Supplementary Information (SI) for Journal of Materials Chemistry B.

Supporting Information

Galactosylated Silver Nanoparticles as a Biocompatible Intrinsic SERS Probe for Bladder Cancer Imaging and Ex Vivo Tumor Detection

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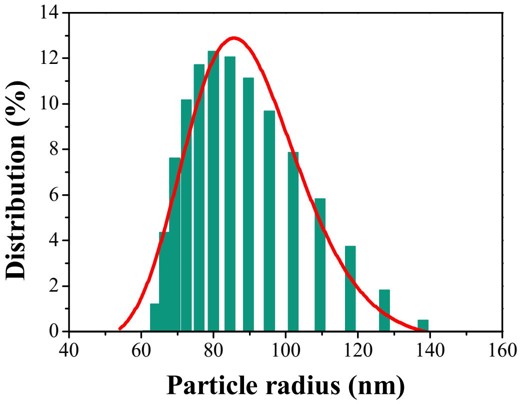

Fig. S1 Particle size distribution of Ag@PGlyco-PSMA NPs by a DLS measurement.

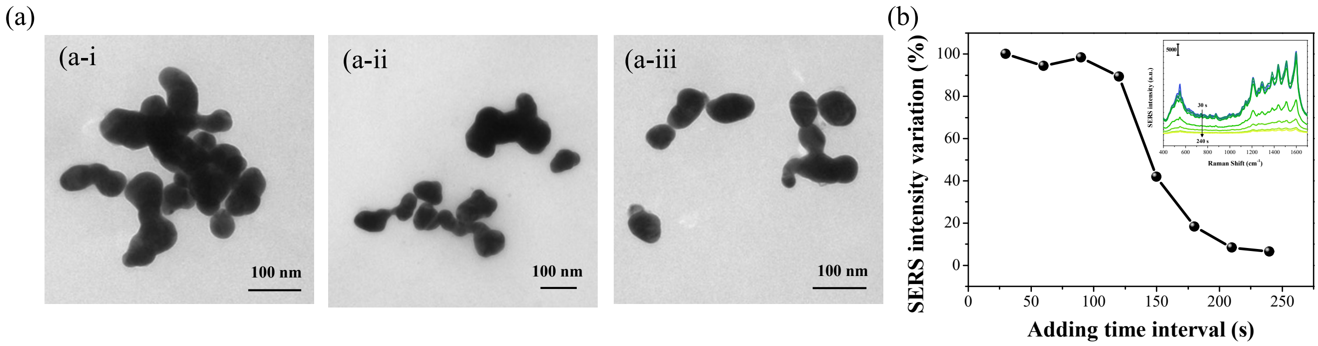

Fig. S2 a) TEM image of Ag@PGlyco-PSMA synthesized by adding PSMA at different times of a-i) 90 s, a-ii) 150 s and a-iii) 210 s. (b) SERS intensity variation of Ag@PGlyco-PSMA synthesized by adding PSMA at 30, 60, 90, 120, 150, 180, 210, and 240 seconds. Inset in (b): SERS intensity record.

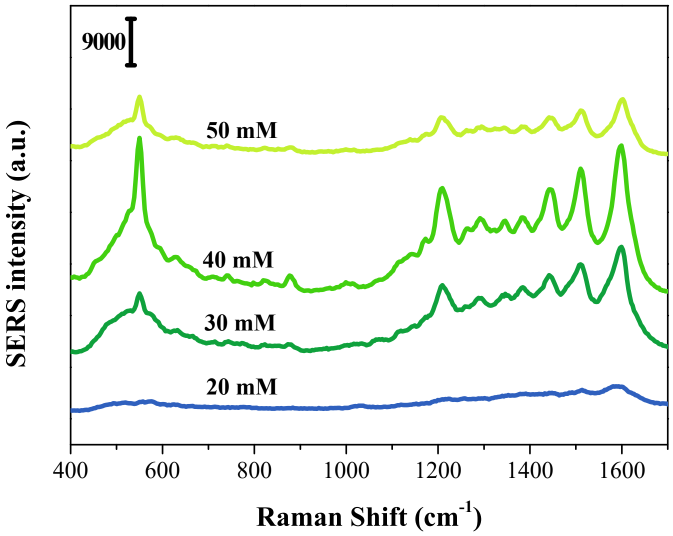

Fig. S3 SERS spectrum of Ag@PGlyco-PSMA synthesized by different concentration (20-50 mM) of $NaBH_4$.

