

Electronic Supplementary Information (ESI) available

Ni-Au core-shell nanowires: Synthesis, microstructures, biofunctionalization, and the toxicologic effects in pancreatic cancer cells

In Tak Jeon,^a Moon Kyu Cho,^a Jin Woo Cho,^b Boo Hyun An,^a Jun Hua Wu,^c Rosemarie Kringel,^d

Daniel S. Choi^{*d} and Young Keun Kim^{*a}

^a Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea.

^b Korea Electronics Technology Institute, Gyeonggi 463-816, Korea

^c Pioneer Research Center for Biomedical Nanocrystals, Korea University, Seoul 136-713, Korea

^d Department of Chemical and Materials Engineering, University of Idaho, Moscow, ID 83844, USA

1. Cost assessment for core-shell nanowire synthesis

In our experiment, Ni nanowires were prepared by electrodeposition with anodized aluminum oxide (AAO) nanotemplate (typically with a pore diameter of 200 nm, a pore length of 60 μm , and a pore density of 10^9 pores/ cm^2) at RT. It is generally accepted that the AAO template-assisted electrodeposition provides a simple, high throughput and cost effective solution for the fabrication of 1D nanostructures.¹ The following cost assessment is based on a 2 cm^2 AAO nanotemplate. A solution cost to grow Ni nanowires is \$5.1 (\$4.22/anodisc, \$0.57 for 300 nm thick Ag evaporation, and \$0.29 for Ni electrobath solution). Au coating was performed on the nanowires through an electroless-plating process in an aqueous solution (3 ml, \$137/L) of $\text{KAu}(\text{CN})_2$ and KCN at an elevated temperature (90 $^\circ\text{C}$) that is relatively lower temperature than CVD and the cost for Au shell formation on Ni nanowires (2×10^9) is \$0.41. The overall cost for Ni-Au core-shell nanowires excluding glassware cost is \$2.76/1 billion NWs.

2. Cross-sectional TEM sample preparation

Figure S1 presents the process for the transmission electron microscopy (TEM) sample preparation by cross-sectioning the Ni-Au core-shell nanowires using the focused ion beam (FIB) lift-out technique (FEI Quanta 3D FEG). First, an electron beam Pt stripe was deposited in a rectangular shape ($3 \times 1 \mu\text{m}$) over the freestanding Ni nanowire area on a Si wafer and a second ion Pt beam deposit was conducted to reduce possible damage of the nanowires from the first Pt deposition (the Pt stripe is about 3 μm thick). Then, the Pt covered region along the

vertical axis of the nanowire is milled away by Ga^+ ions on both sides of the Pt stripe. The edge of the sheet is also milled away to free it by a manipulator. The resultant sheet was transferred to a TEM grid for further thinning. Figure S1b shows the sample sheet attached to the TEM grid by depositing a Pt foil (60~90 nm in thickness). Figure S1c is the field-emission scanning electron microscopy (FE-SEM) cross section image of the Ni-Au core-shell nanowires after milling. In the figure, the right hand-side nanowires have voids probably from the long-time milling. Actually, the transition metal Ni is more easily milled by Ga^+ ions than the noble metal Au. The inset shows the enlargement of a representative single Ni-Au core-shell nanowire in the foil after milling. In the image, the inner dark region is the Ni core and the outer bright region is the Au nanoshell. The original diameter of the Ni nanowires is ~200 nm but increases to ~250 nm after coating. The coating of the Au shell retains the robustness of the nanowires in the foil attached on the TEM grid. We noted that the SEM images of Ni-Au core-shell nanowires are not circular, following the shape of the AAO nanotemplate pore and/or due to stress and deformation arising from the process.

