Electronic Supplementary Information (ESI)

Mesoporous Alloy Chiral Nanoparticles with High Production Yield and Strong Optical Activities

Yicong Ma,[a] Lin Yang,[b] Yu Chen,[c] Xiaopeng Bai,[d] Geping Qu,[e] Tao Yao,[f] Xiangchen Hu,[c] Jianfang Wang,[d] Zongxiang Xu,[e] Yi Yu,[c] and Zhifeng Huang[*f]*

[a]Department of Physics, Hong Kong Baptist University (HKBU), Kowloon Tong, Hong Kong SAR, China

[b]HKBU Institute for Research and Continuing Education Shenzhen, Guangdong 518057, China

[c]School of Physical Science and Technology, ShanghaiTech University, Shanghai, 201210, China

[d]Department of Physics, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR, China

[e]Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, China

[f]Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR, China
E-mail: zfhuang@cuhk.edu.hk

Experimental Methods

GLAD of the host Ag CNPs

The host CNPs were made of Ag. In a custom-built physical vapor deposition system (JunSun Tech Co. Ltd., Taiwan) with a high vacuum of 10^{-7}-10^{-6} Torr, metal pellets (Ag (99.999%), Fuzhou Innovation Photoelectric Technology Co., China) were evaporated at a rate of ≈0.3 nm s^{-1} as monitored by a quartz crystal microbalance (QCM) located near a substrate, using an electron-beam accelerating voltage of 8.0 kV, and emission current of 17–20 mA. At a deposition angle (a) of 86° with respect to the normal direction of a substrate, Ag was evaporated on Si wafers (Semiconductor Wafer Inc., Taiwan) and sapphires (Meco Technology Ltd., Hong Kong) in an area of 1.5 × 1.5 cm^2. The substrate temperature was controlled at ≈-45 °C, using an ethanol cooling system. To produce the RH- and LH-host with a given nominal helical pitch P, a substrate was rotated in clockwise and counterclockwise, respectively, at a rate R_r (in units of degree per second, or ° s^{-1}) given by

$$R_r = 360\, R_d/P_d \quad \text{(S1)}$$

where R_d is the deposition rate of Ag at the substrate surface calibrated as 0.045 nm s^{-1} at a of 86°, and P_d is the as-designed nominal P. The nominal P was experimentally evaluated by

$$P = H/m \quad \text{(S2)}$$

where H is the CNP height measured with scanning electron microscopy (SEM, Oxford, LEO 1530), and m is the number of substrate rotation during GLAD.

Physical vapor deposition of Au adhesion layers

The Au adhesion layer was deposited with Au (99.999%, Fuzhou Innovation Photoelectric Technology Co., China) at a of 0° and R_d = 0.3 nm s^{-1}, with an electron-beam accelerating voltage of 8.0 kV and emission current of 68–70 mA. The substrate was not rotated (R_r = 0 ° s^{-1}), and the substrate temperature was controlled as ≈-45 °C. T_{AL} was adjusted as a function of deposition duration.

GLAD of the host $Ag_{1-x}Au_x$ CNPs

GLAD of the host binary $Ag_{1-x}Au_x$ CNPs involved three sequential GLAD processes. The first and third step was the GLAD of the host Ag CNPs having a nominal P of roughly 8 nm and H of 40 nm. The second step was the deposition of dopant Au on the Ag CNPs, performed at a of 86°, substrate temperature of ≈ -45 °C, R_r = 0 ° s^{-1} (without substrate rotation) and R_d = 0.3 nm s^{-1}, using an electron-beam accelerating voltage of 8.0 kV and emission current of 68–70

mA. The binary host was deposited on the adhesion layer of Au covering the supporting substrate.