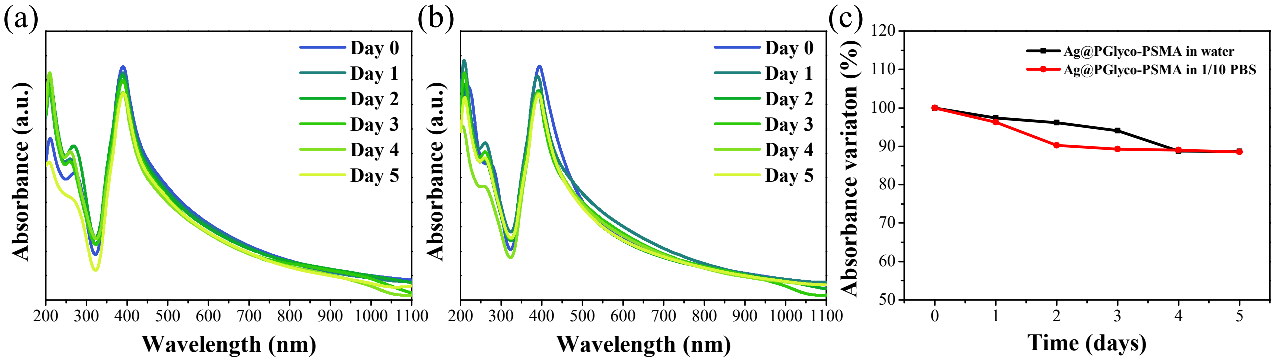

Fig. S4 Absorption spectrum of Ag@PGlyco-PSMA NPs stored in a) D.I. water and b) 1/10 PBS for 5 days and c) corresponding absorbance variation record.

The analytical enhancement factor (AEF), as expressed in the equation, serves as a convenient method to compare the SERS amplification effect of enhanced substrates on analytes.

$$AEF = \frac{I_{SERS}/C_{SERS}}{I_{Raman}/C_{Raman}}$$

I_{SERS} and I_{Raman} are the SERS intensity of analytes enhanced by substates and the Raman intensity of analytes in solutions. C_{SERS} and C_{Raman} are concentrations of analyte in SERS and Raman measurement conditions.

To calculate the AEF of Ag@PGlyco-PSMA NPs, the 15 $\mathrm{ppm}_{[\mathrm{Ag}]}$ of Ag@PGlyco-PSMA NPs were mixed with 8×10^{-8} M (C_{SERS}) MG for measurement. In this condition, the SERS signal was 520 ($\mathrm{I}_{\mathrm{SERS}}$).

Then the 8×10^{-4} M (C_{Raman}) MG was measured for normal Raman signal. In this condition, the Raman signal intensity of MG was 304 (I_{Raman}).

The AEF value of Ag@PGlyco-PSMA NPs is calculated as $1.71*10^{4}$.

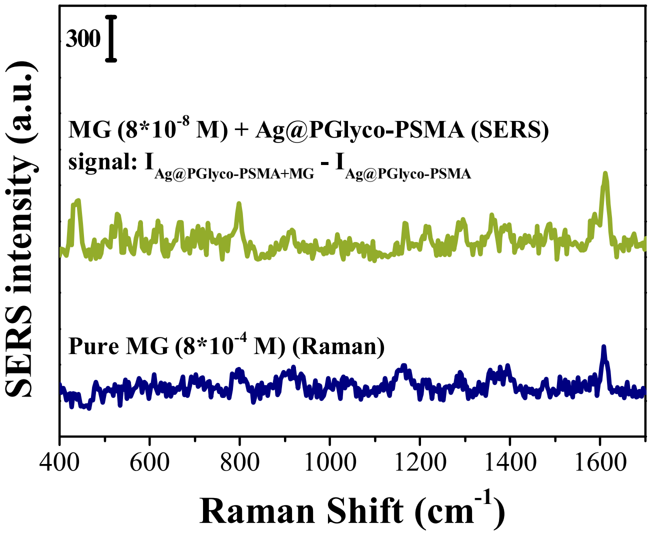

Fig. S5 SERS and Raman spectra on MG molecules using portable 671 nm Raman system.

