# Electronic Supplementary Information (ESI) for

# A New Heterostructured SERS Substrate: Free-standing Silicon Nanowires Decorated with Graphene-encapsulated Gold Nanoparticles

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**Experimental details**

Materials and Methods. Silicon wafer (111) was purchased from IWS (Colfax, CA). Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%) was purchased from Sigma-Aldrich (St. Louis, MO). Sodium borohydride ($NaBH_4$, powder, 98%) was purchased from Acros Organics (New Jersey, NJ). DI water (18.1 MΩ-cm) was obtained using a Barnstead International DI water system (E-pure D4641). All chemicals were used without further purification. Growth and annealing of Si nanowires were carried out inside a GSL-1100X Tube Furnace (MTI Corporation) with a quartz tube from ChemGlass (Vineland, NJ). Oxygen plasma treatment was performed in a Nordson March Jupiter III Reactive Ion Etcher (Concord, CA).

Atmosphere-pressure CVD of Si nanowires. Silicon wafer (111) was pre-cleaned with Acetone, DI-water and then placed in a buffered oxide etch (BOE) solution for 30 s to remove the native surface oxide layer. This was followed by the galvanic deposition of Au film on the substrate in 1 mM $KAuCl_4$ + 1% HF aqueous solution. The as-prepared Si/Au substrate was immediately placed in the center of a GSL-1100X tube furnace. The following growth of Si nanowires was executed *via* an atmosphere pressure CVD method. Briefly, the furnace was first heated up to 850 ºC with a feeding of 5% $H_2$ in Ar. This temperature was maintained for 10 minutes, allowing the pre-coated Au film to convert Au nanoparticles. These Au nanoparticles were expected to serve as catalysts during the following VLS growth of Si nanowires. After this annealing, the temperature was reduced to the growth temperature. The silicon source was 2% $SiH_4$/He carried by 10% $H_2$/Ar. When the growth was completed, the furnace was self-cooled to ambient temperature with flowing of pure Ar.

Surface decoration of Si nanowires. The as-produced Si nanowires were treated with BOE solution for 5 s and then placed in the galvanic deposition solution (1 mM $KAuCl_4$ + 1% HF) for 30 s to deposit gold shells or gold clusters on the nanowires. Followed by annealing the sample in the quartz furnace for 10 min at 625º, Au nanoparticles were uniformly decorated on the surface of Si nanowires. To further grow multilayer graphene shells on these Au nanoparticles, a typical xylene-based CVD process previously reported the authors were employed.[1,2] Briefly, Au nanoparticles decorated on the surface of Si nanowires were surface-oxidized with oxygen plasma for 15 min. The sample was then placed in the center of a quartz tube furnace. The growth of multilayer graphene shell on Au nanoparticles was carried out at 675 ˚C for 1 h. Xylene was used as the carbon source with a feeding rate of 10 mL/h, carried by 10% $H_2$/Ar with a total flow rate of 1.15 SLM. This step led to the structural evolution of final SiNW-GNP heterostructures.

Plasmonic modeling. Discrete dipole approximation (DDA) method was used to demonstrate the plasmonic properties of the surface-decorated Si nanowire heterostructures. This includes the theoretical calculation of the light-induced extinction (composed of absorbance and scattering) on the heterostructures and simulation of the distribution of electromagnetic field that generated by their LSPR. The DDA method is based on the solution of the 3D Maxwell equation *via* the DDSCAT code developed by Draine and Flatau.[3] Detailed simulation procedures have

been demonstrated previously by the authors.[4] Briefly, DDSCAT 7.2 was utilized to mathematically calculate the normalized electric field or surface plasmon generation on a 3D geometrical target that created according to the morphology and structure of the Si nanowire heterostructures. The normalized electric field intensity is defined as the ratio between the electric field generated near the target surface and the incident electric field ($|E|/|E_0|$). The target generation was conducted using 3ds Max® (Autodesk). The effective radius of the dipoles was calculated using: $r_{eff} = (3V/4\pi)^{1/3}$, where $V$ is the total volume of the target and is calculated with $V = Nd^3$ ($N$ is the number of dipoles and $d$ is the lattice spacing in cubic array).