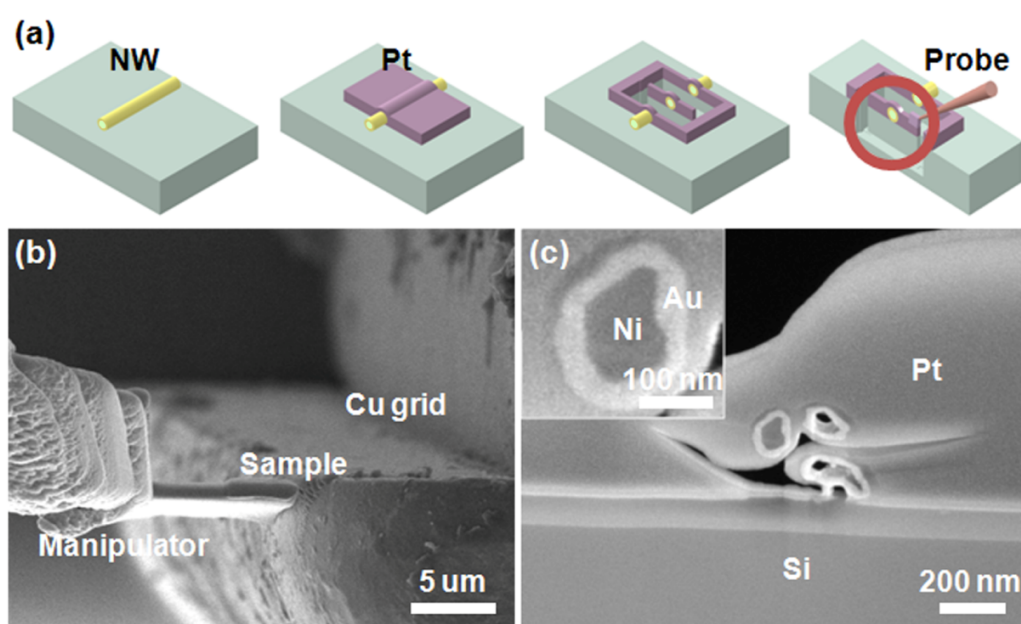


Figure S1. (a) Process for the TEM sample preparation by cross-sectioning the Ni-Au nanowires via the FIB lift-out technique. (b) The sample sheet is attached to the TEM grid by depositing Pt. (c) Cross-sectional image of the Ni-Au core-shell nanowires covered with Pt on the Si wafer and enlargement of the cross-section of the Ni-Au core-shell nanowire.

3. Magnetic property measurement

Figure S2 shows the hysteresis loops for Ni nanowire and Ni-Au core-shell nanowire arrays. For each nanowire array, external magnetic field was applied in two directions, parallel and perpendicular to nanowire axis. Magnetic anisotropy was developed where magnetic easy direction is along the axis predominantly due to shape effect. Coercivity changes before and after nonmagnetic Au shell formation appears negligible: under parallel field, 287 to 288 Oe, and under perpendicular field, 160 to 174 Oe.

