Electronic Supplementary Material (ESI) for Dalton Transactions

Yolk-type Au@Fe_3O_4@C nanospheres for Drug Delivery, MRI and Two-photon Fluorescence Imaging

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1、Synthesis of the yolk-type Au@Fe_3O_4@C nanospheres

Au nanoparticles were prepared according to a previous article: $HAuCl_4$ (2.5 ml, 0.01M) was added to 50 ml of deionized water and heated the water to boiling for 5 minutes. Then, 3.0 ml of sodium citrate (10mg/ml) was added, and the mixture was kept boiling for 30 minutes under stirring, then cooled to room temperature naturally. At last, 0.32 ml aqueous solution of polyvinylpyrrolidone (PVP, 15 mg/ml) was added and the product was kept stirring for 24h to promote the absorption of PVP on the surface of Au NPs. The products were collected by centrifugation, and re-dispersed in 6ml of deionized water.

Preparation of Au@SiO_2 nanoparticles: The above Au colloids were mixed with 20 ml of ethanol, 1ml of ammonia solution and 0.28 ml Tetraethyl Silicate (TEOS). The mixture was kept at room temperature under magnetic stirring for 12 hours. Then the resulting Au@SiO_2 particles were centrifuged and washed with ethanol each twice and kept in 4 ml of water for future use; the preparation of Au@SiO_2@Fe_3O_4@C and SiO_2 etching were carried out following the method reported with some modification nanoparticles to get the yolk-type Au@Fe_3O_4@C architectures:Au@SiO_2 colloidal nanoparticles (1ml) were dispersed in acetone (30ml) which contained 0.15g ferrocenes. Subsequently, 0.7 ml of hydrogen peroxide (30 wt %) was added dropwise. After continuous magnetic stirring at room temperature for 1 hour, the mixture was transferred into a Teflon-lined stainless autoclave (50ml) and maintained at 210 °C for two days. The product was then separated and washed with acetone for several times; Lastly ammonia solution (28wt%) was added to the as-prepared Au@SiO2@Fe3O4@C solution (30ml) before the mixture was transferred into a Teflon-lined stainless autoclave and maintained at 160°C for 8h. The yolk-type Au@Fe_3O_4@C three-ply composite nanoparticles was separated by a magnet and washed with water several times.

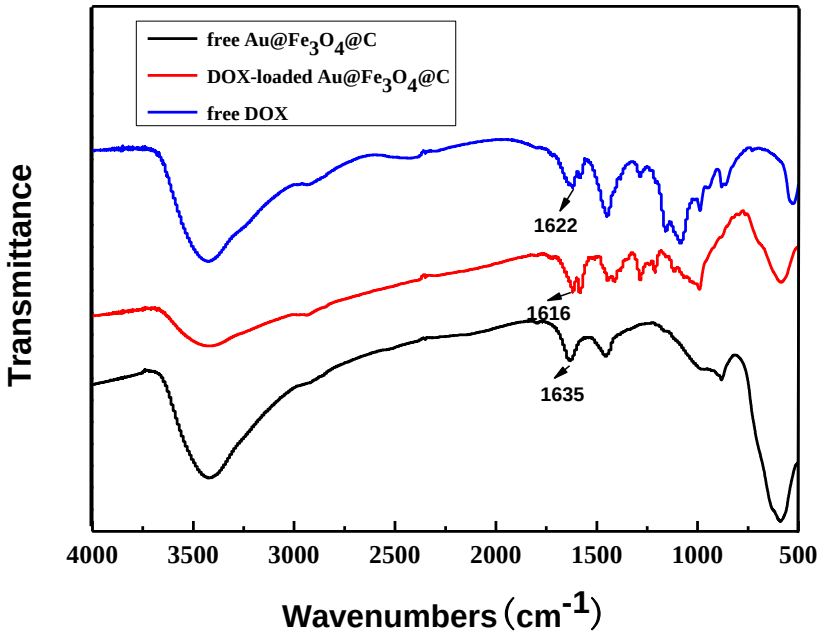
2、Rough evaluation of the weight and drug loading content per nanoparticle

According to the size of the Au@Fe_3O_4@C described in TEM image (140 nm)and the diameter of Au@SiO_2 nanoparticle (about 90 nm), the loading content 1237 mg/g as

well as the densities of Fe_3O_4 (5.18 g/cm^3) and Au (19.3 g/cm^3) from which we can roughly deduce the volumes of Au and Fe_3O_4 to be 1.77×10^{-18} cm^3 and 1.05×10^{-15} cm^3 respectively and By taking these rough dates into consideration, we evaluated that the weight of per particle was about 5.44×10^{-15}g and approximately 6.74×10^{-12} mg DOX was loaded in a single nanoparticle. It was note that during the evaluation, we ignored the weight of carbon for ammonia water corrosion making the carbon much thinner as mentioned above.

