

## Light-Induced Selective Deposition of Other Metals on Metal-Tipped Asymmetric Semiconductor Nanorods

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### 1. Chemicals

Cadmium acetylacetonate ( $\text{Cd}(\text{acac})_2$ , 99.9%), cadmium oxide ( $\text{CdO}$ , 99.5%), dodecylamine (DDA, 98%), gold (III) chloride ( $\text{AuCl}_3$ , 99%), Potassium tetrachloroaurate ( $\text{KAuCl}_4$ , 99.995%), 1,2-hexadecanediol (HDDO, 90%), 1-hexadecylamine (HDA, 90%), 1-octadecene (ODE, 90%), sulfur (S, reagent grade), selenium (Se, 99.99%), tetraoctylammonium bromide (TOAB, 98%), trioctylphosphine oxide (TOPO, 90%) and Iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ , 98%) were purchased from Sigma Aldrich. Trioctylphosphine (TOP, 90%), Oleic acid ( $\text{C}_{17}\text{H}_{33}\text{CO}_2\text{H}$ , 90%) and oleylamine ( $\text{C}_{17}\text{H}_{33}\text{NH}_2$ , 70%) were purchased from Singma Aldrich. Diisooctylphosphinic acid (DIPA, 90%) was purchased from Fluka. n-Octadecylphosphonic acid (ODPA, 97%), trioctylphosphine oxide (TOPO, 99%) and n-hexylphosphonic acid (HPA, 97%) were purchased from Strem. Palladium chloride ( $\text{PdCl}_2$ , >99%) was purchased from Fisher. AR grade ethanol, methanol, and toluene were used. All the chemicals were used as received without further purification. Unless stated otherwise, all the reactions were conducted in oven-dried glassware under nitrogen atmosphere using standard Schlenk techniques.

### 2. Synthesis of spherical CdSe seeds

Synthesis of monodispersed CdSe NCs proceeded based on a previously reported procedure with slight modifications<sup>1</sup>. A mixture bath of 9 g TOPO (90%), 6 g HDA and 0.25 ml of DIPA was degassed at 100°C for 1.5 h. A precursor solution comprising of 317 mg  $\text{Cd}(\text{acac})_2$  and 567 mg HDDO in 6 mL of ODE was degassed at 120°C for 1.5 h, followed by addition of 4 mL of 1.5 M trioctylphosphine selenide at room temperature. The precursor solution was then rapidly injected into the bath at 360°C and allowed to cool to 80 °C. As-synthesized CdSe QDs were subsequently processed by 3-4 cycles of precipitation in a butanol/ methanol mixture and re-dispersion in hexane for further use.

### 3. Preparation of stock solution of CdSe QDs

Processed CdSe QDs were dispersed in a minimum amount of hexane and their concentration was determined by measuring their absorbance at 350 nm, whose molar absorption coefficient is known<sup>2</sup>. The hexane was then removed under vacuum and TOP was added to make up a QD concentration of 400  $\mu$ M. This mixture will subsequently be referred to as the CdSe stock solution.

### 4. Synthesis of CdSe seeded CdS heterostructured nanorods

CdSe seeded CdS nanorods were prepared according to the modified method of Manna<sup>3</sup>. 3g TOPO (99%), 93 mg CdO, 290 mg ODPa and 80 mg HPA are mixed in a 50 mL three-neck round bottled flask (RBF) and degassed at 150 °C for about 1.5 h. The reaction mixture was then heated to 360°C under N<sub>2</sub> atmosphere. Separately, a mixture of S, TOP and CdSe seeds was obtained by first dissolving 120 mg S in 1.8 mL TOP at 50 °C before adding 200  $\mu$ L of the prepared CdSe stock solution. Upon reaching the desired temperature, 1.8 mL TOP was added, and the temperature was allowed to recover to 360 °C before the mixture of S, TOP and CdSe was swiftly injected. The temperature was again allowed to recover to 360 °C and the anisotropic shell was grown at this temperature for about 6-8 minutes. The heating mantle was then removed and the solution was allowed to cool to 80 °C. As-synthesized CdSe seeded CdS nanorods (NRs) were then processed by repeated cycles of precipitation in methanol and re-dispersion in toluene. The concentration of the processed CdSe seeded CdS NRs were determined using a published molar extinction coefficient at 350 nm<sup>4</sup>.