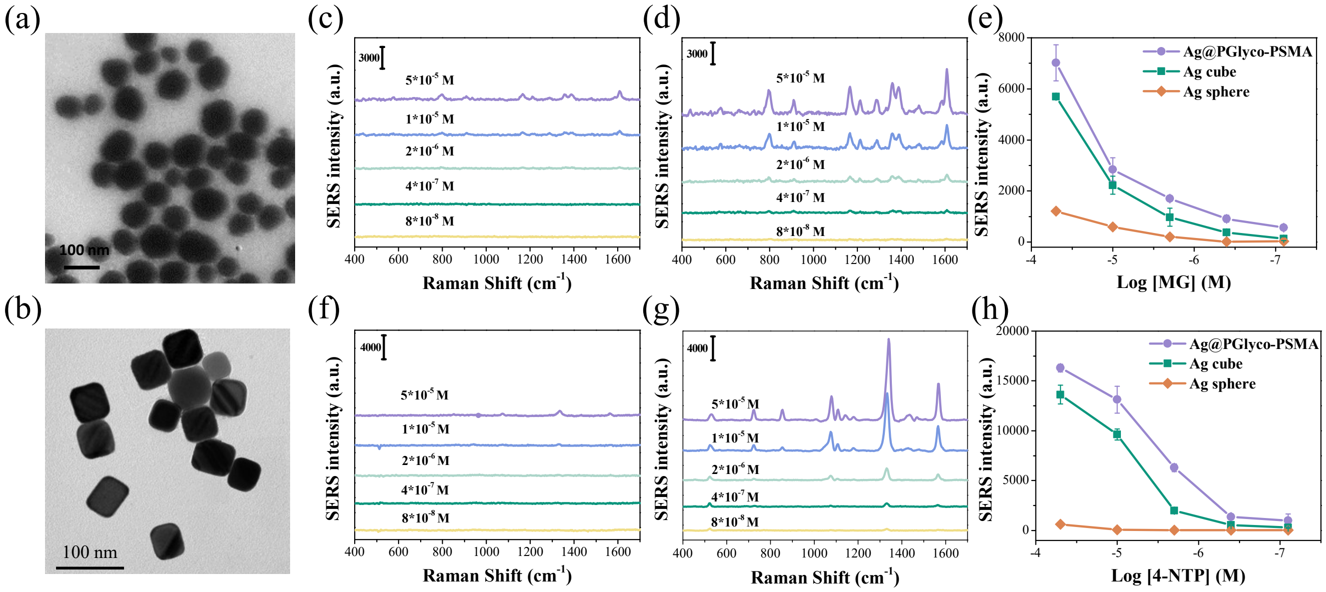

Fig. S6 TEM images of a) Ag nanosphere and b) Ag nanocube. SERS spectra measurement of c) Ag nanosphere and d) Ag nanocube mixed with different concentration of MG and e) SERS intensity record at 1608 cm^{-1}. SERS spectra measurement of f) Ag nanosphere and g) Ag nanocube mixed with different concentration of 4-NTP for 1 hr and h) SERS intensity record at 1339 cm^{-1}.