Characterizations. The JEOL-7000 field-emission SEM and Tecnai F-20 TEM were used for the morphological and structural characterization. To conduct the SERS sensing experiments, the Si nanowire heterostructures were first treated with oxygen plasma for 15 s to adjust the thickness of the multilayer graphene shell on Au nanoparticles. The samples were further treated with BOE for 10 s to create possible surface Si-H bonds on Si nanowires. This was followed by incubating the treated substrates in a dye solution containing $10^{-6}$ M R6G solution for 10 h at room temperature. The substrates were washed with DI-water and dried in flowing $N_2$. For SERS test, a 785-nm Raman laser and another 532-nm Raman laser was respectively used. The laser power was ~1 mW. The integration time was set for 10 s with a co-condition of 2.

(1) Chopra, N.; Bachas, L. G.; Knecht, M. R. Fabrication and biofunctionalization of carbon-encapsulated Au nanoparticles. *Chem. Mater*. **2009**, *21*, 1176-1178.

(2) Chopra, N.; Wu, J.; Summerville, L. Controlled assembly of graphene shells encapsulated gold nanoparticles and their integration with carbon nanotubes. *Carbon* **2013**, *62*, 76-87.

(3) Draine, B. T.; Flatau, P. J. User guide for the discrete dipole approximation code DDSCAT 7.3. *arXiv preprint arXiv* **2013**, 307, 1305.6497.

(4) Wu, J.; Shi, W.; Chopra, N. Optical properties of gold/multilayer-graphene/carbon nanotube hybrid materials. *Carbon* **2014**, *68*, 708-717.

**Figure S1.** (A) SEM image of Au film prepared by galvanic deposition for 3 min. (B) SEM image of corresponding Au nanoparticles after external annealing. (C) Dependence of particle size on the galvanic deposition time.

