

SUPPORTING INFORMATION

for

TiO₂ Core-Shell and Core-Dual-Shell Nanoparticles with Tunable Heterojunctions and Visible to Near-IR Extinctions

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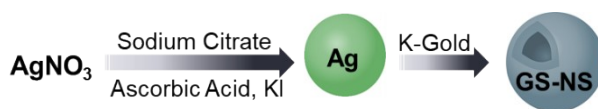
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MATERIALS AND METHODS

Scheme S1. Synthesis Route for Ag NPs and GS-NSs



Materials

Silver nitrate, potassium iodide, ascorbic acid, tetraethyl orthosilicate (TEOS), sodium stannate trihydrate, hydroxypropyl cellulose (HPC, MW \sim 100,000), titanium butoxide (TBOT), and commercial TiO_2 nanopowder (<25 nm particle size) were purchased from Sigma-Aldrich and used without further purification. Hydrogen tetrachloroaurate(III) hydrate (Strem), trisodium citrate (EM Science), and potassium carbonate (J. T. Baker) were purchased from the indicated suppliers and used without modification. Water was purified to a resistance of 18 $\text{M}\Omega\text{-cm}$ (Academic Milli-Q Water System, Millipore Corporation). All glassware and reaction vessels used during the experiments was cleaned twice in an aqua regia solution (3:1 HCl: HNO_3), rinsed with water and acetone, and then dried in the oven prior to each use. After repeated use, the glassware was also occasionally cleaned in a base bath followed by piranha solution (3:1 $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) and then again by aqua regia.

Characterization Methods

A LEO-1525 scanning electron microscope (SEM) was used to image the nanoparticles with an accelerating voltage of 15 kV. All SEM samples were prepared by depositing on a silicon wafer, pre-cleaned with water and ethanol. The nanoparticles were also imaged using a JEOL JEM-2010 transmission electron microscope (TEM) and JEM-2000 FX TEM operating at an accelerating voltage of 200 kV. All TEM samples were deposited on 300 mesh holey carbon-coated copper grids and dried overnight before analysis. Energy-dispersive X-ray spectroscopy (EDX) data were collected by an EDX attached to the JEM-2010 TEM instrument, providing the elemental composition of the particles. X-ray diffraction (XRD) patterns for the nanoparticles were obtained using a X'PERT PRO PANalytical X-ray diffractometer. A glass slide was cleaned with piranha and a concentrated sample of the nanoparticles in water was deposited onto the cleaned glass slides. The XRD data were

obtained using Cu K α radiation over the 2 θ range of 10°-80° over 15 minutes. A PHI 5700 X-ray photoelectron spectrometer X-ray photoelectron was used to collect spectroscopy (XPS) data. A monochromatic Al K α source with 10 mA emission current and 15kV emission bias was used as the measurement parameters. Concentrated samples of the nanoparticles in water were dropped on copper-tape-covered silicon wafers. Before sample preparation, the copper-tape-covered slides were washed with Milli-Q water followed by ethanol and dried with nitrogen gas. UV-Vis extinction spectra were obtained using a Cary 50 Scan UV-vis spectrometer. Particle concentration was measured using nanoparticle tracking analysis (NTA) with a Malvern Nanosight NS300 instrument. Photoluminescence measurements were carried out using a Perkin-Elmer LS55 fluorometer. Excitation wavelengths of 300 nm with cut-off filters at 390 nm, were used to ensure complete excitation and minimize background noise. All original nanoparticle solutions were diluted ~50-fold. PL intensities were normalized by the particle concentration and UV-vis extinction intensity of the exact samples used for PL measurements.