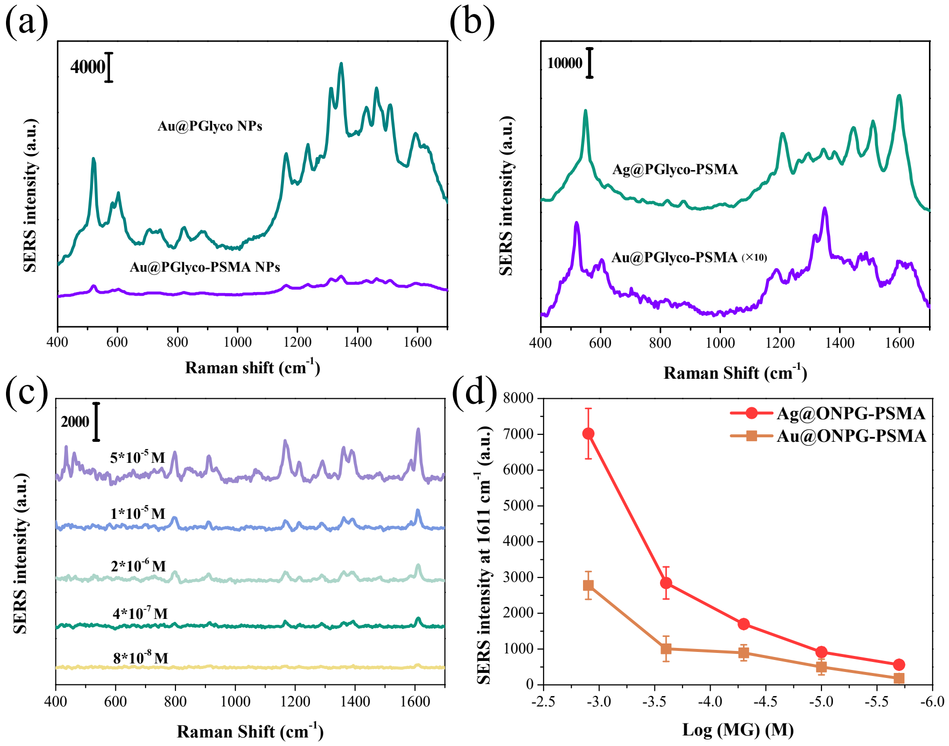

Fig. S7 a) SERS spectrum of Au@PGlyco and Au@PGlyco-PSMA NPs. b) SERS spectrum of Ag@PGlyco-PSMA and Au@PGlyco-PSMA nanoparticles. The SERS spectra of Au@PGlyco-PSMA NPs is increased by a factor of 10. c) SERS spectrum measurement and d) SERS intensity record of Au@PGlyco-PSMA NPs mixed with different concentration of MG.