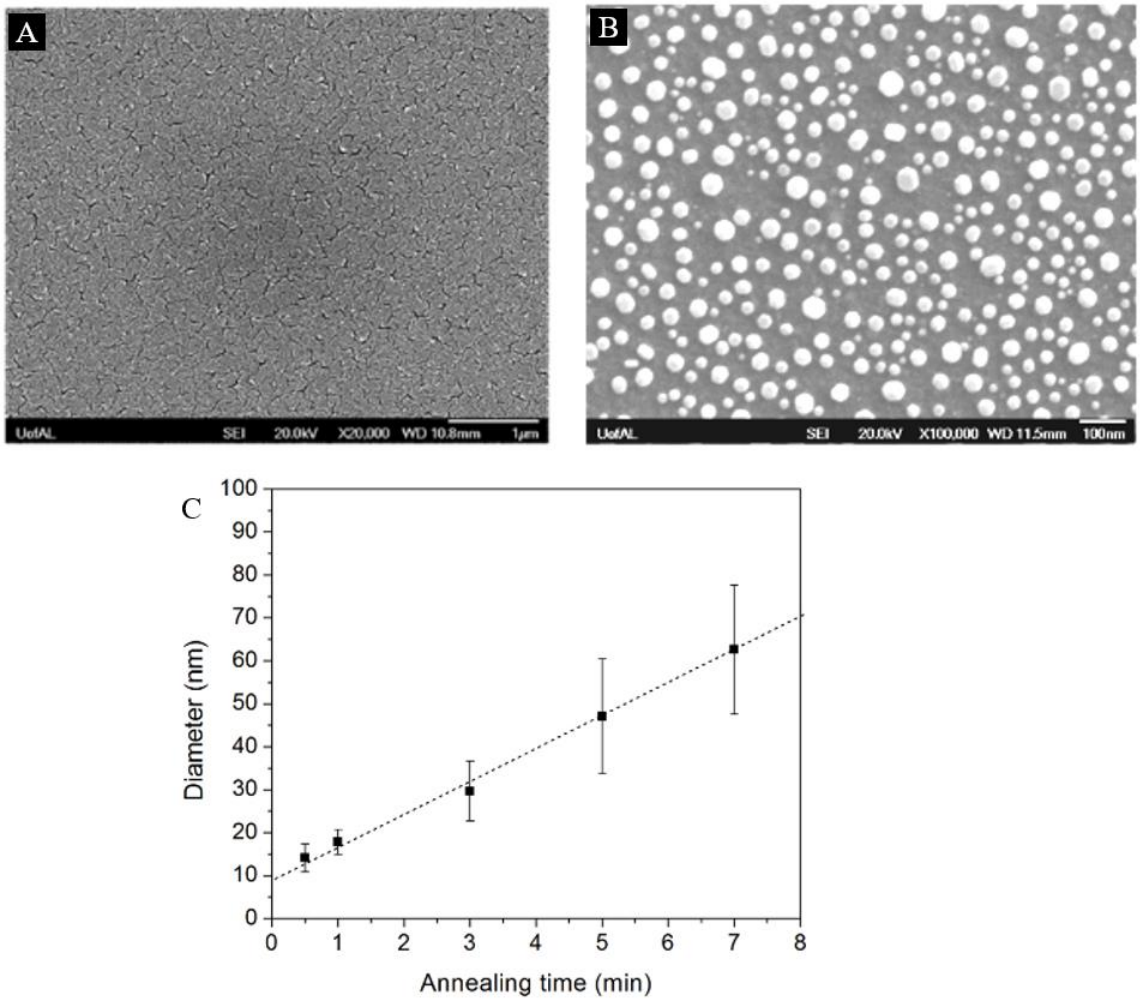

**Figure S2.** (A) Low-resolution and (B) high-resolution SEM images of the as-coated Si-Au nanowire heterostructures. (C) Low-resolution and (D) high-resolution SEM images of the annealed Si-Au nanowire heterostructures.