GRR of the host

In a homemade Teflon beaker, sapphire and silicon substrates deposited with the host were insert in a homemade Teflon holder and then immersed into a 200-mL electrolyte containing 20 μmol L^{-1} chloroauric acid ($HAuCl_4 \cdot 3H_2O$, 99.999%, Sigma-Aldrich) at a stirring rate of 380 rpm under 25°C. Before the GRR, the Teflon holder and beaker were degreased in Piranha (98% H_2SO_4: 30% H_2O_2 = 3:1, v/v) for 15 min at room temperature, sufficiently rinsed with DI water (18.2 MΩ, Milli-Q reference water purification system fed with campus distilled water), and dried with N_2 gases. After the GRR for 1–2 hr, the samples were removed out of the electrolyte to terminate the GRR and thoroughly rinsed with DI water and dried with N_2 gases.

Optical Characterization

Under ambient conditions, BioLogic CD (MOS 500) was used to monitor UV–visible–NIR extinction and CD spectra of a close-packed CNP array deposited on sapphire, under an irradiative incidence along the normal direction of sapphires. An extinction spectrum was monitored with an irradiation of linearly polarized light. For a given sample, four CD spectra in a wavelength range of 200-800 nm were subsequently recorded. After monitoring a CD spectrum, the sample was manually rotated at an angle of 90° around its normal axis before measuring the next CD spectrum. Then, the four CD spectra were algebraically averaged to obtain a CD spectrum of the sample, to eliminate linear birefringence and linear dichroism.

Structure Characterization

The as-deposited samples were mechanically split, leaving the freshly exposed surfaces for the SEM-EDX (Carl Zeiss: LEO 1530) characterization. The CNPs were scratched off the substrates and well dispersed in water via ultrasonication for 30 min. Several drops of the mixture were applied to a TEM grid with lacey carbon film (Electron Microscopy Sciences, Inc., USA). The grid was dried under ambient conditions and characterized by TEM (Tecnai G2 20 STWIN). The High-resolution TEM, HAADF-STEM and EDS mapping were performed with a JEOL JEM-F200 field-emission gun microscope (200 kV, fitted with a JEOL silicon drift detector). Without post-deposition treatment, the samples were characterized by XRD (Bruker, non-monochromated Cu Ka X-ray with wavelength of 0.15418 nm, Advance

D8 multipurpose X-ray diffractometer) and XPS (ULVAC PHI 5000 VersaProbe III, Al Ka radiation of 1486.6 eV, at a current of 4.5 mA, voltage of 10 kV, and takeoff angle (between the sample and detector) of 45°, and in a vacuum of $\approx 2 \times 10^{-9}$ mbar).

