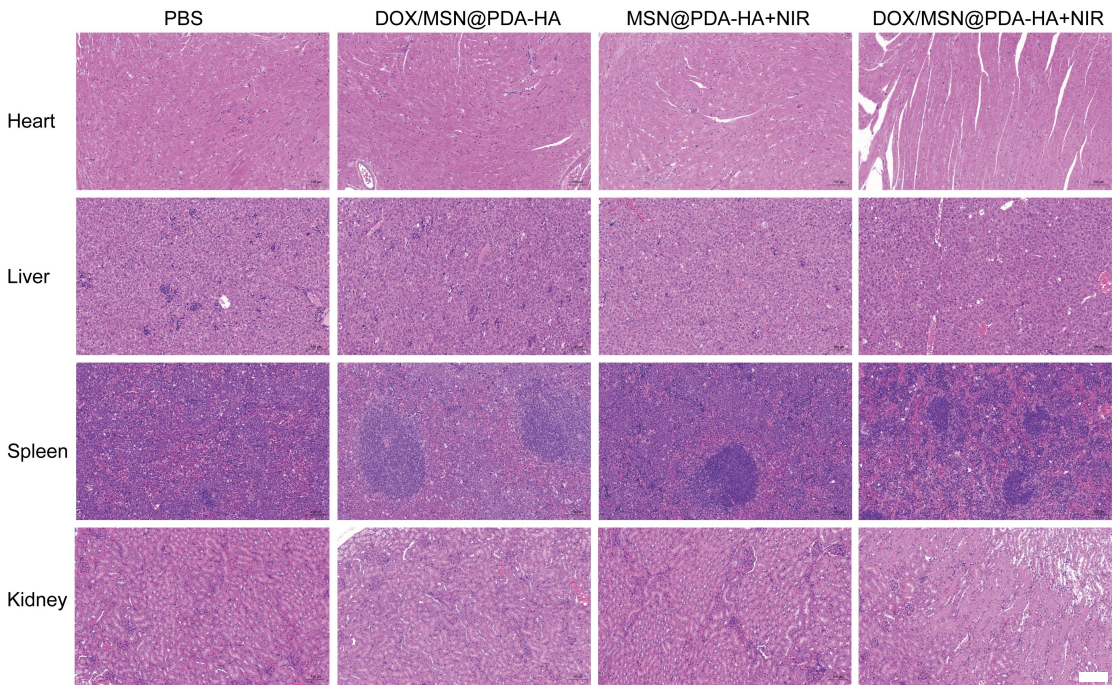

Fig.S18 H&E staining images of major organs (heart, liver, spleen, and kidney) collected from various groups at the endpoint of the treatments (scale bar: 100 μm).

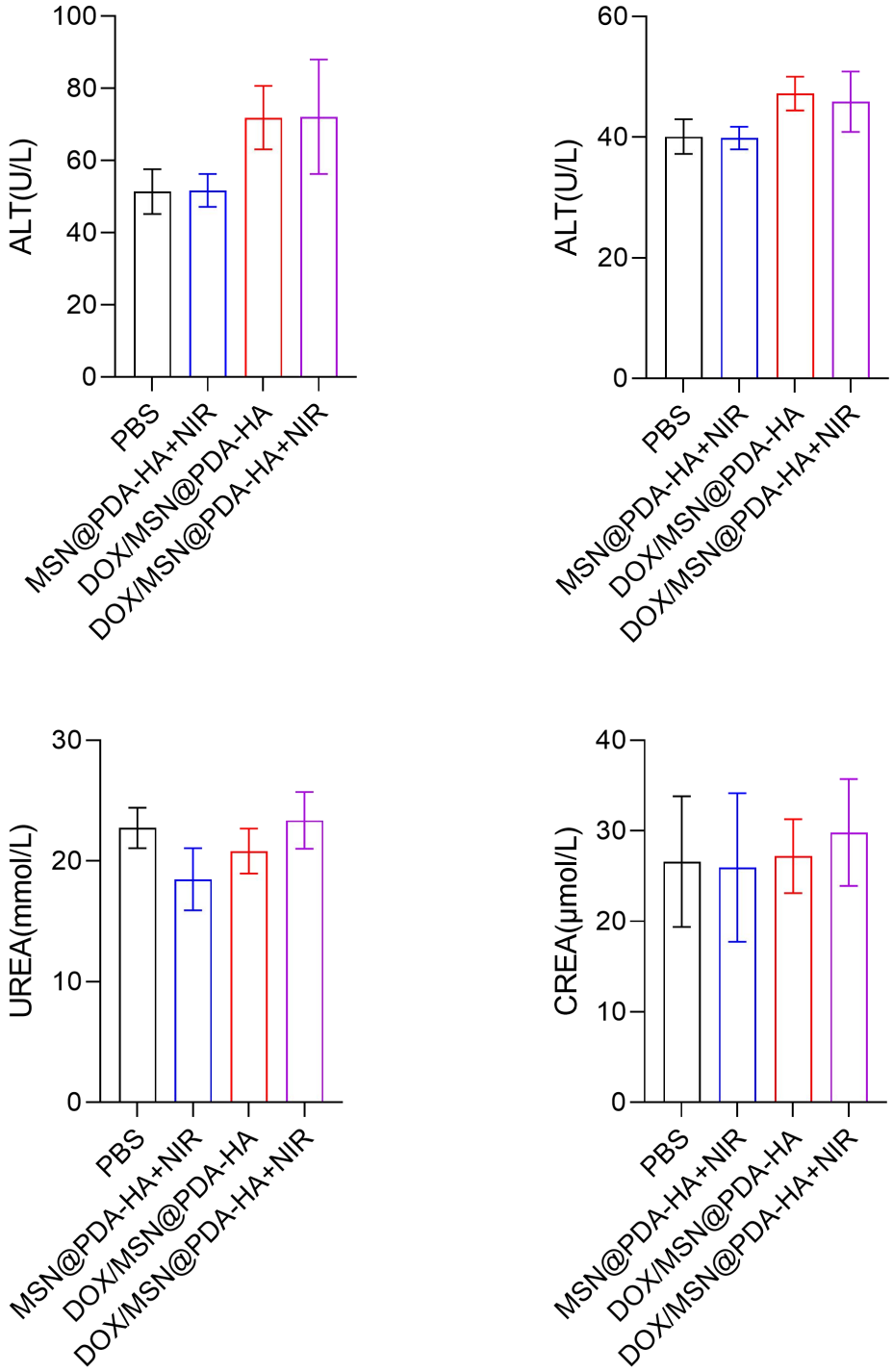

Fig.S19 Main physiological indexes (AST, ALT, UREA and CREA) of mice after treatments of different groups (n = 3).