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Supporting Information

Scattering-Mediated Absorption from Heterogeneous Nanoparticle Assemblies in Diblock Copolymer Micelles for SERS Enhancement

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Experimental details on the encapsulation of Au NPs in the core of PS-PAA micelles

A mixture solution of 2-naphthalenethiol-coated Au NPs and the PS-PAA copolymers was prepared in *N*,*N*-dimethylformamide (DMF). Since DMF is a good solvent for both the Au NPs and PS-PAA copolymers, micellization could not occur at this stage. To prepare micelles, deionized water was added to the DMF solution (H_2O/DMF = ~18 vol%) and the solution was heated to 110 °C for 2 h. Although water is a selective solvent for the PAA block, the PS-PAA copolymers were present in their unimeric state without aggregation under these conditions because the temperature was above the critical micelle temperature.[1,2] During the cooling process, however, the PS-PAA copolymers started to associate into spherical micelles consisting of a PS core and a PAA corona. At the same time, 2-naphthalenethiol-coated Au NPs were encapsulated into the core of micelles to avoid unfavorable contact with H_2O/DMF. The resulting solution was dialyzed against deionized water, purified by centrifugation, and re-dispersed in deionized water to completely remove DMF and residual chemicals.

Experimental details on the synthesis of Ag NPs in the corona of PS-PAA micelles

To synthesize Ag NPs, an aqueous solution of $AgNO_3$ was added to the solution of Au@PS-PAA micelles to coordinate the carboxylate anions in the PAA block with Ag^+ ions. In this step, it must be noted that the –COOH groups in the PAA block are weak acids. Owing to the low degree of ionization of –COOH ($pK_a = 4.5 – 6.5$),[3] the added Ag^+ ions could not be fully coordinated to PAA blocks. Otherwise, many Ag^+ ions were present in the free state in the aqueous solution. For this reason, the simple addition of common reducing agents such as $NaBH_4$ to the micellar solution entailed the uncontrolled reaction of Ag^+ in the solvent phase, and precipitates occurred at the bottom of the solution. To solve this problem, we applied a photo-reduction method by irradiating the micellar mixture with UV light as described in our previous report.[2] The carboxylate anions in the PAA block can be photo-excited by UV irradiation to assist the reduction of the immobilized Ag^+ ions. In this study, we modified the method by employing hydroquinone as secondary reducing agent. After UV treatment for 3 h, hydroquinone was added to the micellar solution and the reaction mixture was allowed to stand for at least 3 h. Here, hydroquinone provided another selective condition; the standard reduction potential of hydroquinone ($E^0 = -0.699$ V) was unable to overcome the potential barrier for the reduction of the Ag^+ ions themselves ($E^0 = -1.8$ V), but Ag^+ ions could be reduced when pre-formed seeds or Ag NPs were present in the solution ($E^0 = +0.799$ V).[4,5]

TEM image of PS-PAA micelles with Au NPs without surface modification

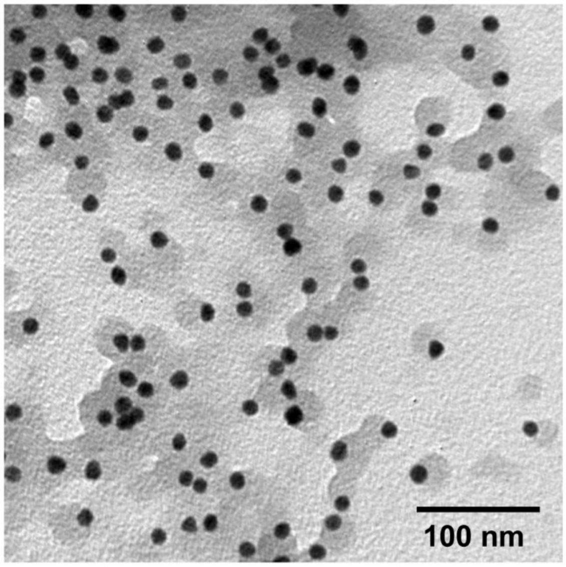

Figure S1. TEM image of PS-PAA micelles with Au NPs. The NPs were mostly placed at the peripheral region of micelles, forming cherry-like morphology.