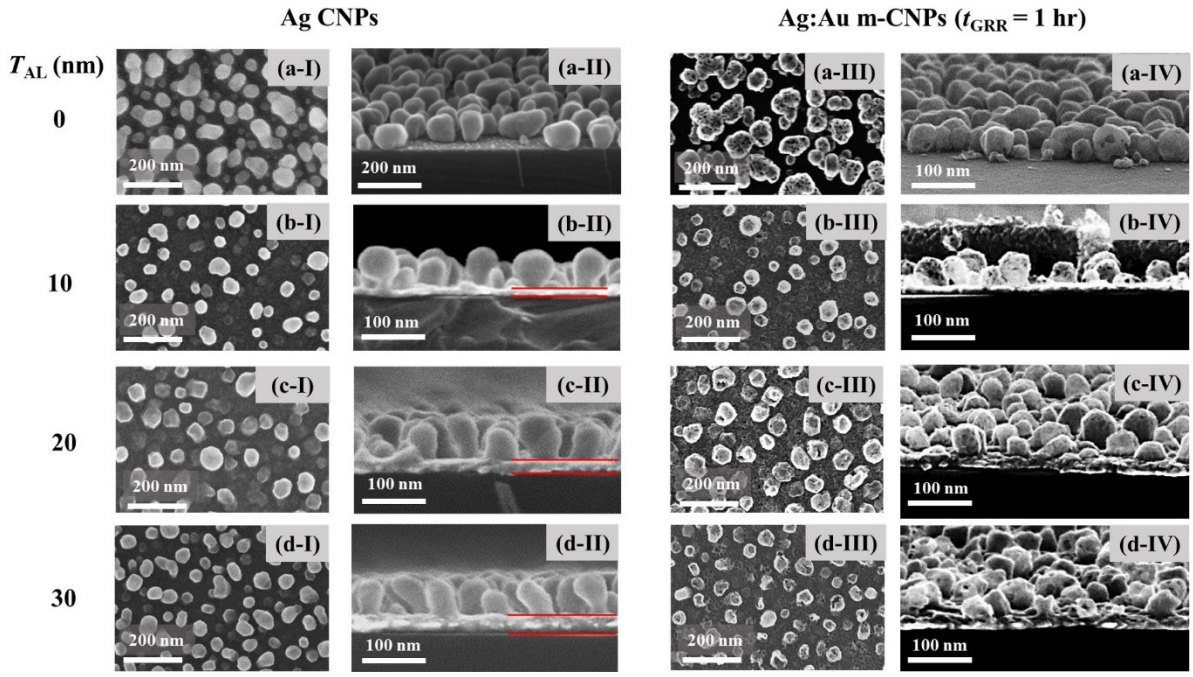

Figure S1. The GRR (t_{GRR} of 1 hr) of RH-Ag CNPs (with a nominal P of 8 nm and H of 80 nm) deposited on an Au adhesion layer with a T_{AL} of (a) 0 nm, (b)10 nm, (c) 20 nm, and (d) 30 nm. (I, II) Ag CNPs; (III, IV) Ag:Au m-CNPs. (I, III) SEM top-down images; (II, IV) SEM cross-sectional images. (b-II, c-II, and d-II) The red lines show T_{AL}.

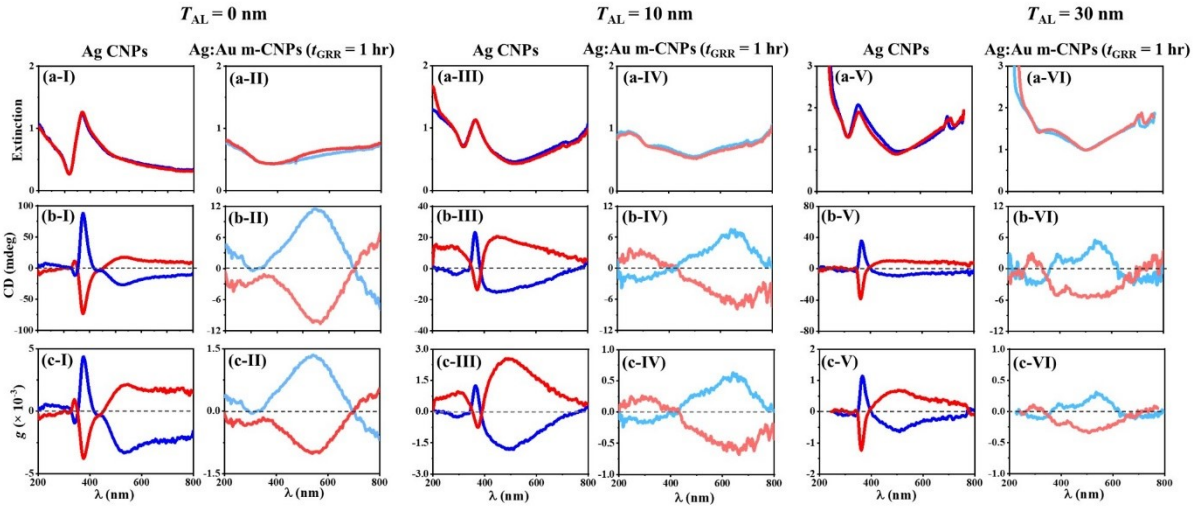

Figure S2. The 1 hr-GRR of Ag CNPs (with a nominal P of 8 nm and height H of 80 nm) deposited on an Au adhesion layer with a T_{AL} of (I, II) 0 nm, (III, IV)10 nm, and (V, VI) 30 nm, characterized with the UV-visible-NIR spectroscopies of (a) extinction, (b) CD, and (c) anisotropic g-factor. (I, III, V) Ag CNPs; (II, IV, VI) Ag:Au m-CNPs produced with the 1-hr GRR. LH: red and pink lines; RH: blue and cyan lines.