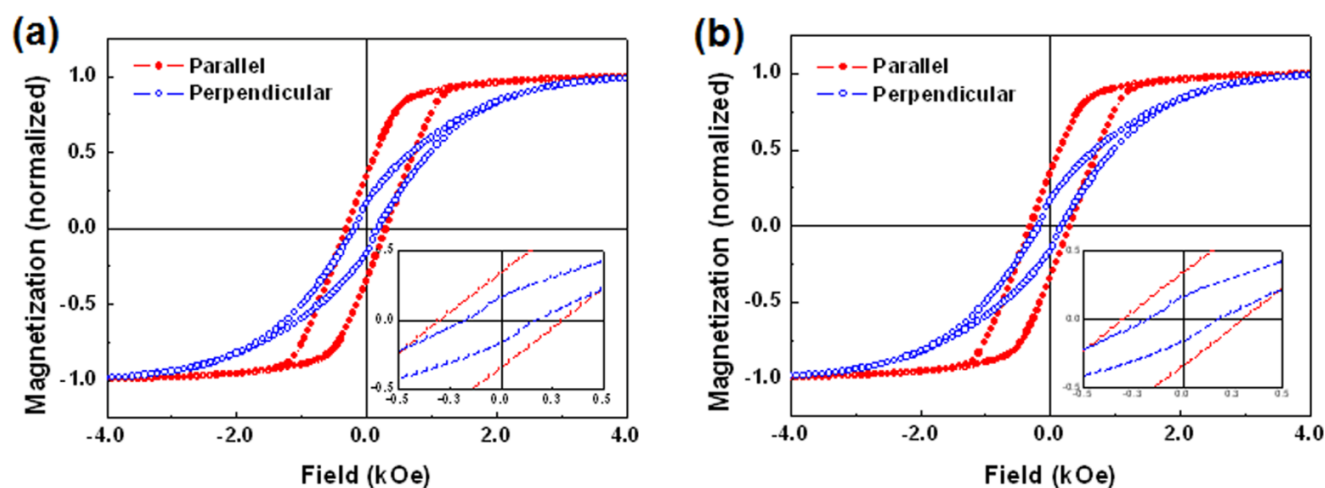


Figure S2. Magnetic hysteresis curves measured under external field parallel and perpendicular to the nanowire axis: (a) Ni nanowire array with coercivity values of 287 Oe (parallel) and 160 Oe (perpendicular), and (b) Ni-Au core-shell nanowire array with coercivity values of 288 Oe (parallel) and 174 Oe (perpendicular).

4. Bioconjugation procedure

A schematic illustration of nanowire surface functionalization steps is shown in Figure S3. Functionalizing the surface of nanowires by chemical modification to tailor surface properties, impart other properties (fluorescence), and introduce molecular recognition for small molecules (drugs), biopolymers (peptides, proteins, and DNA), and protein assemblies (viruses) has become an important tool in nanobiotechnology.²⁻⁴ To develop a platform for biomedical system, we successfully conjugated streptavidin-fluorescent dyes on the biotinylated Ni-Au core-shell nanowires which are found to be good candidates for clinical materials through biofunctional surface modification of the Au nanoshell layers. The interaction between streptavidin and biotin is one of the strongest non-covalent interactions in nature. The high affinity of the biotin-streptavidin binding offers useful biofunctional advantages on inorganic nanostructures.

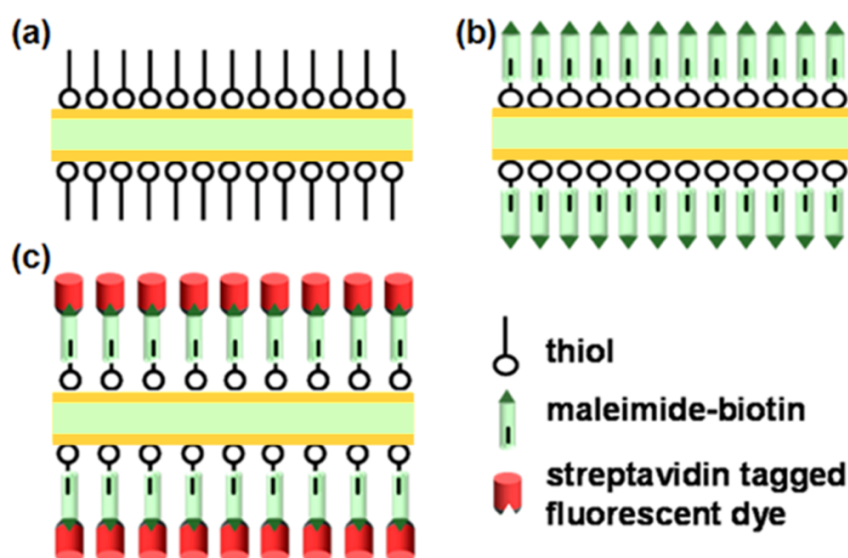


Figure S3. Bioconjugation procedure of the Ni-Au core-shell nanowires. (a) Thiolation on the Au shell. (b) Biotinylated shell through thiol-maleimide bonding. (c) Conjugation of streptavidin-fluorophores to biotin.