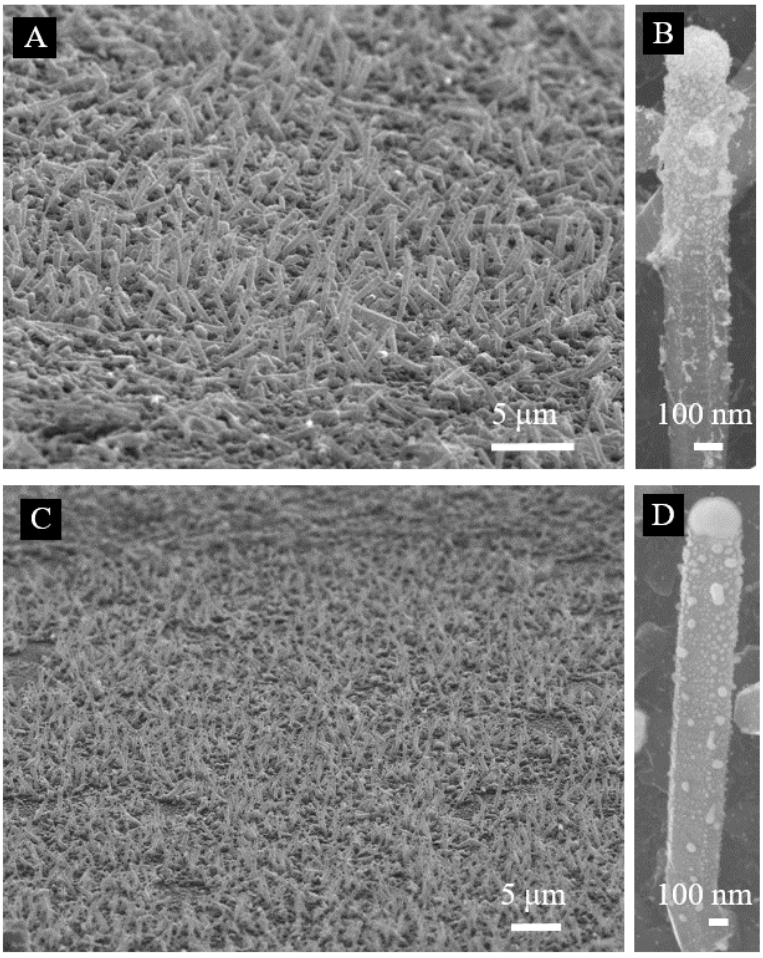

**Figure S3.** (A) Low-resolution and (B) high-resolution SEM images of the as-coated Si-Au nanowire heterostructures. (C) Low-resolution and (D) high-resolution SEM images of the annealed Si-Au nanowire heterostructures.