### 5. Gold, Palladium stock solution

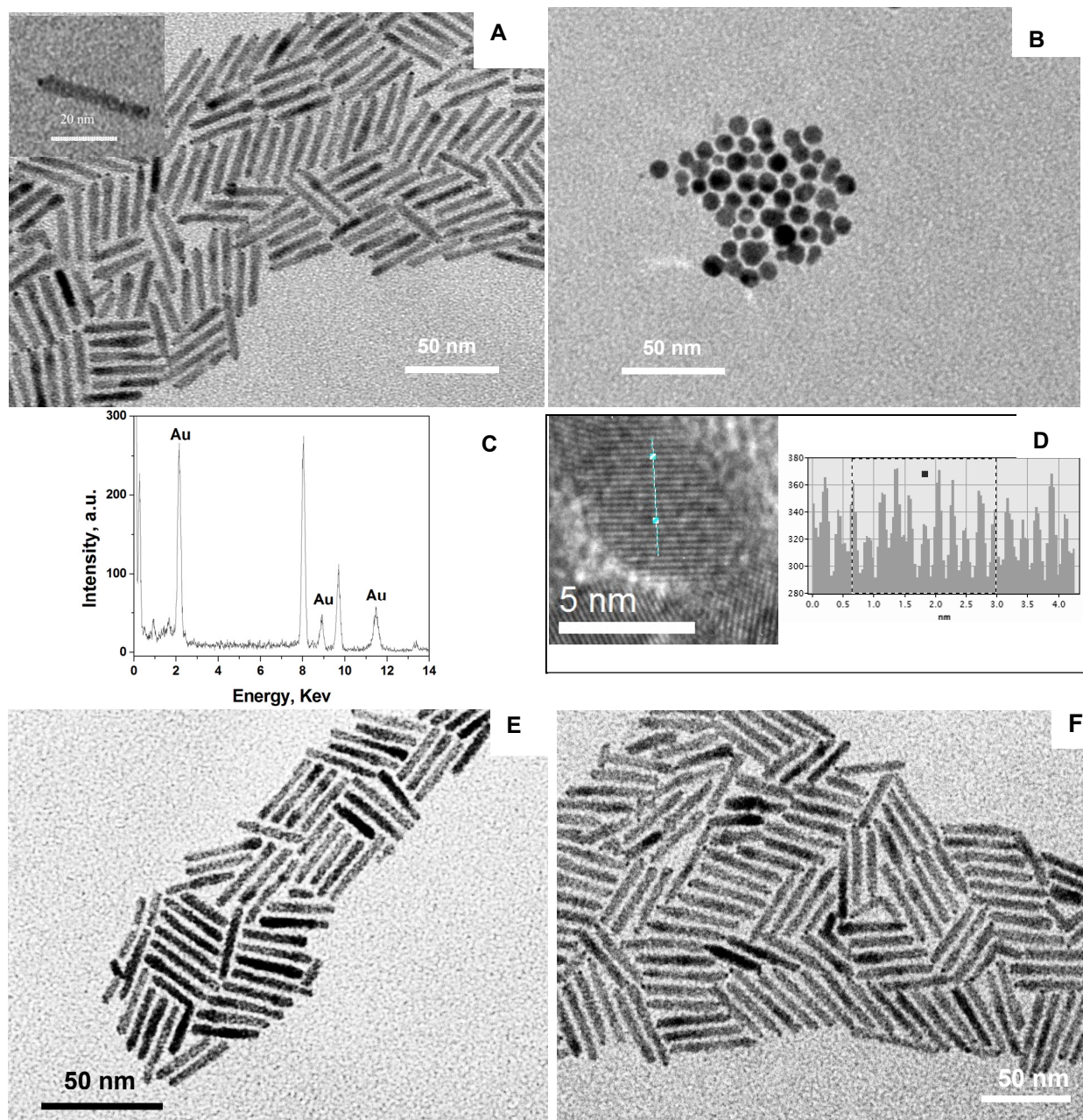
For the Au stock solution, 48 mg of AuCl<sub>3</sub> (0.16 mmol) and 88 mg of TOAB (0.16 mmol) were dissolved in 5 mL of toluene. The suspension was sonicated for 5 minutes at room temperature until a dark red solution was obtained. This mixture will be referred to as Au stock solution (1). The mixture was then further diluted by a factor of 32 in toluene and will subsequently be referred to as Au stock solution (2). For the Pd stock solution, 10 mg of PdCl<sub>2</sub> (0.06 mmol) and 52 mg of TOAB (0.076 mmol) were dissolved in 5 mL of toluene. The suspension was stirred at room temperature overnight until a dark red clear solution was seen. This mixture will be referred to as the Pd stock solution