5. Optical property measurement

Subsequently, we studied the UV-Vis absorption spectra of the biotinylated Ni-Au core-shell nanowires before and after the conjugation of the streptavidin-fluorescent dyes (Atto425, FITC and Atto655).⁵⁻⁷ During the absorbance measurements, the solution consisting of DMSO and PBS (50:50) was used at pH~7.0. Before the bonding of the streptavidin-fluorescent dye on the core-shell nanowires, the absorption spectrum I in Figure S4a showed the typical surface plasmon band of nanostructured gold. After the biotinylated core-shell nanowires were conjugated to the streptavidin-fluorescent dyes (Figure S4b~d), however, changes in the optical properties were observed that the Au plasmon disappeared. The biofunctionalized core-shell nanowires showed the characteristic absorbance peaks at the expected excitation wavelengths. The maximum absorbance peaks before and after biofunctionalization are 440 nm for solution of streptavidin-Atto425 conjugated core-shell nanowires (I) and 438 nm for the solution of streptavidin-Atto425 (II); 502 nm for the solution of streptavidin-FITC conjugated core-shell nanowires (I) and 498 nm for the solution of streptavidin-FITC (II); and 663 nm for the solution of streptavidin-Atto655 conjugated core-shell nanowires (I) and 662 nm for the solution of streptavidin-Atto655 (II).

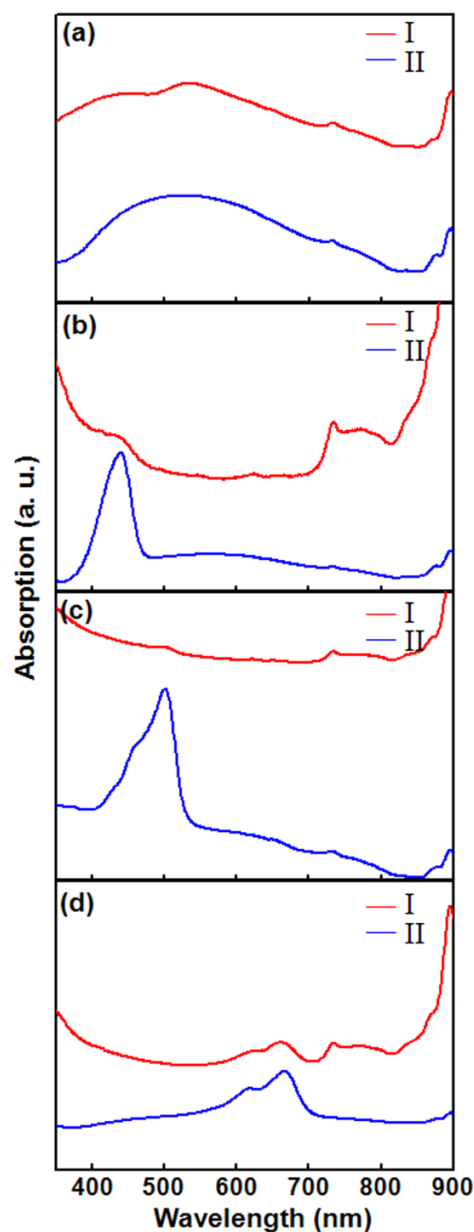


Figure S4. Absorbance spectra analysis of the dyes before and after surface functionalization. (a) Solution of DMSO, PBS and core-shell nanowires (I) and solution of DMSO and PBS (II). (b) Solution of streptavidin-Atto425 conjugated core-shell nanowires (I) and solution of streptavidin-Atto425 (II). (c) Solution of streptavidin-FITC conjugated core-shell nanowires (I) and solution of streptavidin-FITC (II). (d) Solution of streptavidin-Atto655 conjugated core-shell nanowires (I) and solution of streptavidin-Atto655 (II).