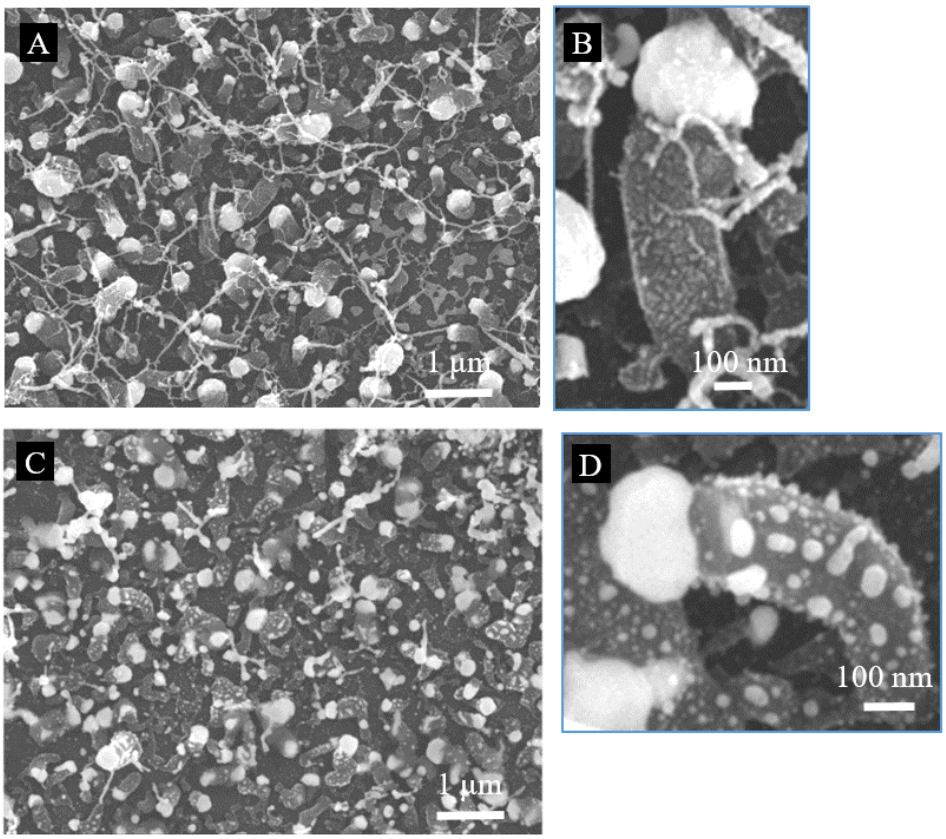

**Figure S4.** (A, B) SEM and (C, D) TEM images demonstrating the direct CVD growth of graphene on Si nanowires.

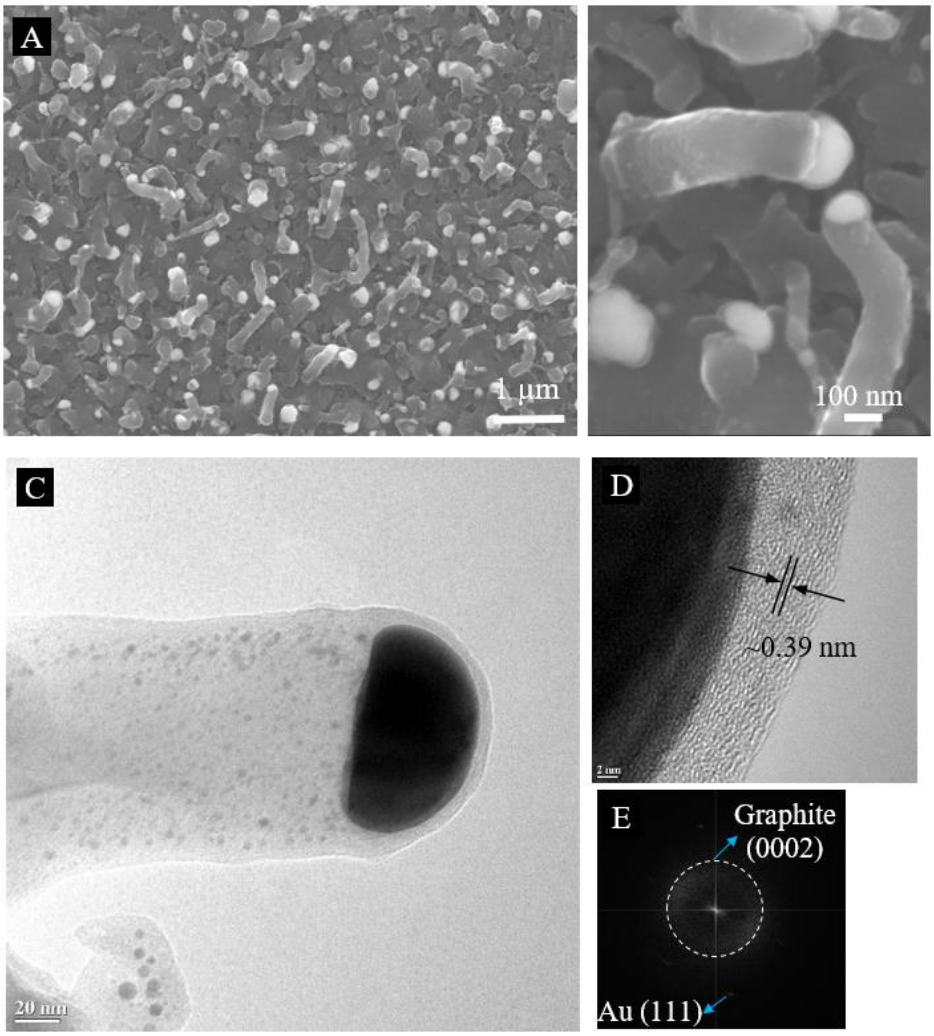

**Figure S5.** (A, B) SEM and (C, D) TEM images demonstrating the direct CVD growth of graphene on Si nanowires.

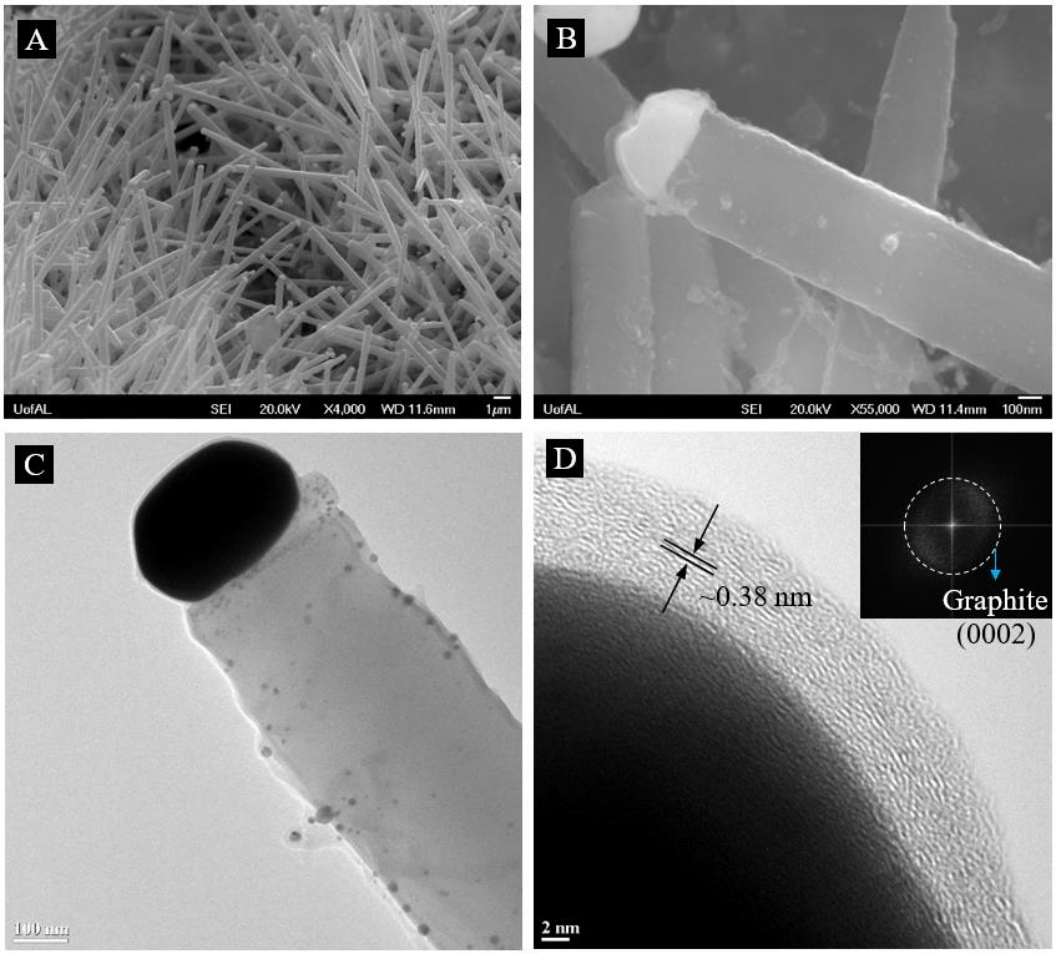

**Figure S6.** TEM images of the SiNW-GNP heterostructures. For these samples Au nanoparticles were formed on Si nanowire using a chemical nucleation method. Briefly, the as-produced Si nanowires were dispersed in ethanol by sonicating the substrate (1×1 $cm^2$) for 10 min. This was followed by addition of ~30 µL as-prepared $NaBH_4$ solution (60 g/L) into the nanowire dispersion. After slightly stirred for 1 min, ~50 µL of $HAuCl_4$ (~5 x $10^{-3}$ M) was further added. The nucleation reaction was continued for 10 min. The product was washed with ethanol for 3 times and finally dispersed in ~1 mL ethanol.