### 6. Preparation of Au-tipped NRs

#### *Matchstick-like structure*

In a 10 mL flask, 1 mL of Au stock solution (2) and 1 mL of a 0.15M DDA toluene solution were mixed and sonicated at room temperature for 15 mins to give a light yellow solution. In a separate vial, a mixture comprising of 0.5 ml of a solution of CdSe seeded CdS NRs (~ 50  $\mu$ M) and 12 mg of ODPa was prepared. This mixture was then rapidly delivered into the solution containing the Au precursors and stirred vigorously under N<sub>2</sub> at room temperature.

The reaction was allowed to proceed for a fixed amount of time, typically 20 mins and then quenched with 2.5 mL of MeOH. After purification with MeOH, the final solution was diluted 10 times in toluene for use. Figure S1A is a representative TEM image of the rods obtained.

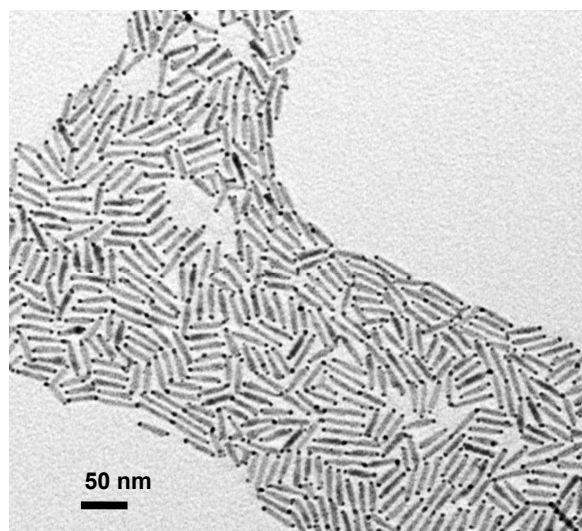


**Figure S1.** (A) TEM image of Au-tipped CdSe seeded CdS nanorods with a length of  $\sim 30$  nm, rod diameter of  $\sim 4.1$  nm and a tip diameter of  $\sim 1.4$  nm. Inset in A is a magnified image of a typical Au-CdSe/CdS nanorod. (B) is a TEM image of control experiments for Pd deposition on bare Au nanoparticles under UV excitation. No Pd deposition was observed. (C) EDX analysis of sample (B), showing no traces of Pd present. (D) HRTEM image of sample, where the only discernible lattice spacings are those of Au, suggesting the absence of Pd. The diagram on the right in D is the

distance measurement of the lattice line profiles, which correspond to those of Au(111). (E) TEM image of control experiment for Pd deposition on bare CdSe seeded CdS nanorods under UV excitation. (F) TEM image of control experiment for Pd deposition on Au-tipped CdSe seeded CdS nanorods without UV excitation. In both (E) and (F), no Pd deposition was observed.