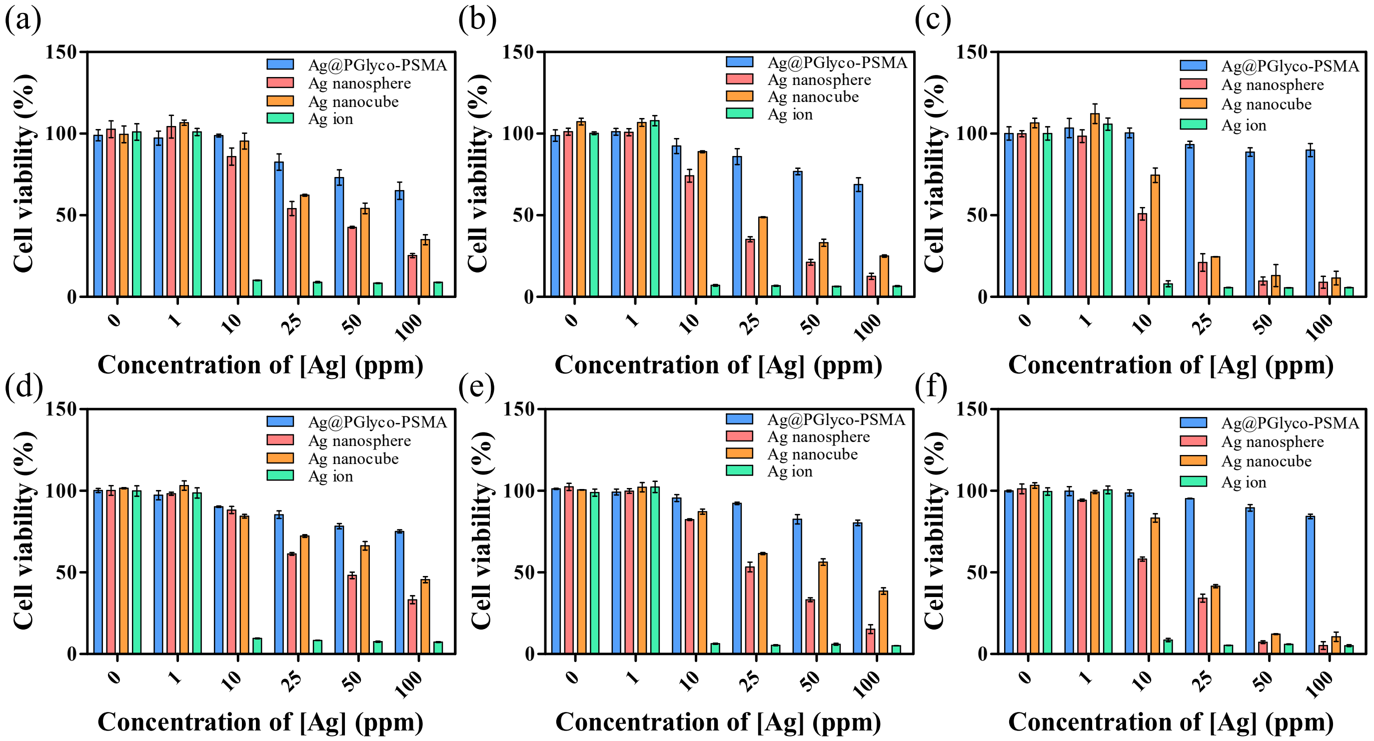

Fig. S8 MTT assays of (a-c) T24 cells (n=4) and (d-f) SV-HUC-1 (n=4) cultured with Ag@PGlyco-PSMA NPs, Ag nanospheres, Ag nanocubes and Ag ions for a,d) 24 hours, b,e) 48 hours and c,f) 72 hours.

