

**Supporting Information for Publication**

**Ultrasensitive Detection of Thyrotropin-  
Releasing Hormone Based on Azo Coupling  
and Surface-Enhanced Resonance Raman  
Spectroscopy**

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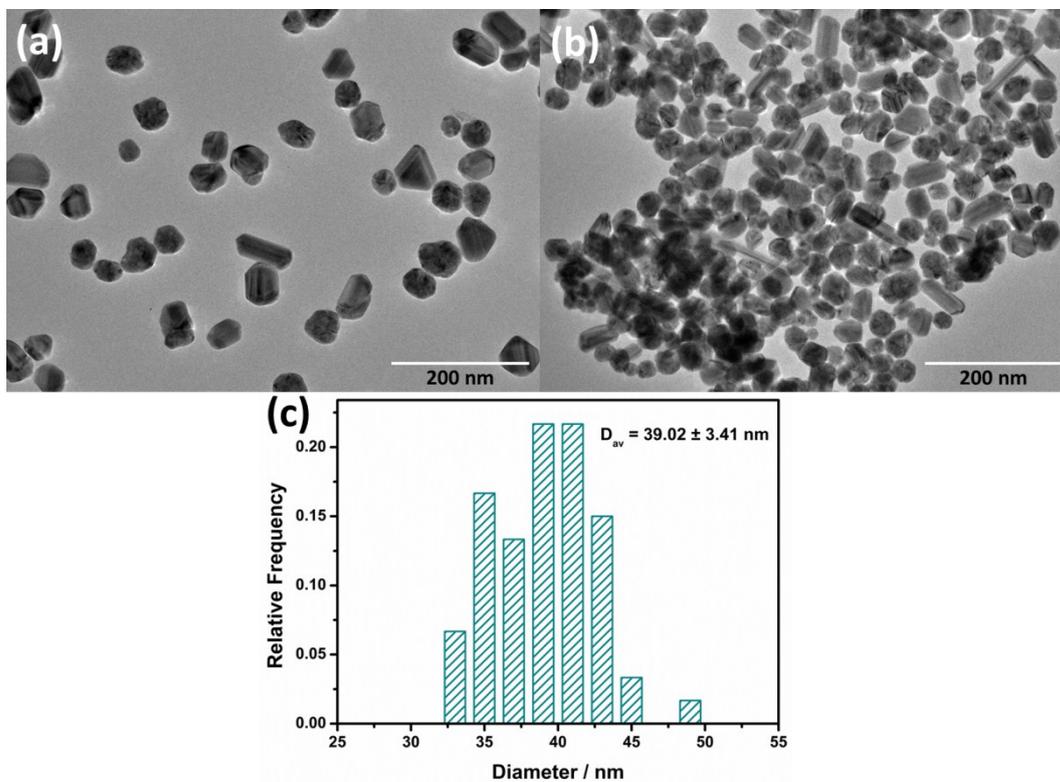
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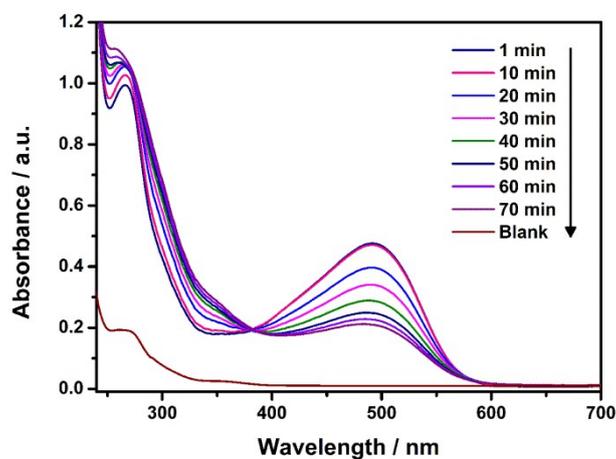
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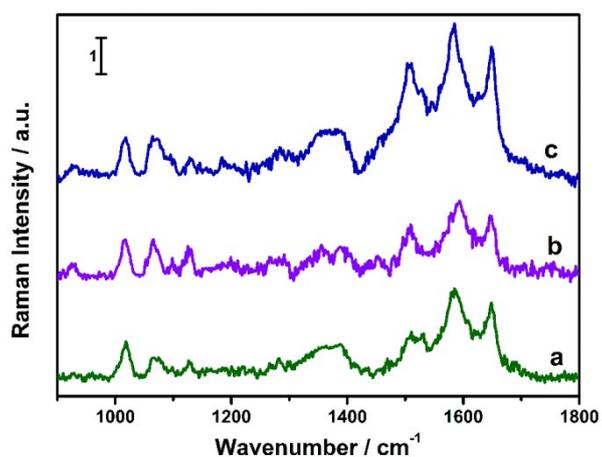


**SI-Figure 1.** HRTEM images of 250  $\mu\text{L}$  colloidal Ag nanoparticles (a) before; (b) after the addition of 50  $\mu\text{L}$  TRH-derived azo solution (scale bar: 200 nm) and (c) size distribution of colloid Ag nanoparticles ( $D_{av}$  is the average particle size).

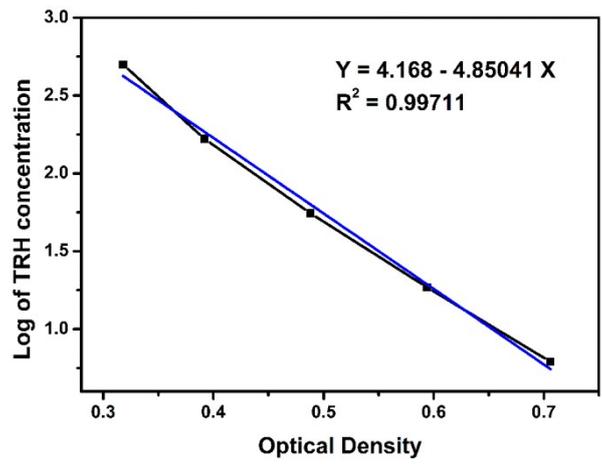
The size measurement and distribution of Ag nanoparticles were performed by software of Nano Measurer. The number of nanoparticles taking into account was 60. Then the diameters of 60 particles were exported into Origin 8.5 to plot the histogram of size distribution and calculate the average diameter ( $39.02 \pm 3.41 \text{ nm}$ ).



**SI-Figure 2.** Time-dependent UV-vis absorption spectra of the azo compound derived from TRH at a concentration of 1 mg/mL during the progress of the coupling reaction in 70 minutes.



**SI-Figure 3.** SERRS spectra of azo dye derived from (a) hyperthyroid sample; (b) euthyroid sample; (c) euthyroid sample with addition of TRH. Excitation wavelength: 532 nm.



**SI-Figure 4.** Standard Curve of ELISA Kit for TRH.