#### *Dumbbell-like structure*

In a 10 mL flask, 0.1 mL of Au stock solution (1), 0.9 mL of toluene and 1 mL of a DDA toluene solution (0.15 M) were mixed and sonicated at 40 °C for 15 mins to give a light yellow solution. In a separate vial, a mixture solution comprising of 0.5 mL of a solution of CdSe seeded CdS NRs (~ 50  $\mu$ M) and 12 mg of ODPA was prepared and then rapidly delivered into the Au solution with vigorous stirring at 90 °C. The reaction was allowed to proceed for a fixed amount of time, typically 6 hr and then quenched with MeOH. Re-dispersion in 0.5 mL toluene and this solution will subsequently be referred to be stock solution. Figure S2 gives a TEM image of the rods obtained.



**Figure S2.** TEM image of dumbbell-like Au-tipped CdSe seeded CdS nanorods. The ~3 nm diameter NRs have an average length of ~29 nm with a Au tip diameter of ~2.8 nm.

#### **7. TEM characterization**

JEOL 2010 and 3010 (with accelerating voltages of 200keV and 300keV respectively) microscopes were used to obtain normal bright-field TEM images of the nanoparticles. For TEM sample preparation, a drop of the nanoparticle solution was placed onto a 300 mesh size copper grid covered with a continuous carbon film. Excess solution was removed by an adsorbent paper and the sample was dried at room temperature. The High-Resolution TEM images, High-Angle Annular Dark Field Scanning-TEM (HAADF-STEM) studies and detailed elemental composition analysis were carried out on a FEI Titan 80-300 electron microscope operated at 300 KV, which is equipped with an electron

beam monochromator, an energy dispersive X-ray spectroscopy (EDX) and a Gatan electron energy loss spectrometer. The probing electron beam size for the EDX measurement was around 0.3 nm. The dwell time for each EDX spectrum is 10 seconds.

## 8. Optical characterization

UV-visible absorption spectra were obtained with either a Shimadzu UV-1700 spectrophotometer or an Agilent 8453 UV-Visible spectrophotometer.

## 9. Deposition of Pd on matchstick-like Au-tipped NRs and control experiments

In a 10 mL vial, 0.25 mL of Pd stock solution and 0.25 mL of a 0.15M DDA toluene solution were mixed and sonicated at room temperature for 15 min to give a pale colored solution. In a separate vial, a mixture solution comprising of 0.5 ml of match-like Au-tipped NR solution ( $\sim 5 \mu\text{M}$ ) and 6 mg of ODPA was prepared. This mixture was then added into the Pd solution. And 0.1 mL ethanol was dripped afterwards. A UV lamp (4 W,  $\lambda=365\text{nm}$ ) was held at a fixed distance to the reaction vial, yielding an approximate excitation intensity of  $0.11 \text{ W/cm}^2$  as measured by a power meter. The reaction solution went on at room temperature under ambient atmosphere for a fixed amount of time, typically 1 hr. The reaction was finally quenched with 1 mL of MeOH and processed at least twice before characterization.

### *Control (1): using free Au nanoparticles*

In this control experiment (see Fig. S1B, S1C, and S1D), free gold nanoparticles with a diameter  $\sim 6 \text{ nm}$  were used instead of Au-tipped nanorods while all other conditions were kept the same. No Pd deposition was observed.

### *Control (2) : using CdSe seeded CdS bare nanorods*

In this control experiment (see Fig. S1E), CdSe seeded CdS nanorods without Au attachment were used while all other conditions were kept the same. No Pd deposition was observed.

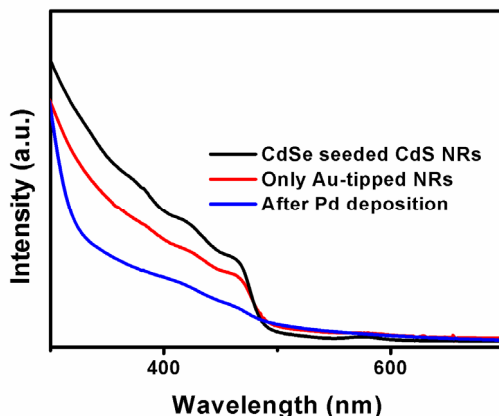
### *Control (3) : Au-tipped NRs without UV irradiation*

In this control experiment (see Fig. S1F), matchstick-like Au-tipped NRs were used while all other conditions were kept the same, with the exception that no UV excitation was employed. No Pd deposition was observed.



