## **Supporting Information for**

Controllable synthesis of tetrapod gold nanocrystals with precisely tunable near-infrared plasmon resonance towards high efficient surface enhanced Raman spectroscopy bioimaging

Jing Cai,<sup>ab</sup> Vijay Raghavan,<sup>b</sup> Yu Jie Bai,<sup>c</sup> Ming Hui Zhou,<sup>d</sup> Xiao Li Liu,<sup>a</sup> Chun Yan Liao,<sup>d</sup> Pei Ma,<sup>a</sup> Lei

Shi,<sup>c</sup> Peter Dockery,<sup>e</sup> Ivan Keogh,<sup>f</sup> Hai Ming Fan, \*ab and Malini Olivo<sup>bg</sup>

<sup>a</sup>School of Chemical Engineering, Northwest University, Xi'an 710069, P. R. China

<sup>b</sup>School of Physics, National University of Ireland, Galway, Ireland

<sup>c</sup>Department of Physics, Fudan University, Shanghai 200433, P. R. China

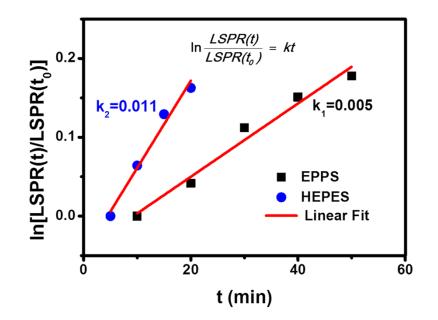
<sup>d</sup>Department of Physics, Northwest University, Xi'an 710069, P. R. China

<sup>e</sup>Department of Anatomy, National University of Ireland, Galway, Ireland

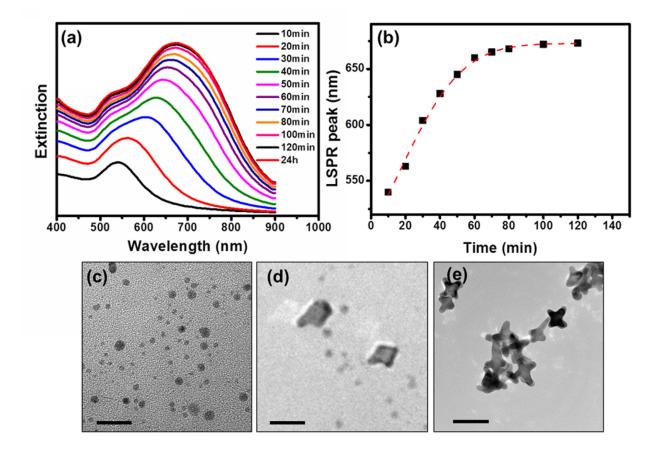
<sup>f</sup>Department of Surgery, National University of Ireland, Galway, Ireland

<sup>g</sup>Singapore Bioimaging Consortium, Agency for Science Technology and Research, Singapore 138667, Singapore

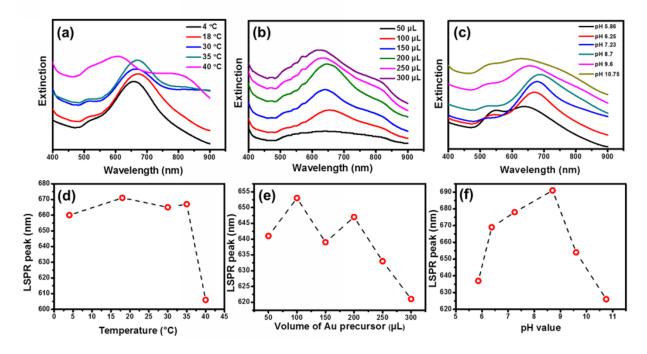
\* Corresponding author: Prof. Dr. Hai Ming Fan: <a href="mailto:fanhm@nwu.edu.cn">fanhm@nwu.edu.cn</a>;