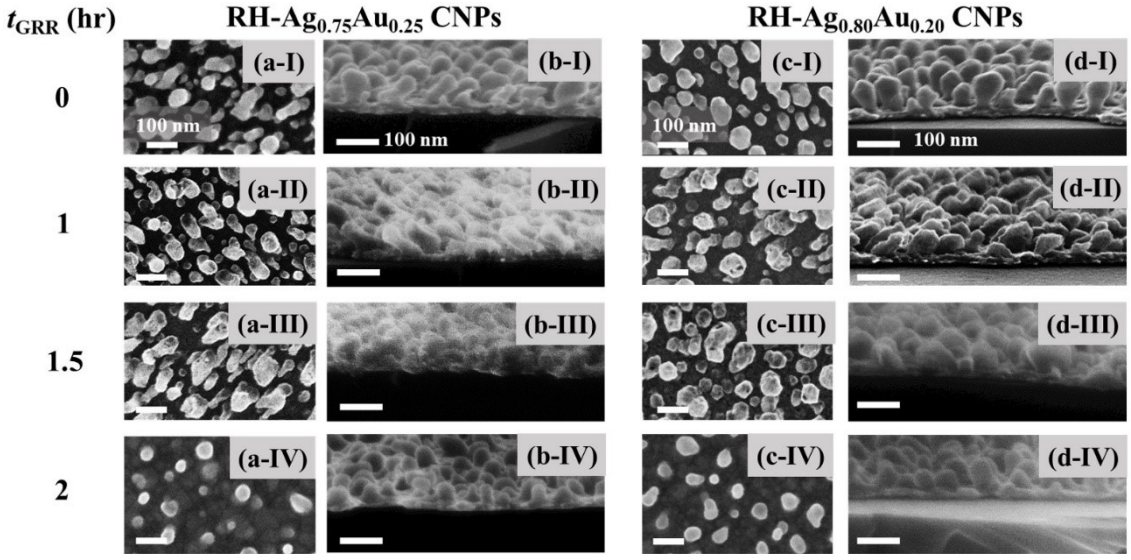

Figure S3. The GRR of (a, b) RH-$Ag_{0.75}Au_{0.25}$ and (c, d) RH-$Ag_{0.80}Au_{0.20}$ CNPs deposited on the Au adhesion layer (with T_{AL} of 20 nm), with the t_{GRR} of (I) 0, (II) 1, (III) 1.5 and (IV) 2 hr. SEM (a, c) top-down and (b, d) tilted images. Scale bars: 100 nm.