UV-Vis spectra in the absence PS-PAA micelles

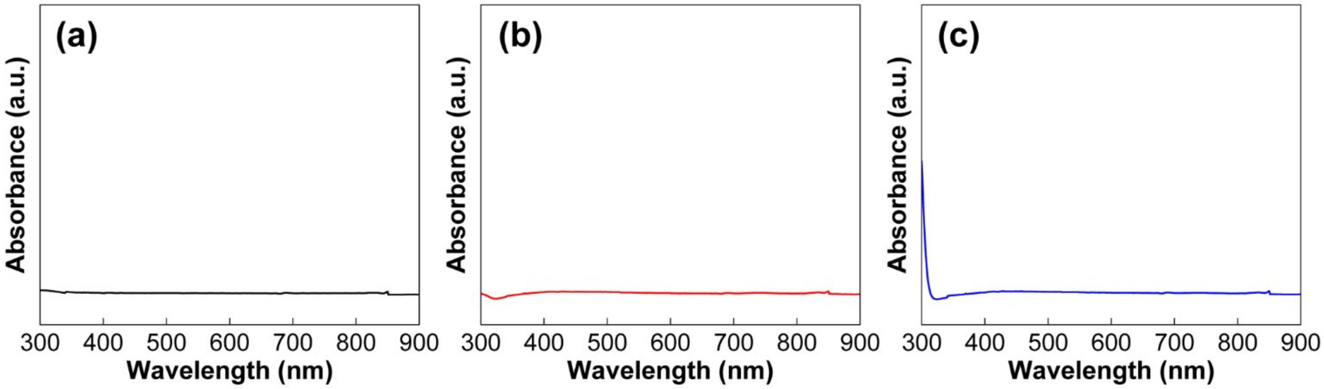

Figure S2. UV-Vis spectra: (a) aqueous $AgNO_3$ solution; (b) after being exposed to UV light; (c) after the addition hydroquinone. The experimental condition including the concentration of $AgNO_3$ and hydroquinone was identical to that described in the main text.

Additional TEM image of Au@PS-PAA@Ag assemblies

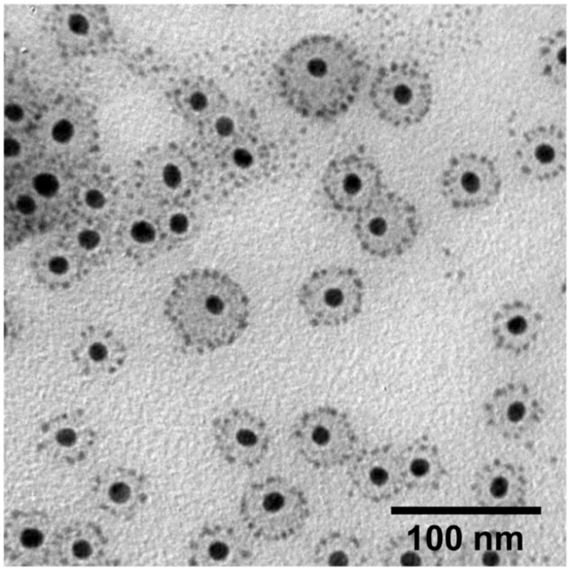

Figure S3. TEM image of Au@PS-PAA@Ag assemblies with unbound Ag NPs.

EDX spectra from Au@PS-PAA@Ag assembly

For the chemical analysis of Au@PS-PAA@Ag assembly, EDX spectra were collected from the circled and crossed points in the TEM image of Figure S4a. From the circled point, the characteristic X-ray peaks corresponding to Au were solely obtained in Figure S4b. From the crossed point, the characteristic X-ray peaks for Ag were obtained in Figure S4c.