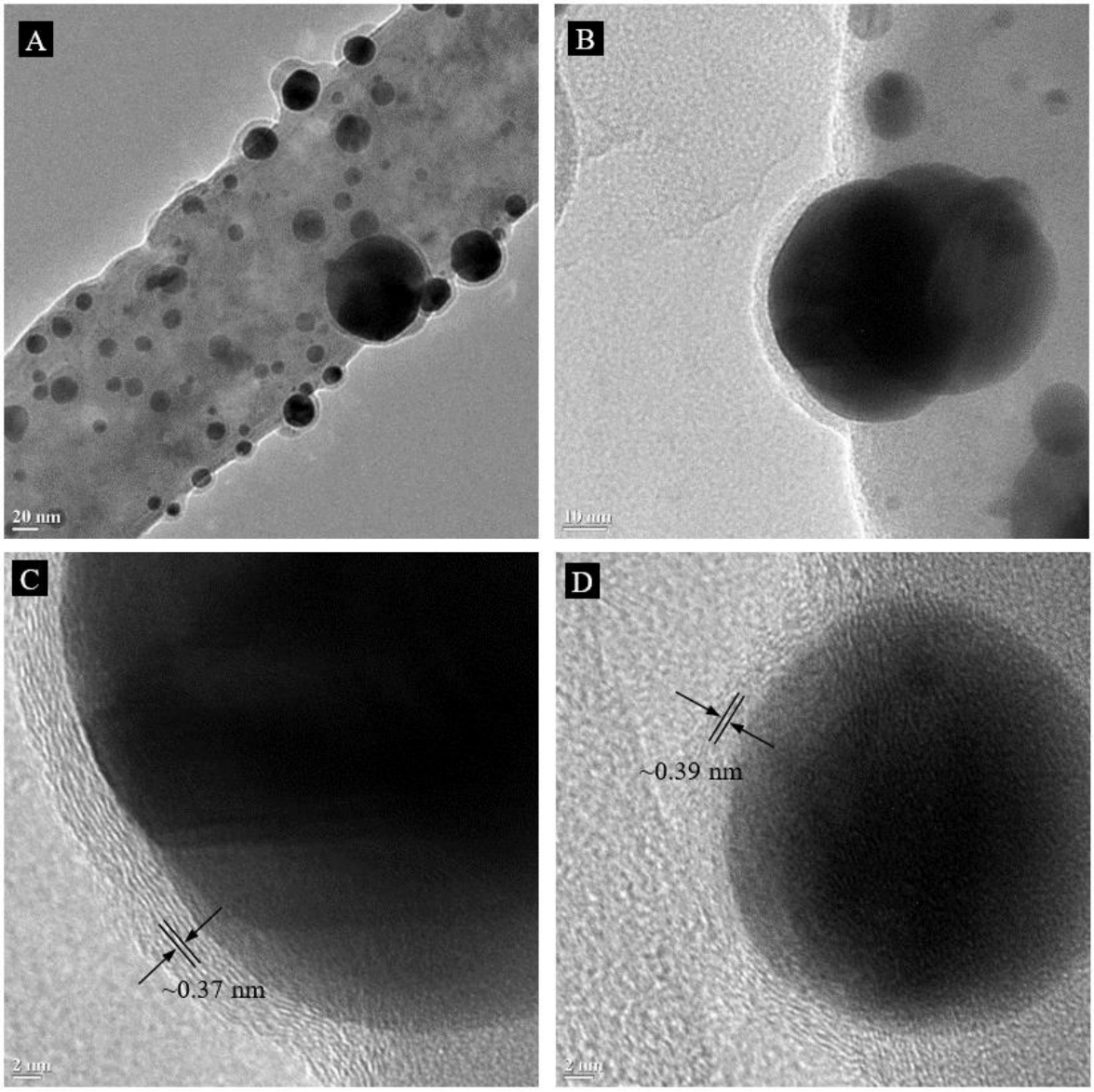

**Figure S7.** Deconvolution of extinction spectra to absorption component and scattering component: (A) the SiNW-AuNP target and (B) the SiNW-GNP target corresponding to Figure 7 in the main text.