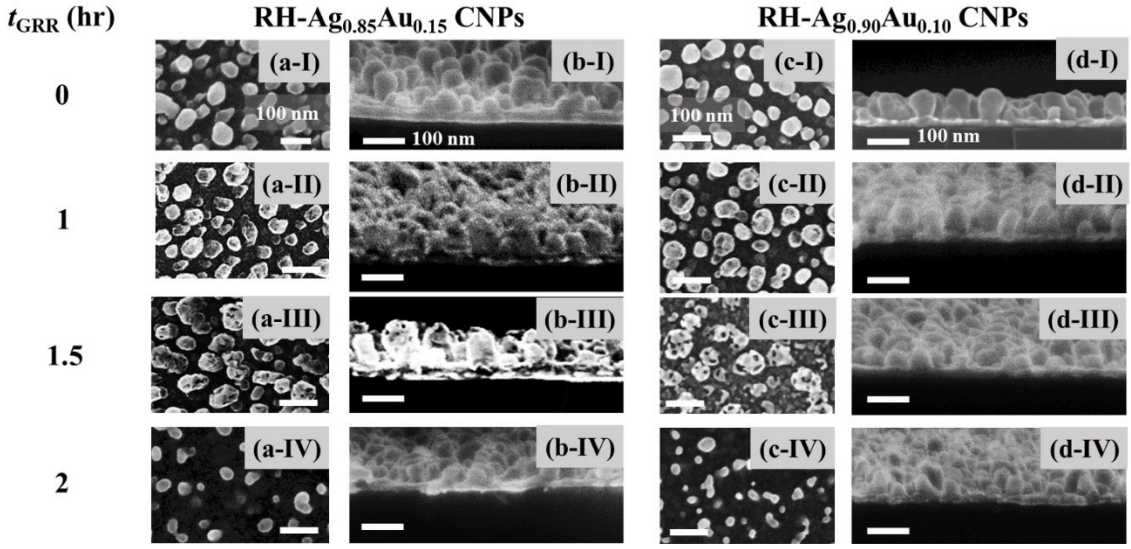

Figure S4. The GRR of (a, b) RH-$Ag_{0.85}Au_{0.15}$ and (c, d) RH-$Ag_{0.90}Au_{0.10}$ CNPs deposited on the Au adhesion layer (with T_{AL} of 20 nm), with the t_{GRR} of (I) 0, (II) 1, (III) 1.5 and (IV) 2 hr. SEM (a, c) top-down and (b, d) tilted images. Scale bars: 100 nm.

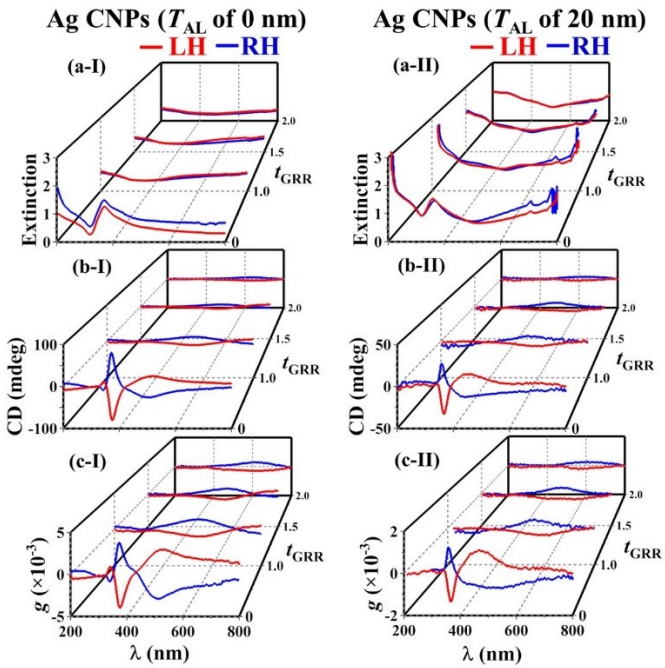

Figure S5. The GRR of Ag CNPs deposited on the Au adhesion layer with T_{AL} of (I) 0 nm and (II) 20 nm with the t_{GRR} increasing from 0 to 2 hr, characterized with UV-visible-NIR spectroscopies of (a) extinction, (b) CD, and (c) anisotropic *g*-factor. LH: red lines; RH: blue lines.