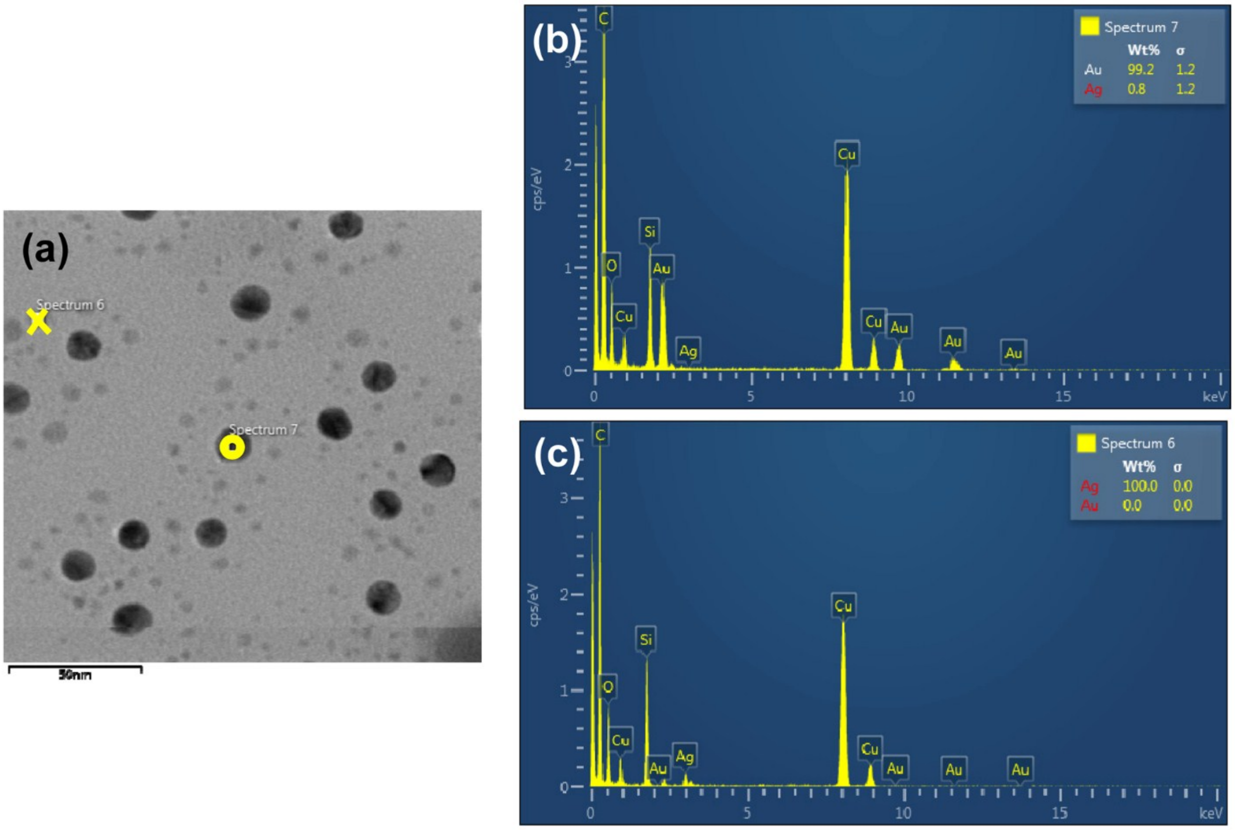

Figure S4. (a) TEM image of Au@PS-PAA@Ag assembly. (b, c) EDX spectra from the circled (b) and crossed (c) points in the TEM images, respectively.

Comparison of Raman spectra from 2-naphthalenethiol-coated Au NPs, Au@PS-PAA micelles, and Au@PS-PAA@Ag assemblies

Since SERS effect of 12 nm-sized Au NPs is relatively weak, we utilized 50 nm-sized Au NPs for the comparison in Figure S5. The Raman spectra from Au@PS-PAA micelles and Au@PS-PAA@Ag assemblies were extracted from Figure 4e (Main Text) and re-plotted in a different y-scale. On the other hand, Raman spectrum of 2-naphthalenethiol-coated Au NPs (50 nm in a diameter) were collected after dropping the NP solution on glass slide.

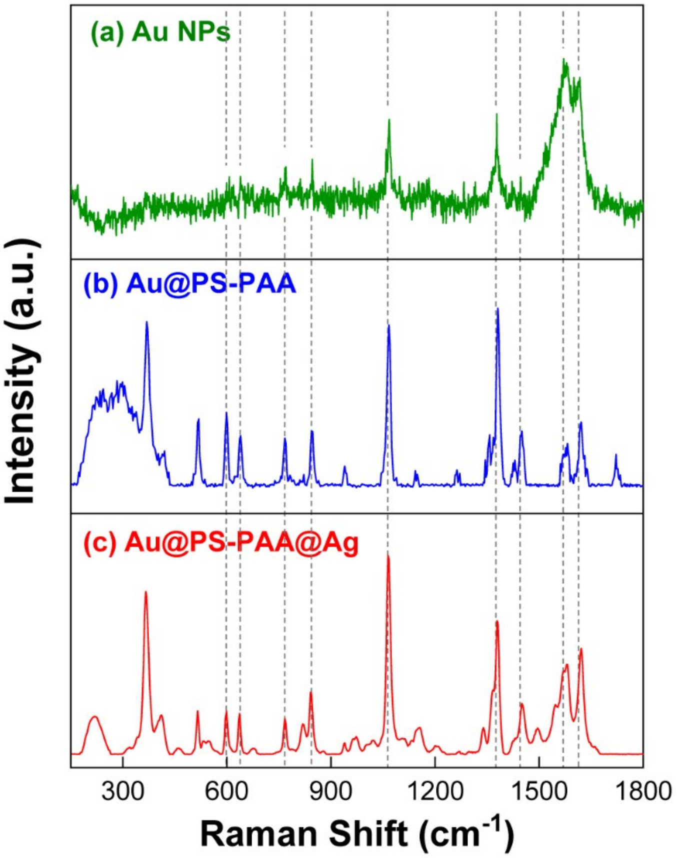

Figure S5. Raman spectra from 2-naphthalenethiol-coated Au NPs (a), Au@PS-PAA micelles (b), and Au@PS-PAA@Ag assemblies (c).