## 10. UV-vis spectra of Pd/Au-tipped CdSe seeded CdS nanorods

A comparison between the UV-vis spectra of NRs with and without Pd deposition revealed progressive loss of absorption features upon Pd deposition, as shown in Fig S3. The Pd/Au alloyed tipped rods did not yield any discernible peak at ~520 nm, which is characteristic of the plasmon resonance in similar sized Au.



**Figure S3.** UV-vis spectra of bare CdSe seeded CdS NRs (black), Au-tipped NRs (red), and Pd/Au-tipped NRs (blue). The NRs used here are the same as those in Fig. 1A.

## 11. Deposition of Fe on dumbbell Au-tipped NRs and control experiments

0.5 mL of ~50  $\mu$ M Au NR stock solution, oleylamine, oleic acid and HDDO were co-dissolved in 6 mL ODE in a 25 mL three-neck flask. The mixture was degassed under vacuum for 1.5 hr at 80  $^{\circ}$ C, after which it was heated under  $N_2$  to 95  $^{\circ}$ C. Subsequently, 0.1 mL of 0.1-1.0 M  $Fe(CO)_5$  in ODE was rapidly injected into the above-mentioned three-neck RBF containing the Au-tipped NRs. The flask was then put in a UV reactor (350 nm, 350 W) for 1 hr. Finally, the solution was exposed to air for approximately 30 mins to facilitate complete oxidation of the iron, and then processed via 3-4 cycles of dispersion/precipitation using a toluene/butanol-methanol mixture. An optimized molar ratio of ligands oleylamine: oleic acid: HDDO was found to be 2.35: 1: 1.85.