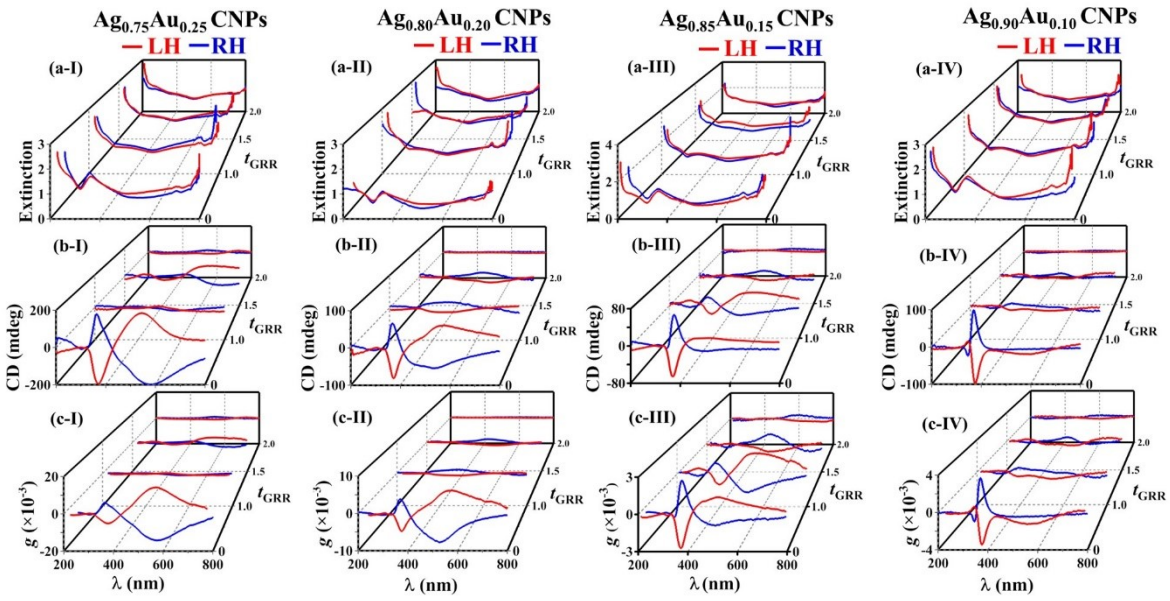

Figure S6. The GRR of (I) $Ag_{0.75}Au_{0.25}$, (II) $Ag_{0.80}Au_{0.20}$, (III) $Ag_{0.85}Au_{0.15}$, and (III) $Ag_{0.90}Au_{0.10}$ CNPs (deposited on the Au adhesion layer with the T_{AL} of 20 nm) with the t_{GRR} increasing from 0 to 2 hr, characterized with UV-visible-NIR spectroscopies of (a) extinction, (b) CD, and (c) anisotropic *g*-factor. LH: red lines; RH: blue lines.