RESULTS AND DISCUSSION

SEM Images of Ag NPs and GS-NSs:

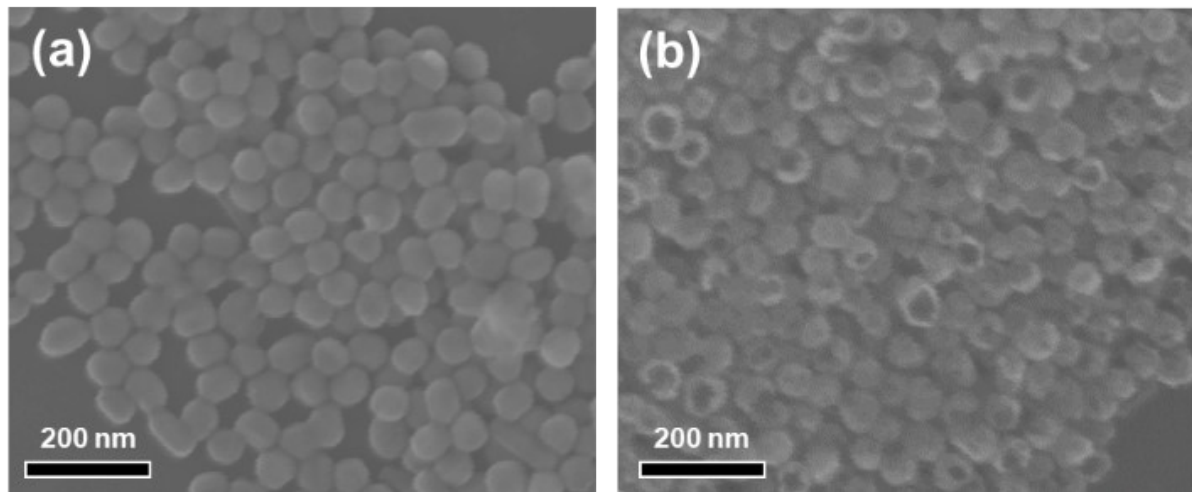


Figure S1. SEM images of (a) Ag NPs and (b) GS-NSs.

TEM Images of Nanoparticles:

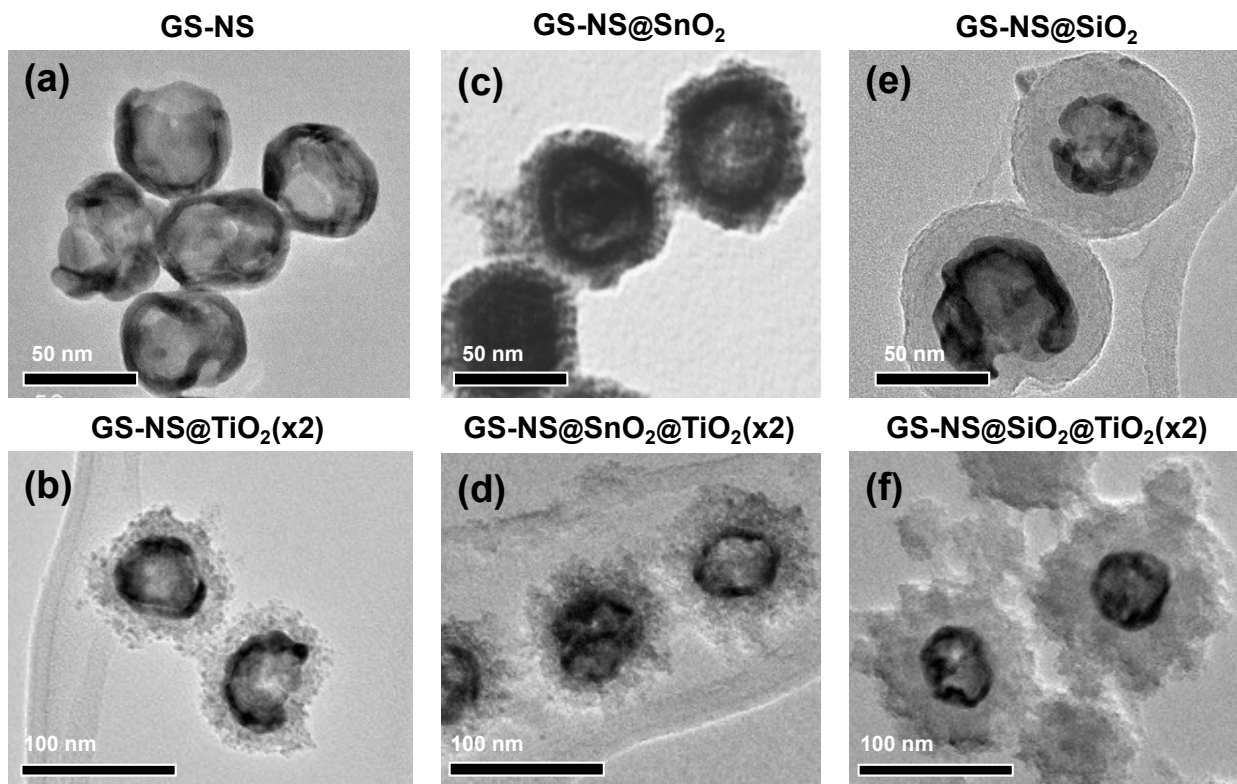


Figure S2. Additional TEM images of nanoparticles before and after 2 rounds of coating with TiO_2 ($\times 2$): (a,b) GS-NS and GS-NS@ $\text{TiO}_2(\times 2)$, (c,d) GS-NS@ SnO_2 and GS-NS@ SnO_2 @ $\text{TiO}_2(\times 2)$, and (e,f) GS-NS@ SiO_2 and GS-NS@ SiO_2 @ $\text{TiO}_2(\times 2)$, respectively.

SEM Image of Annealed TiO₂-Coated Nanoparticles:

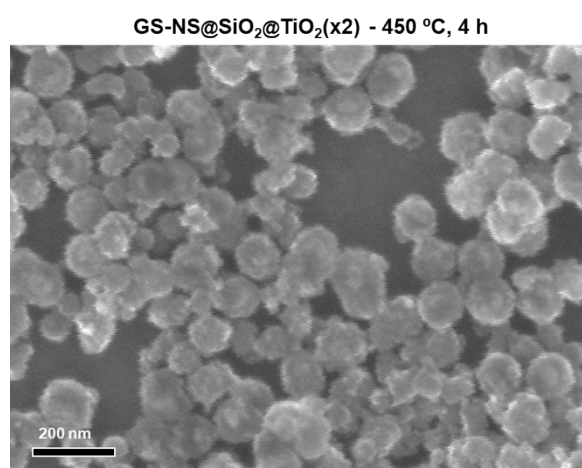


Figure S3. SEM image of the nanoparticles after annealing at 450 °C for 4 h, GS-NS@SiO₂@TiO₂(x2) shown as an example here.

SEM-EDX Spectra:

Table S1. EDX-Derived Relative Atomic Concentration of Ti, O, Ag, Au, Si, and Sn in the Various TiO₂-Coated Samples

Sample	Relative Atomic Concentration (%)					
	Ti	O	Ag	Au	Si	Sn
GS-NS@TiO ₂ (x2)	19	61	13	8	-	-
GS-NS@SnO ₂ @TiO ₂ (x2)	13	67	6	5	-	9
GS-NS@SiO ₂ @TiO ₂ (x2)	9	60	3	3	25	-

The SEM-EDX spectra show that all of the nanoparticles contain peaks characteristic for Ti L α , K α , and K β at 0.45 eV, 4.51 eV, and 4.93 eV, respectively. All of the nanoparticles also contain peaks characteristic for Au M, L α , and L β at 2.12 eV, 9.71 eV, and 11.58 eV, respectively. Since the GS-NS core is an alloy of gold and silver, the spectra also shows the peaks characteristic for Ag L α , K α , and K β at 2.98 eV, 22.16 eV, and 24.94 eV, respectively. Also, the oxygen K α peak at 0.525 eV was observed for all of the nanoparticles. The nanoparticles with a SnO₂ interlayer exhibit the peaks for Sn L α and K α at 3.44 eV and 25.27 eV, respectively. On the other hand, in the nanoparticles with a SiO₂ interlayer, the peak corresponding to Si K α at 1.74 eV can be observed.