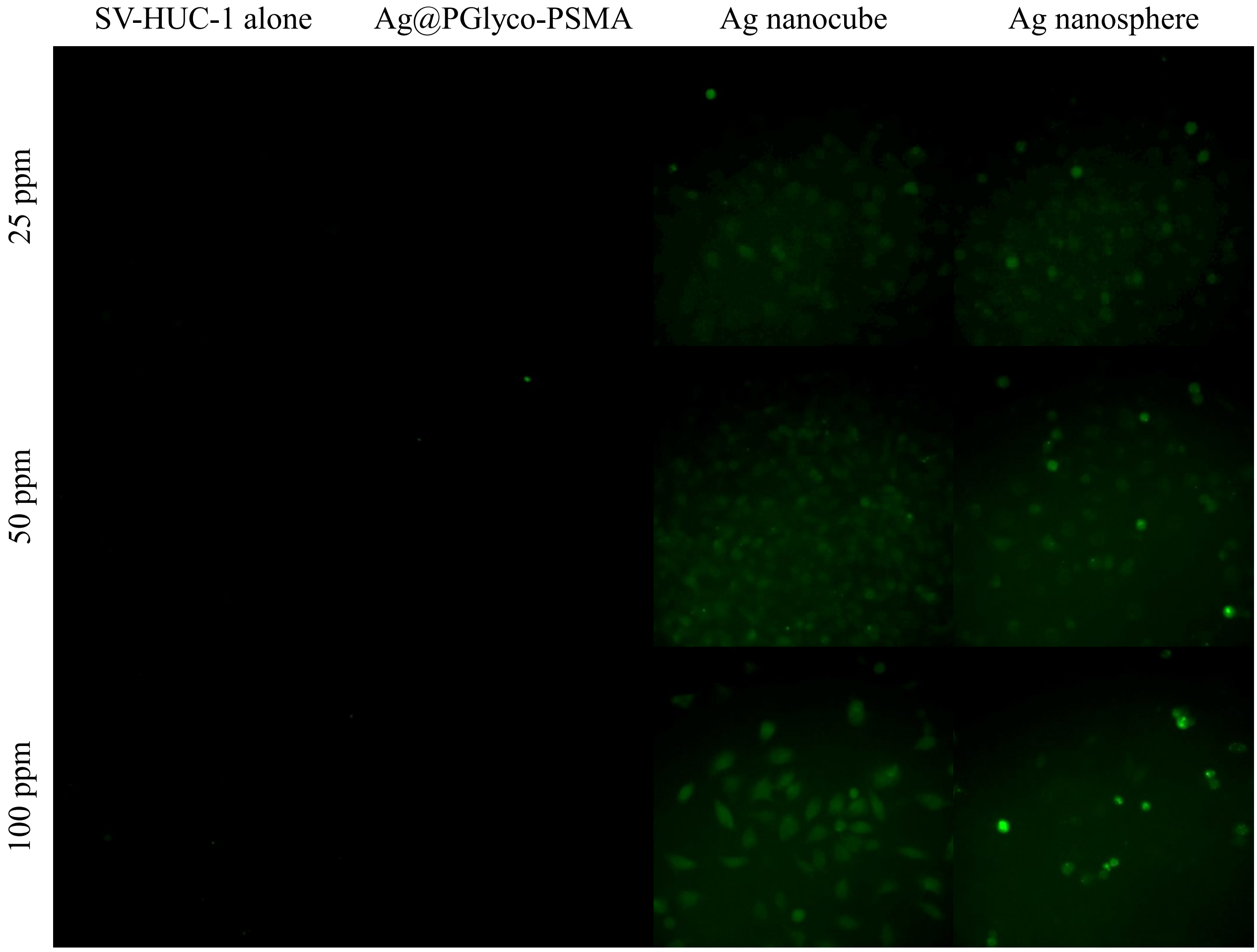

Fig. S9 DCFH-DA staining of SV-HUC-1 cells cultured with 25, 50, and 100 $\mathrm{ppm}_{[Ag]}$ Ag@PGlyco-PSMA NPs, Ag nanospheres, and Ag nanocubes for 24 hours.

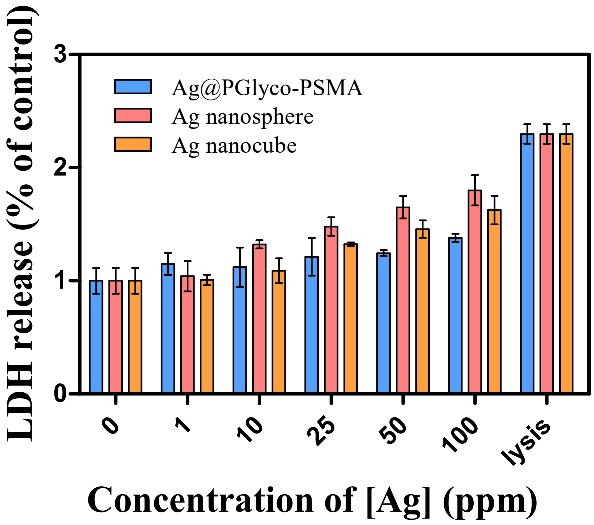

Fig. S10 LDH assays of SV-HUC-1 cells cultured with Ag@PGlyco-PSMA NPs, Ag nanospheres and Ag nanocubes for 24 hours (n=4).