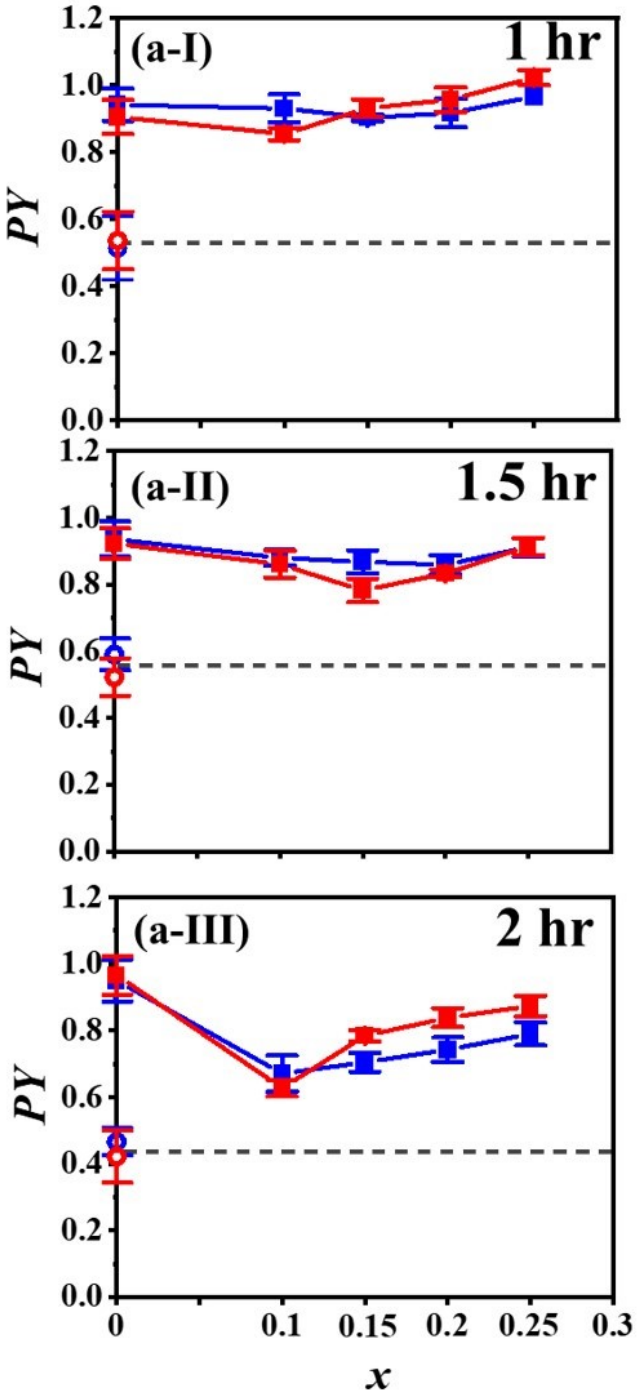

Figure S7. Plots of PY versus x for the GRR of binary $Ag_{(1-x)}Au_x$ CNPs (deposited on the Au adhesion layer with the T_{AL} of 20 nm) with the t_{GRR} of (I) 1 hr, (II) 1.5 hr, and (III) 2 hr. LH: red solid squares; RH: blue solid squares. The results for the GRR of LH- and RH-Ag CNPs (without the Au adhesion layer) are shown with red and blue hollow spheres, respectively.

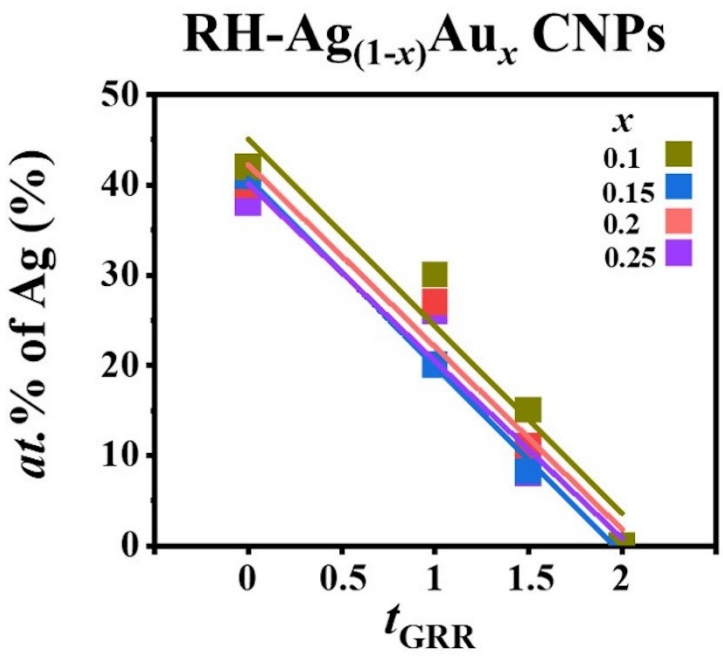

Figure S8. Plot of atomic percentage (at.%) of Ag in the RH-Ag:Au m-CNPs versus t_{GRR}, for the GRR of RH-$Ag_{(1-x)}Au_x$ CNPs deposited on the Au adhesion layer with the T_{AL} of 20 nm. x of 0.10 (Olive-green squares), 0.15 (blue squares), 0.20 (pink squares), and 0.25 (purple squares). The linear fitting leads to the evaluation of r_{GRR} as a function of x, as shown in **Figure 2c**.