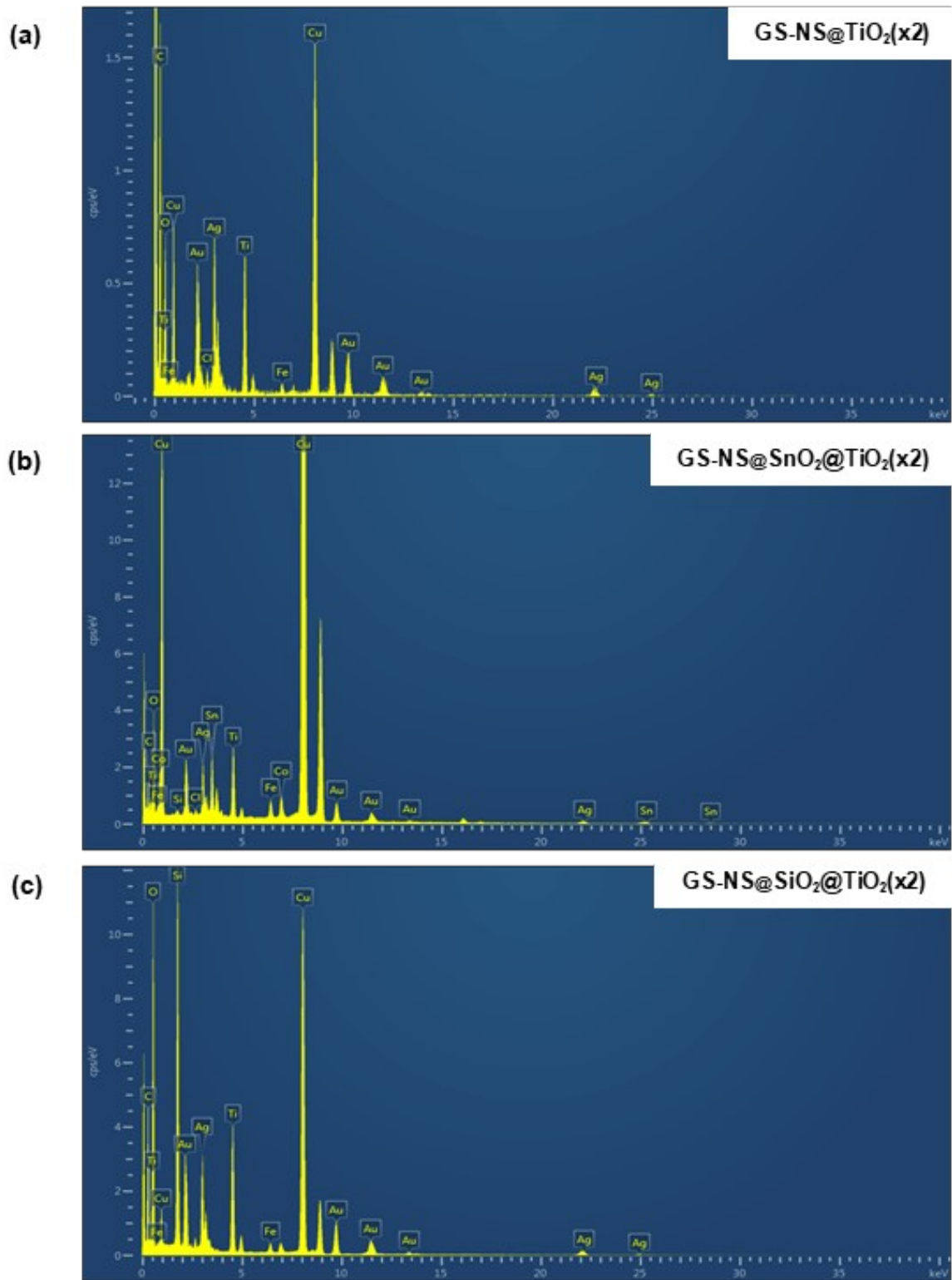


Figure S4. STEM-EDX spectra of the (a) GS-NS@TiO₂(x2), (b) GS-NS@SiO₂@TiO₂(x2), and (c) GS-NS@SnO₂@TiO₂(x2) nanoparticles.