3、Analysis of FTIR spectrum for DOX loading mechanism of Au@Fe3O4@C nanoparticles.

The IR absorption band at 1635 cm^{-1} was due to the stretching vibration of carboxyl group on the surface of Au @Fe_3O_4@C nanoparticles. The band near 1622 cm^{-1} belongs to amide I, peak of free DOX red shifts to 1616 cm^{-1} compared with the spectrum of DOX-Au@Fe3O4@C demonstrating the formation of weakly non-covalent hydrogen bonding between the amide group (DOX) and carboxyl group (Au@Fe3O4@C nanoparticles)[1,2]. And electrostatic force between the positively charged DOX and the negatively charged Au@Fe_3O_4@C spheres was suggested as another mechanism for high DOX loading capacity.[3.4]

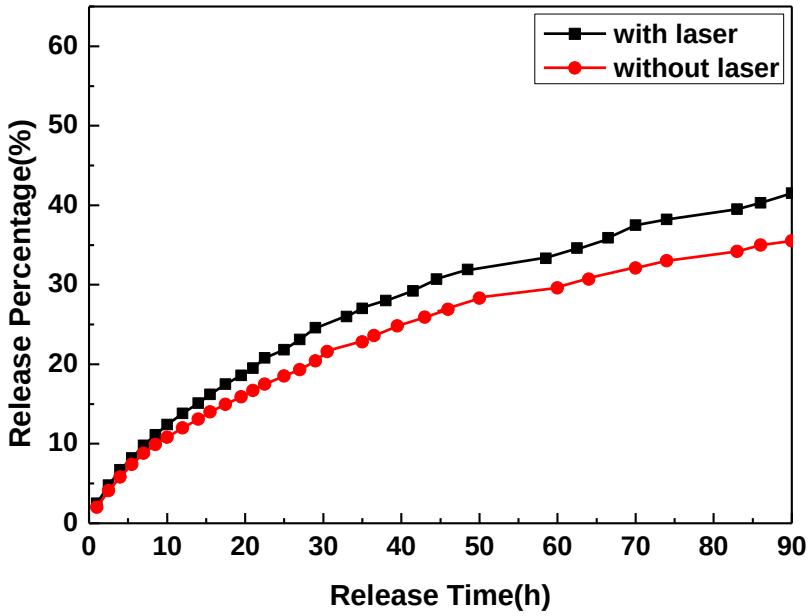


S1. FTIR spectrum of free DOX, free Au@Fe_3O_4@C and DOX- Au@Fe_3O_4@C nanoparticles

4、Controlled release of DOX from hollow Fe_3O_4@C nanoparticles with /without NIR-laser irradiation *in vitro*.

To validate whether the increasement of drug release percentage described in the main text was due to Au nanoparticles encapsulated in the Au@Fe_3O_4@C nanospheres, we introduced DOX- Fe_3O_4@C system for contrast and the DOX content loaded on hollow Fe_3O_4@C was the same as that loaded on Au@Fe_3O_4@C nanospheres. The drug loaded hollow particles were divided into two groups for examining the release rate with and without NIR-laser irradiation(808 nm, 2W cm^{-2})

as that depicted in the main text respectively. DOX release profiles shown in S2 indicated that the difference in cumulative release percentage between NIR-triggered group (red, 41.5%) and no NIR-triggered one (black, 35.5%) was only about 6% after 90 h while it was about 20% as shown in Fig 6 in the main text when compared the drug release from Au@Fe_3O_4@C nanoparticles with and without NIR-laser. We ensured that Au nanoparticles encapsulated in the Au@Fe_3O_4@C nanospheres can facilitate drug release. It was worth noting that the DOX release from hollow Fe_3O_4@C and from Au@Fe_3O_4@C nanoparticles under magnetic stirring at a constant rate at 37 °C were quite similar.



S2. Release profiles of DOX-Fe_3O_4@C nanoparticles with (black) and without (red) laser irradiation for 90h

Reference:

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