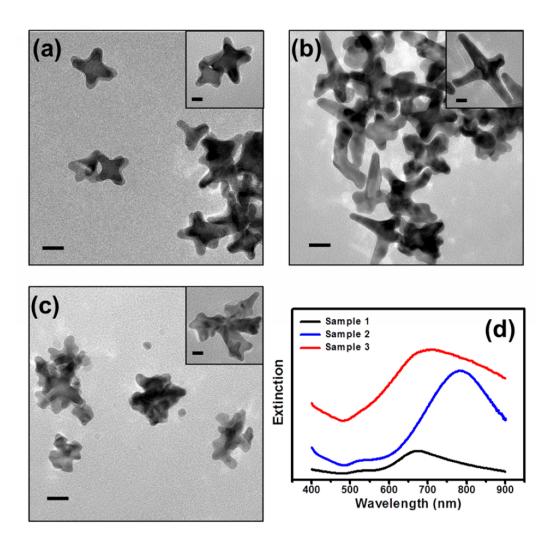
**Fig. S1.** The kinetics plots of tetrapod Au nanocrystals growth with different reducing agents, EPPS and HEPES. The two growth kinetics models both follow pseudo-first order reaction as shown in equation:  $ln[x(t)/x(t_0)]=kt$ , where k is the apparent rate constant (min<sup>-1</sup>), x(t) and x(t\_0) are LSPR peak value at time (t) and (t\_0). t\_0 is 10 min for EPPS and 5 min for HEPES.



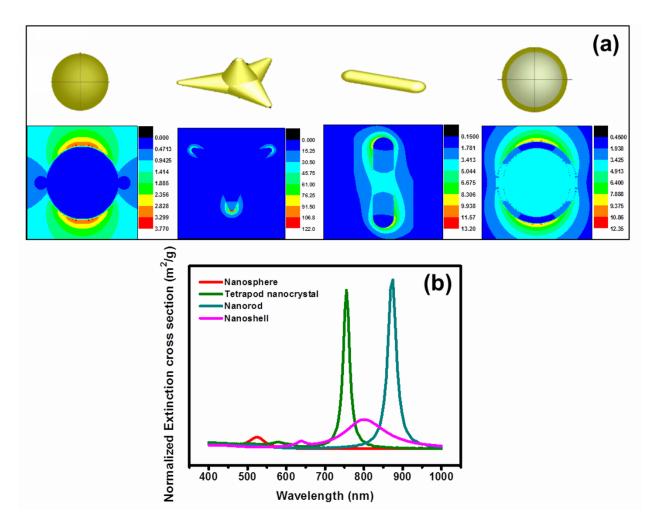
**Fig. S2.** (a) Extinction spectra of tetrapod Au nanocrystals in reaction solution recoded as a function of time. (b) The LSPR peaks of the Au nanocrystals as a function of time. Representative TEM images of products formed after (c) 10, (d) 30 and (e) 60 min of reaction. The scale bars are 20 nm, 20 nm and 50 nm.



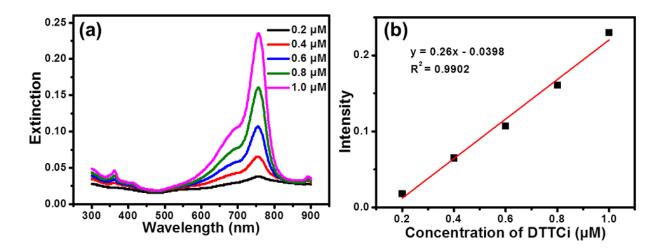
**Fig. S3.** Extinction spectra of tetrapod Au nanocrystals synthesized with varied temperature (a), Au precursor volume (b) and pH value (c). The LSPR peaks of the tetrapod Au nanocrystals as a function of temperature (d), Au precursor volume (e) and pH value (f).



**Fig. S4.** TEM images of (a) tetrapod Au<sub>670</sub> nanocrystals seeds (Sample 1), (b) tetrapod Au nanocrystals synthesized by gradually adding Au precursors up to 300  $\mu$ L (Sample 2) and (c) Au nanoparticles synthesized by immediately adding 300  $\mu$ L Au precursors (Sample 3). The scale bars are 20 nm in (a-c) and 10 nm in inset of (a-c). (d) Extinction spectra of Sample 1-3.



**Fig. S5.** (a) FDTD simulated electromagnetic field distributions of different gold nanostructures, including nanosphere (25.8 nm diameter), tetrapod nanocrystal (7 nm core, 28 nm branches), nanorod (14 nm width, 4.5 aspect ratio), nanoshell (130 nm diameter, 110 nm silica core), from left to right. (b) Normalized simulated extinction spectra of different gold nanostructures.



**Fig. S6.** (a) Extinction spectra of DTTCi with different concentration in DMSO. (b) The Beer's law plot for DTTCi (characteristic peak at 756 nm).