### *Control (1): using free Au nanoparticles*

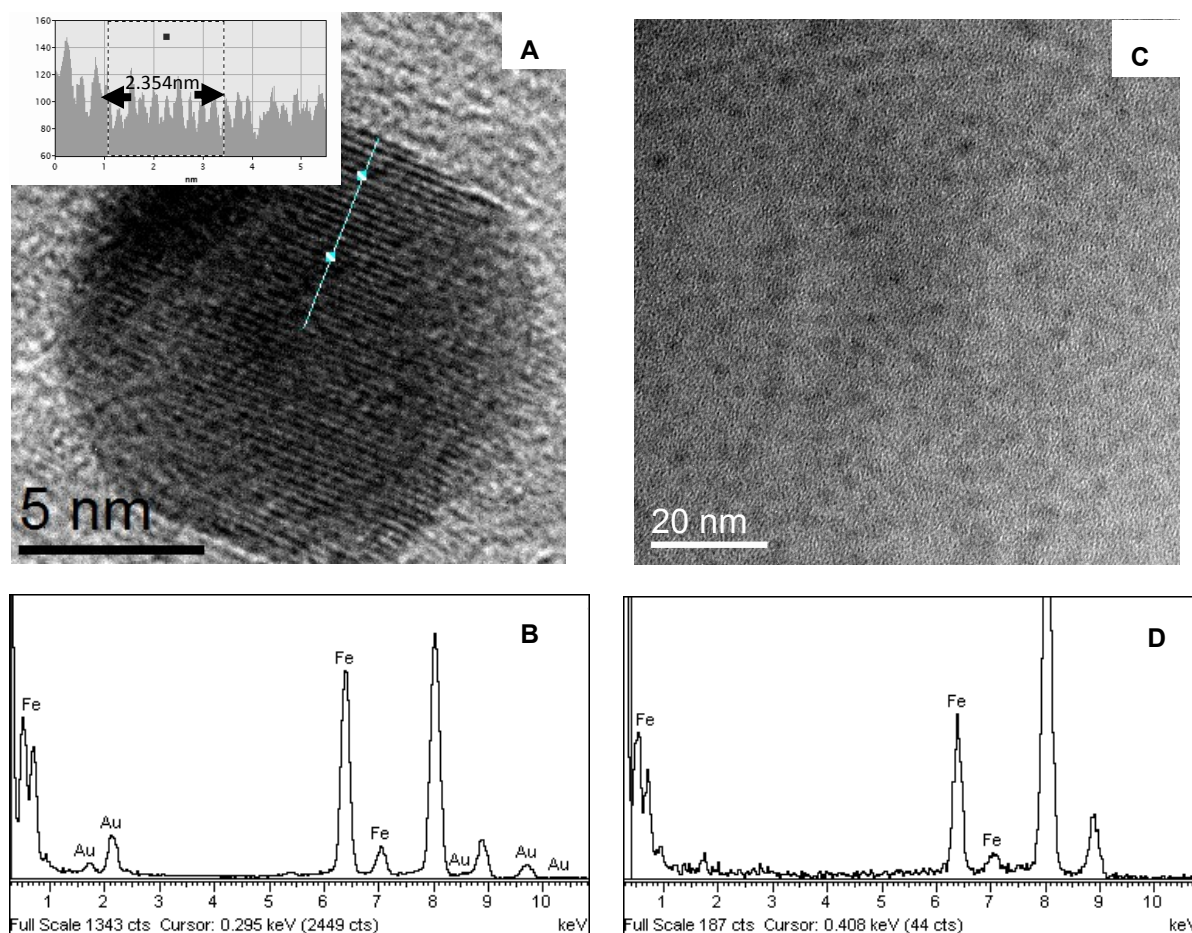
Employing the same Fe deposition conditions, Au nanoparticles with a diameter ~6 nm instead of Au-tipped NRs were used. No attachment of iron oxide to Au nanoparticles was observed, as illustrated in Figure S4.

### *Control (2): using bare CdSe seeded CdS NRs*

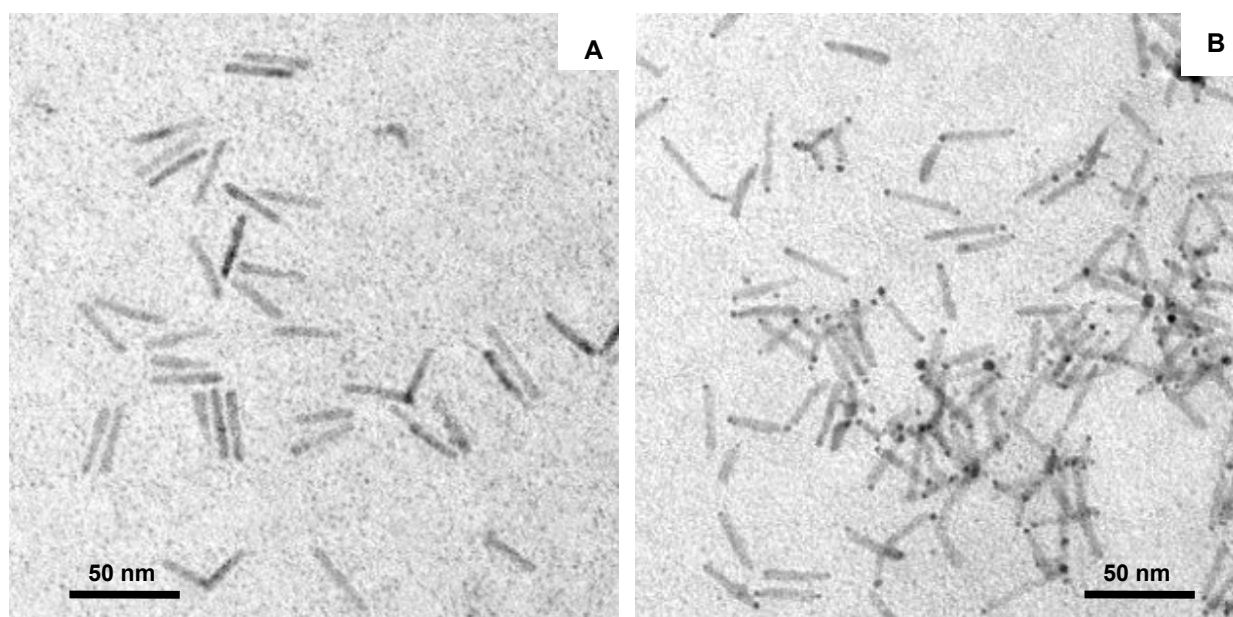
Employing the same Fe deposition conditions, bare NRs were used instead of Au-tipped NRs. No attachment of iron oxide to the NRs was observed, as shown in Figure S5(A).