STEM-EDX Line Spectra:

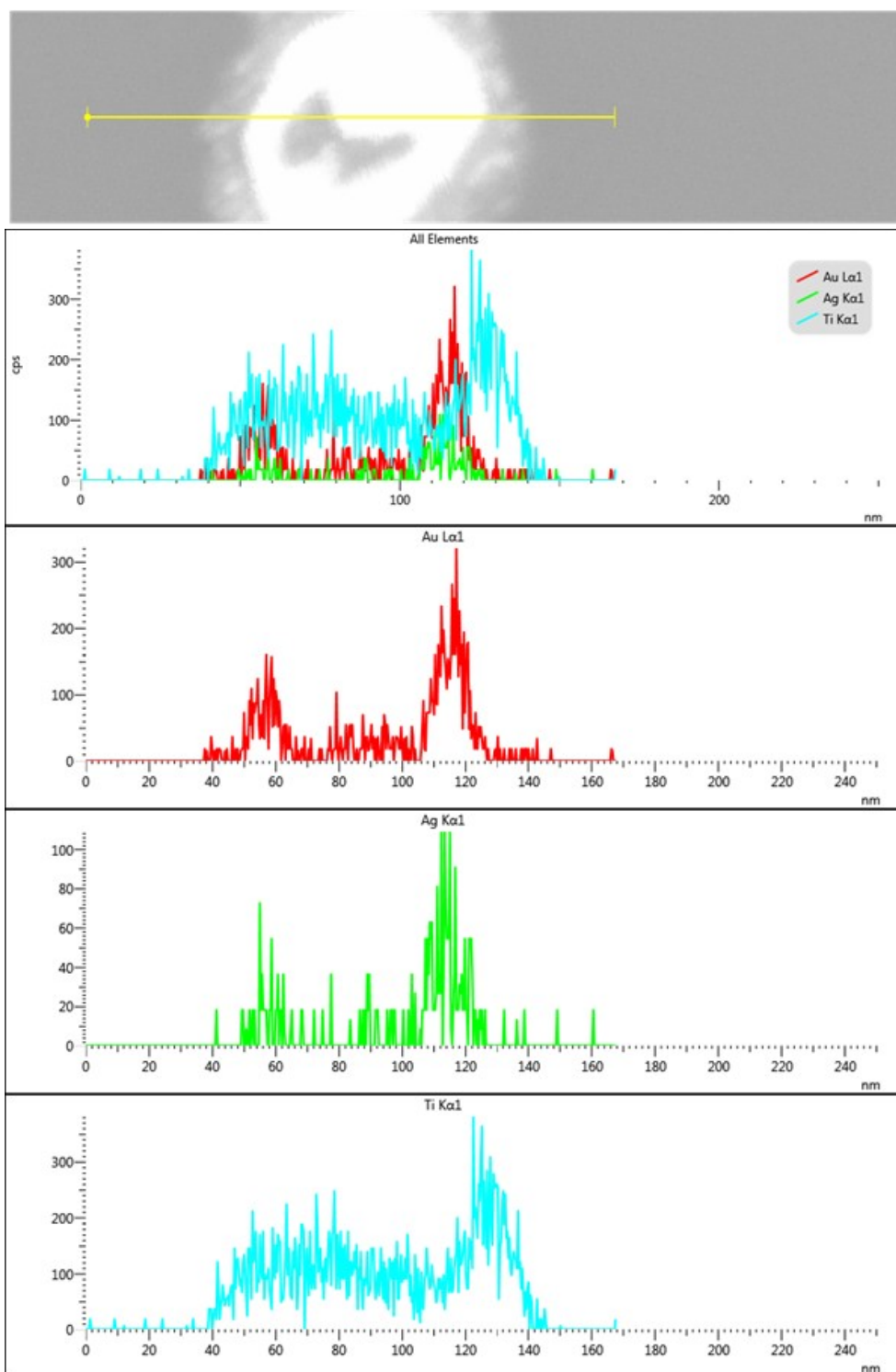


Figure S5. STEM image and corresponding EDX line spectra of GS-NS@TiO₂(×2) nanoparticles showing the distribution of the constituent elements in the nanoparticles.