In this study, we confirmed the surface plasmon resonance (SPR) of the Ni-Au core-shell nanowires over the electroless-plating time as displayed in Figure S5. The analysis was performed using a UV spectrophotometer (UV-Vis, Shimadzu UV-1800) under the conditions: sampling interval (0.5) and slit width (1.0 nm).

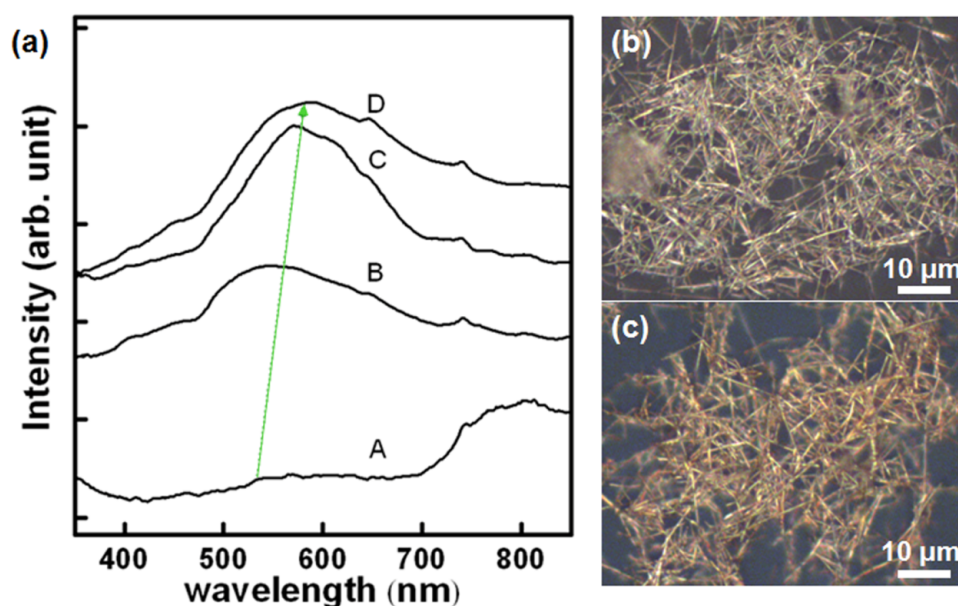


Figure S5. (a) UV-Vis absorption spectra of the Ni-Au core-shell nanowires over the electroless plating time. A – 1 min, B – 2 min, C – 3 min, and D – 4 min. The strong absorption in the long wavelength in the curve A is due to the solvents (refer to the spectrum II in Figure S4a). Bright-field reflectance image of Ni nanowires (b), and Ni-Au core-shell nanowires (c).

References

- 1 J. Burdick, E. Alonas, H. C. Huang, K. Rege and J. Wang, *Nanotechnol.*, 2009, **20**, 065306.
- 2 Y. Cui, Q. Q. Wei, H. K. Park and C. M. Lieber, *Science*, 2001, **293**, 1289.
- 3 F. Patolsky, G. Zheng and C. M. Lieber, *Nanomedicine-Uk*, 2006, **1**, 51.
- 4 E. Katz and I. Willner, *Angew. Chem. Int. Ed.*, 2004, **43**, 6042.
- 5 G. Barbillon, A. C. Faure, N. El Kork, P. Moretti, S. Roux, O. Tillement, M. G. Ou, A. Descamps, P. Perriat, A. Vial, J. L. Bijeon, C. A. Marquette and B. Jacquier, *Nanotechnol.*, 2008, **19**, 035705.
- 6 G. C. A. M. Bokken, R. J. Corbee, F. van Knapen and A. A. Bergwerff, *Fems. Microbiol. Lett.*, 2003, **222**,
- 7 Y. Sun, D. Q. Song, Y. P. Bai, L. Y. Wang, Y. Tian and H. Q. Zhang, *Anal. Chim. Acta.*, 2008, **624**,