*Control (3): Au-tipped NRs without UV irradiation*

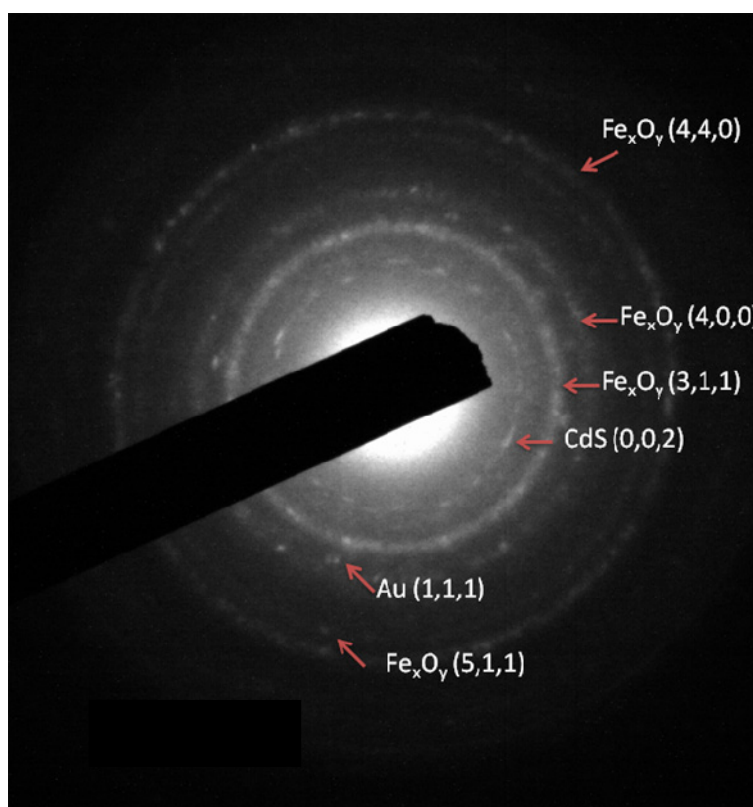
Employing the same Fe deposition conditions, Au-tipped NRs were used, with the exception that no UV excitation was utilized. No attachment of iron oxide to the NRs was observed, as shown in Figure S5(B).



**Figure S4.** (A) HRTEM image of a typical Au nanoparticle after the Fe deposition process. The inset is the distance measurement of 10 facets by line profiles, corresponding to those of Au(111). The corresponding selective-area EDX results, as shown in (B), demonstrate the presence of both Au and Fe. (C) Low resolution TEM image showing the presence of many small particles (< 4 nm in diameter) on the TEM grid. (D) is the corresponding selective-area EDX result of (C) (where Au particles are not present), showing that the small particles are nuclei of Fe.



**Figure S5.** TEM images of control experiments for Fe deposition using (A) bare CdSe seeded CdS NRs and (B) dumbbell-structured Au-tipped NRs but without UV irradiation. In both cases, no selective growth of  $\text{Fe}_x\text{O}_y$  at the tips of the NRs was observed, but homogeneous nucleation of very small particles of iron oxide was evident.