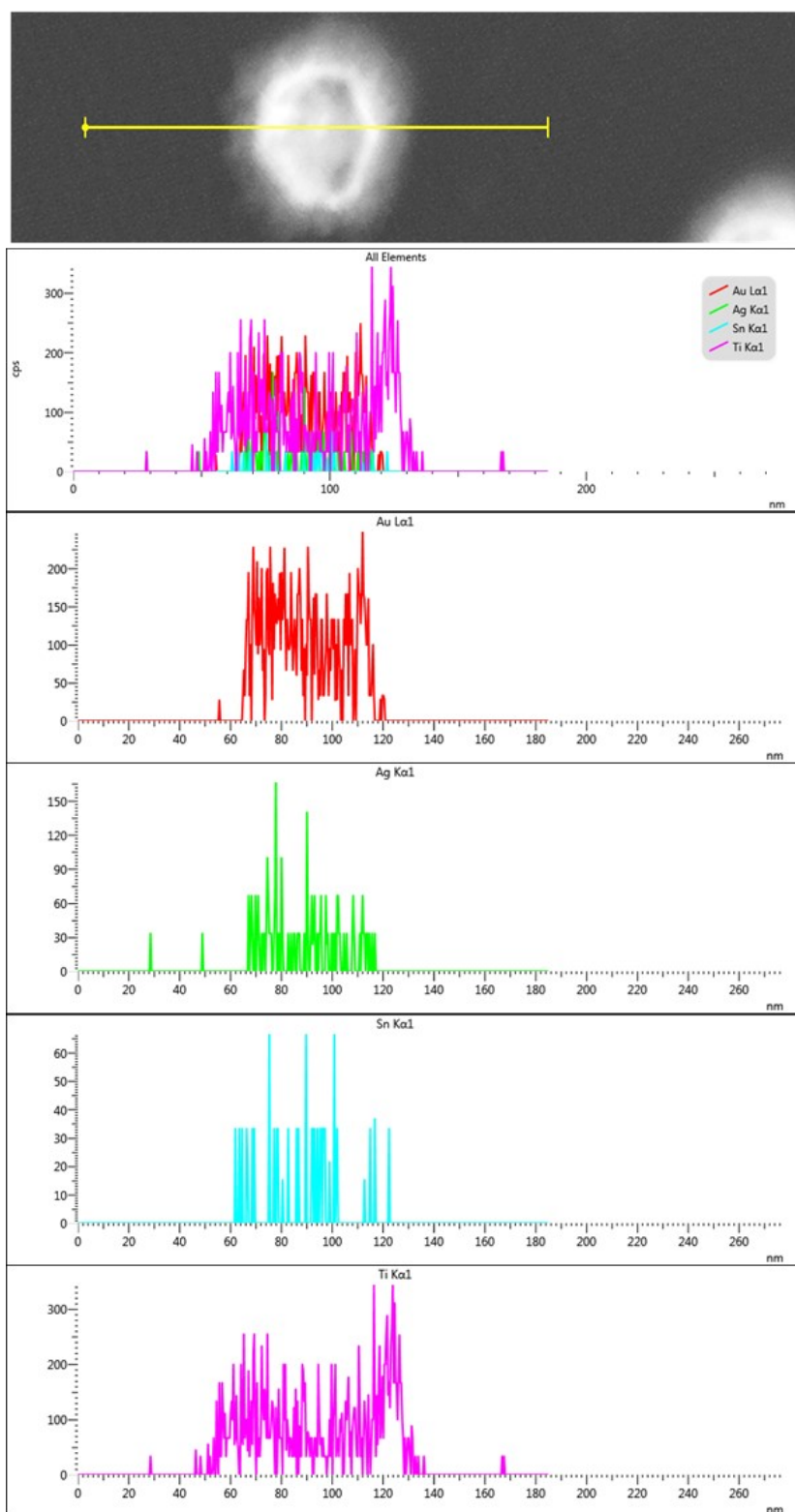


Figure S6. STEM image and corresponding EDX line spectra of GS-NS@SnO₂@TiO₂(×2) nanoparticles showing the distribution of the constituent elements in the nanoparticles.