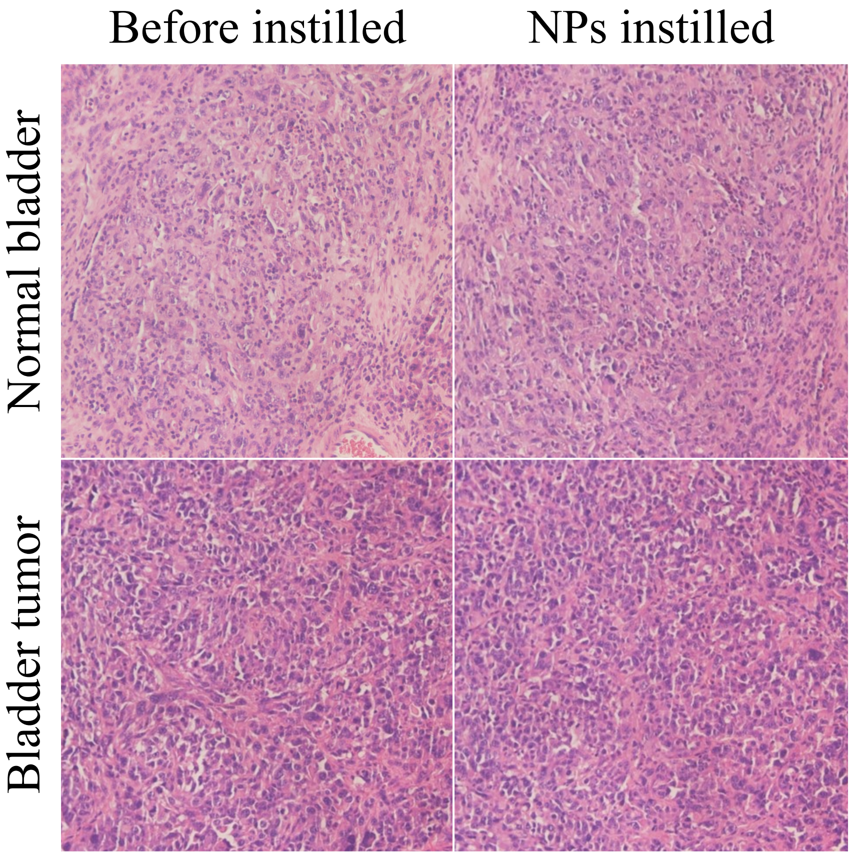

Fig. S11 H&E staining of mice bladder with/without tumor instilled with 250 $\text{ppm}_{[\text{Ag}]}$ Ag@PGlyco-PSMA NPs.

Table S1 SERS peak assignment of Ag@PGlyco-PSMA NPs

Raman Shift (cm^{-1})	Band assignment
876	C-C bending of quinoid ring
1145	C-H bending of Phenylhydrazine
1169	C-H bending of benzenoid and semiquinoid ring
1209	C-N stretching of quinoid
1258	C-N stretching of reduced amine-benzenic ring
1291	C-H bending of benzenoid
1323	C∼N+• stretching of semiquinone segments
1343	C∼N+• stretching vibrations
1383	C~N stretching of semiquinonoid (radical cations)
1441	C-C stretching of benzene ring (radical cations)
1482	C=N stretching in quinoid segments
1510	N-H bending of protonated amine (semiquinone radical cation)
1565	C-C stretching of quinoid ring
1596	C=C stretching of quinonoid ring C~C stretching of semiquinonoid ring
1620	C-C stretching of benzenoid ring C=O stretching of benzoquinone

Table S2 SERS peak assignment of malachite green (MG).

Raman Shift (cm^{-1})	Band assignment
797	C–H bending (out-of-plane) in phenyl rings
911	C–H bending (out-of-plane) in phenyl rings
1170	C–H bending (in-plane) in phenyl rings
1291	C–H bending (in-plane) in phenyl rings
1362	N–C stretching vibration
1394	C–C and C–H motions (in-plane)
1613	C–C stretching in phenyl rings

Table S3 SERS peak assignment of Rhodamine 6G (R6G).

Raman Shift (cm^{-1})	Band assignment
613	C−C bending (in-plane) in phenyl rings
772	C−H bending (out-of-plane) in phenyl rings
1125	C-H bending (in plane) xanthene/phenyl rings
1182	C−H bending (in-plane) in xanthene ring
1307	C-O-C in-plane bending in xanthene ring
1359	C−C stretching in xanthene ring
1507	C−C stretching in xanthene ring
1568	C-C stretching in phenyl ring
1648	C−C stretching in xanthene ring

Table S4 SERS peak assignment of 4-Nitrothiophenol.

Raman Shift (cm^{-1})	Band assignment
1074	C–H bending
1105	C–H bending
1180	C–H bending
1330	NO_2 symmetric stretching
1565	C–C stretching