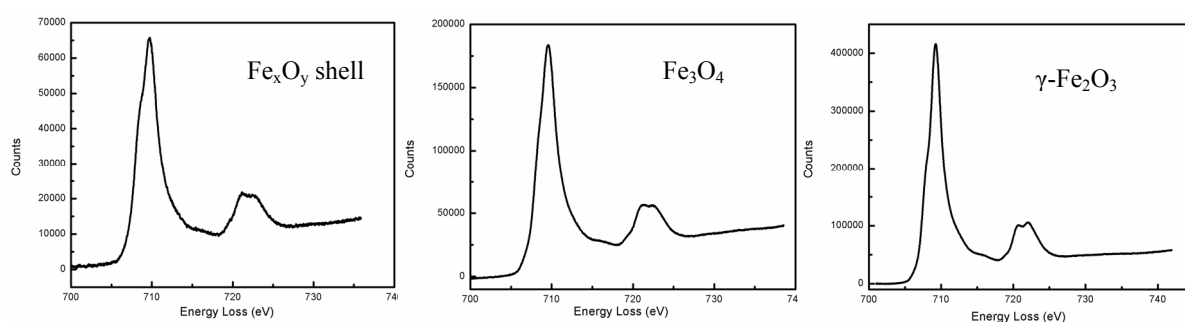


**Figure S6.** SAED pattern of  $\text{Fe}_x\text{O}_y$ -Au-NR composite.



## 12. Electron Energy Loss Spectroscopy measurements

All electron energy loss spectroscopy (EELS) measurements were performed on a Titan TEM at TEM imaging mode with an energy resolution of 0.8 eV and dispersion of 0.02 eV/channel. The acquisition time for each spectrum was 5 s and the collection angle of the transmitted beam was 5.9 mrad. We analyzed 8 to 10 spectra acquired at different areas on the TEM grid for each sample. Figure S7 depicts the Fe  $L_{2,3}$  spectra of as-synthesized Au-Fe<sub>x</sub>O<sub>y</sub> core-shell NRs, standard samples of Fe<sub>x</sub>O<sub>y</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> after background subtraction, from which we were able to determine the Fe  $L_{2,3}$  white line ratio  $I(L_3)/I(L_2)$ . The same integration method was applied to all the spectra for the analysis of the white line. A list of the average width (full width at half maximum) of the white lines and relative intensities  $I(L_3)/I(L_2)$  are listed in Table S1.



**Figure S7.** EELS of Fe L-edge spectra after background subtraction for Fe<sub>x</sub>O<sub>y</sub> -tipped nanorods, Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

	Width of the white lines		Average relative intensity of the white lines
	$\Delta L_3$ (eV)	$\Delta L_2$ (eV)	$I(L_3)/I(L_2)$
Fe <sub>3</sub> O <sub>4</sub>	3.05±0.2	3.55±0.2	2.72±0.2
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	3.02±0.1	3.56±0.1	3.07±0.2
Fe <sub>x</sub> O <sub>y</sub> shell	3.26±0.1	3.75±0.1	2.78±0.2

**Table S1.** EELS analysis of the  $L_3$  and  $L_2$  white lines on the iron L edge for samples of Fe<sub>x</sub>O<sub>y</sub>-tipped nanorods, Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

### 13. Magnetic measurements

The magnetic properties of the samples were investigated by SQUID magnetometry, normalizing the results to the iron oxide mass in the samples. Measurements of static magnetization and hysteresis behavior were performed with a Quantum Design MPMS XL SQUID magnetometer. Zero-field-cooled (ZFC) magnetization curves were measured by cooling samples in a zero magnetic field and then increasing the temperature under an applied field of 1 KOe. Field-cooled (FC) magnetization curves were recorded during cooling of the samples under the same field of 1 KOe. The field dependence of the magnetization (hysteresis loop) was recorded at 10 K and 300 K. The saturation magnetization ( $M_S$ ) values were derived from corresponding plots of  $M$  versus  $1/H$  by extrapolation of the  $M$  values corresponding to  $1/H$  at 0.

#### References:

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