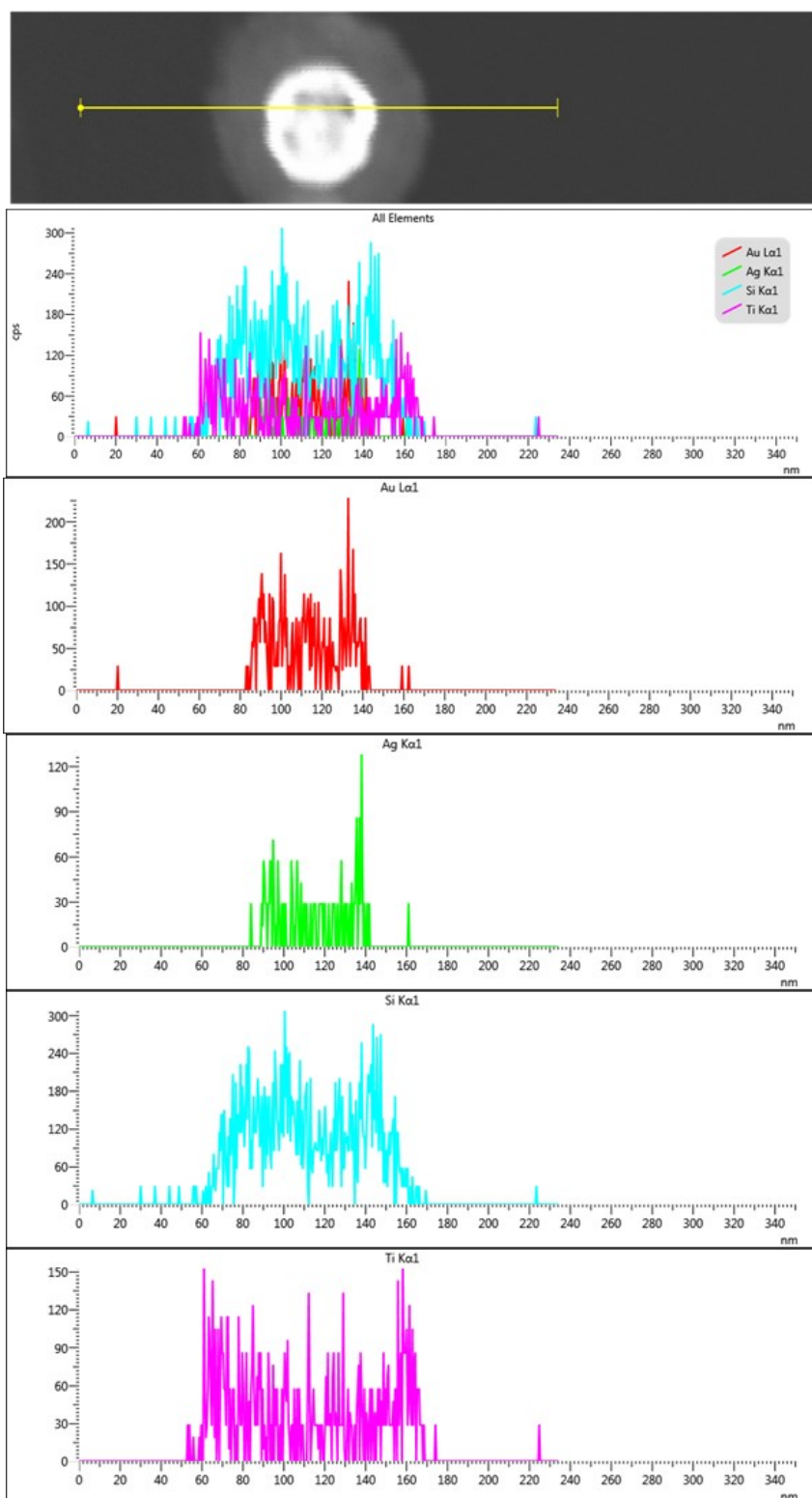


Figure S7. STEM image and corresponding EDX line spectra of GS-NS@SiO₂@TiO₂(x2) nanoparticles, showing the distribution of the constituent elements in the nanoparticles.