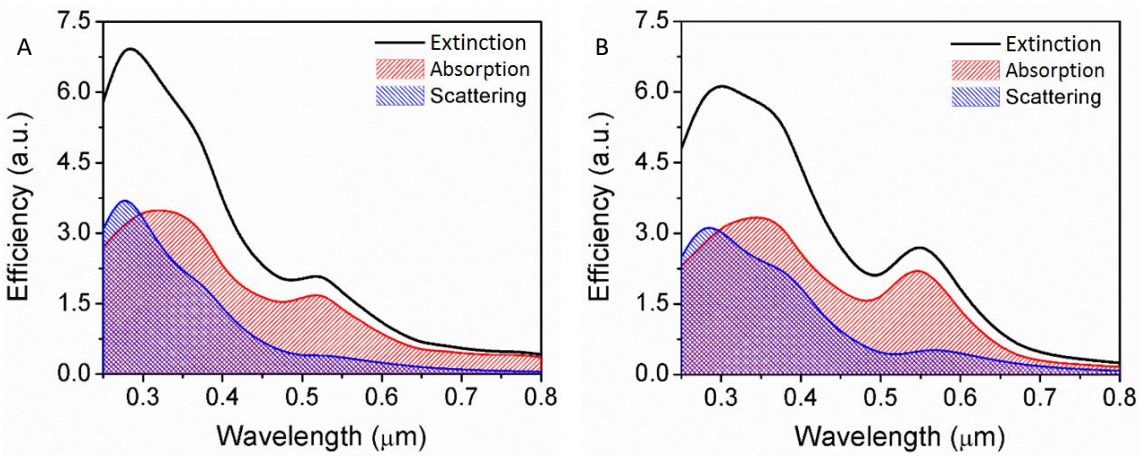

**Figure S8.** Simulated electric filed mapping around (B) the SiNW-AuNP target and (C) the SiNW-GNP target. The incident wavelength is 785 nm for both. The bottom images show the cross-section view of the electric filed distribution.

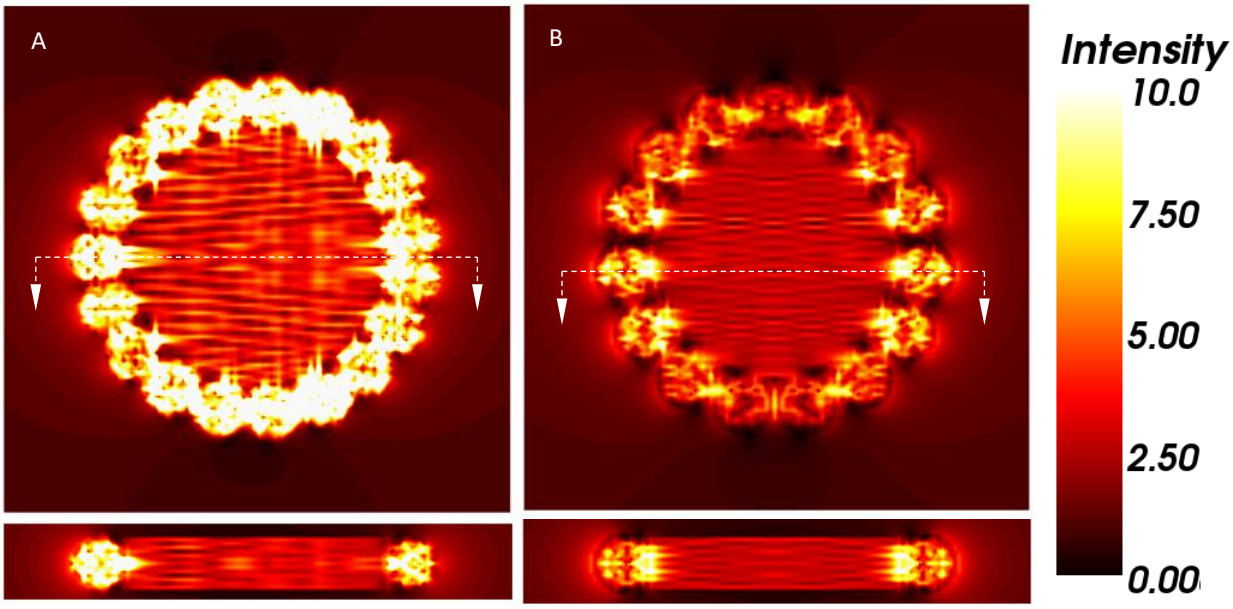

**Figure S9.** Deconvoluted spectra for the Si nanrod target (A) without and (B) with a gold tip. The extinction spectra are corresponding to Figure 6 in the main text.