

Electronic Supplementary Information

Experimental

1. Chemicals

Chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$), sodium borohydride (NaBH_4), cetyltrimethylammonium bromide (CTAB), L-ascorbic acid (AA) and silver nitrate (AgNO_3) were purchased from Sinopharm Chemical Reagent Co. Ltd. EDC and NHS were received from Aldrich and Fluka respectively. Thiol carboxylic polyethylene glycol ($M_w \sim 459$), thiol polyethylene glycol ($M_w \sim 2000$) were obtained from Nanocs Co. Ltd. Streptavidin ($M_w \sim 60$ KD) was purchased from Sigma Aldrich. All aqueous solution were prepared using Ultrapure water ($18 \text{ M}\Omega \cdot \text{cm}^{-1}$).

2. Experiments

2.1. Synthesis of Au nanoparticles (AuNSs)

AuNSs were synthesized according to the classic method reported by Frens [1]. Briefly, 5 ml of 1% sodium citrate was quickly added to 95 ml of 0.01% boiling tetrachloroauric acid solution. The mixture was rapidly stirred until the solution changed to deep wine red color, indicating formation of gold nanosphere suspension and continued to stir for 15 min.

2.2. Synthesis of Au nanorods (AuNRs)

AuNRs were synthesized by a seed-mediated method that had been reported by Murphy [2]. First, Au seeds were prepared by adding NaBH_4 (0.6 mL, 0.01 M) to a mixture of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and cetyltrimethylammonium bromide (CTAB, 7.5 mL, 0.1 M). Then, 0.2 mL of seed solution was added to the growth solution containing CTAB (45 mL, 0.1 M), $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (2 mL, 0.01 M), AgNO_3 (0.35 mL, 0.01M) and ascorbic acid (0.32 L, 0.1 M). Finally, AuNRs were left undisturbed for at least 3 h.

2.3. Preparation of side-by-side AuNSs-AuNRs assemblies

For the AuNRs, the pH of AuNRs solution was firstly adjusted to ~ 8.7 with 0.1 M

NaOH. Then 400 μL of this solution was added to streptavidin solution (240 μL , 100 nM) in dropwise, followed by mixing for 10 min at 25°C. Finally the AuNRs-streptavidin were centrifuged twice (7000 r, 15 min) and resuspended in 0.01M PBS buffer (pH=7.2~7.4) for further use [3]. As for the AuNSs, first, bifunctional PEG (SH-PEG-COOH, 0.55 nmol) was added to 1 mL AuNSs solution followed by adding SH-PEG (1.8 nmol) and shaking for 40 min. The solution underwent one centrifugation and resuspended in MES buffer (0.01 M, pH=6.2) [4]. Second, freshly prepared EDC (0.6 μmol) and Biotin-PEO-Amine (0.06 μmol) was added and reacted for 4 h before two centrifugations and redispersed in 0.01 M PBS buffer. Finally, functionalized AuNSs and AuNRs were mixed together.

2.4. Preparation of end-to-end AuNSs-AuNRs assemblies

For AuNRs, bifunctional PEG (SH-PEG-COOH, 1 μM) was injected to freshly prepared AuNRs solution and stirred for 20 min followed by one centrifugation. After that EDC (0.09 μmol) and Biotin-PEO-Amine (0.01 μmol) were both added and shaken 4 h followed by centrifugations and redispersed in 0.01 M PBS buffer. For AuNSs, PEGylated AuNSs were prepared the same as that practiced in AuNSs-biotin conjugate. Differently, stock solution of EDC (0.4 M) and NHS (0.1 M) was injected afterwards and stirred for 30 min followed by two centrifugations. Then Streptavidin was added to the activated AuNSs mixing for 3 h and resuspended in 0.01 M PBS buffer. Finally, the functionalized AuNSs and AuNRs were mixed together for further analysis.

3. Instruments

The zeta potential measurement was performed on a Malvern Zetasizer ZEN3600 instrument. Transmission electron microscopy (TEM) images were obtained using Tecnai F30 operating at 300 kV. The UV-vis absorption data were collected on a DU 800 UV-vis spectrophotometer.

References

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- 2 Sau T K and Murphy C J. 2004 *Langmuir* 20 6414
- 3 Li X, Qian J and He S L. 2008 *Nanotechnology* 19 355501
- 4 Qian X M, Peng X H, Ansari D O, Yin-Goen Q, Chen G Z, Shin D M, Yang L, Young A N, Wang M D and Nie S M. 2008 *Nature Biotechnol.* 26 83