Raman spectra of 2-naphthalenethiol in acetone

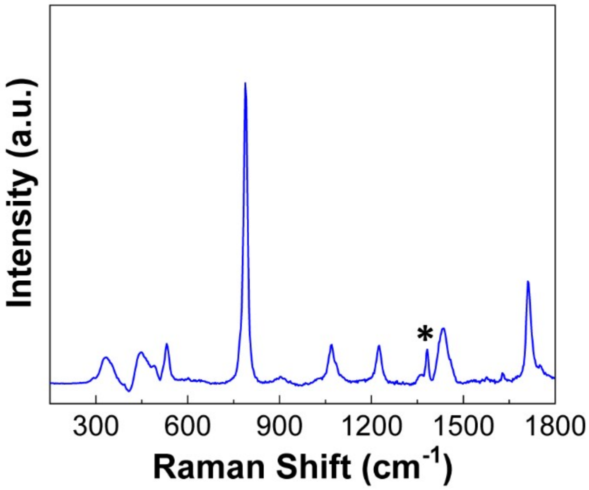

Figure S6. Raman spectra of 2-naphthalenethiol in acetone (0.075 M). Raman peak at 1378 cm^{-1} was marked as asterisk. The excitation wavelength was 633 nm for the evaluation of enhancement factor.

TEM image of citrate-reduced Ag NPs

The citrate-coated Ag NPs had been synthesized according to a literature.[6] Briefly, a reaction medium (55.2 mL) containing $AgNO_3$ (0.021 g) and trisodium citrate dehydrate (0.106 g) in deionized water was prepared. Subsequently, a freshly-prepared 0.1 M $NaBH_4$ solution (4.8 mL) was added dropwise into the reaction medium under vigorous stirring at 60 °C. The synthesis of Ag NPs could be discernible by the color change of the solution. After stirring for 2 hr, the resulting solution was filtered through a 0.45 μm membrane filter and stored at 4 °C in the dark.

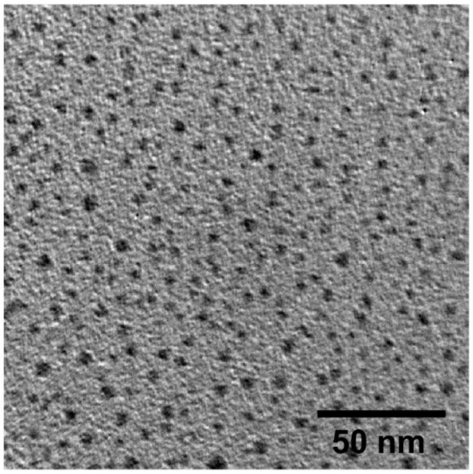

Figure S7. TEM image of citrate-reduced Ag NPs.

Calculated extinction, absorbance, and scattering spectra of Ag and Au NPs

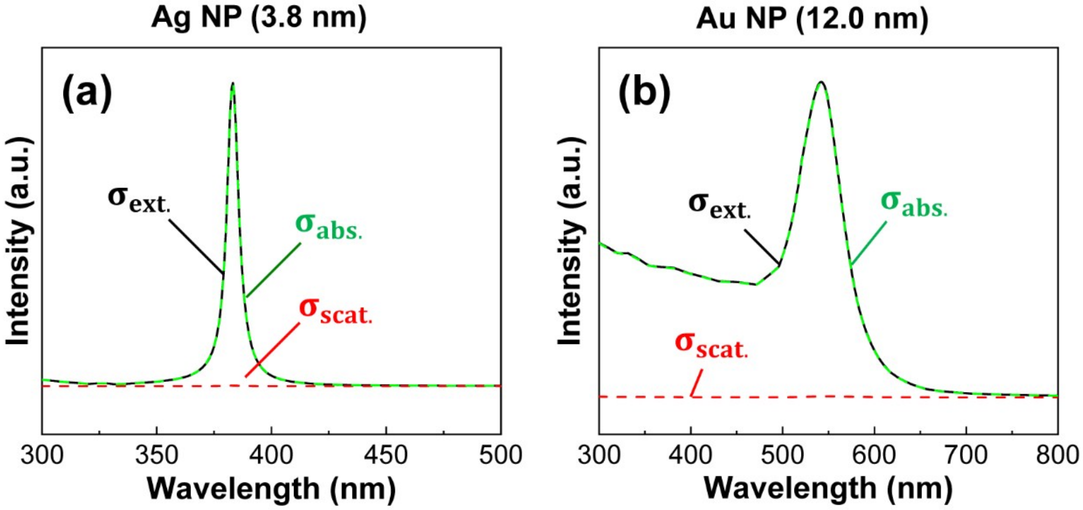

Figure S8. Calculated extinction (black line), absorption (dotted green line), and scattering (dotted red line) spectra of Ag (a) and Au (b) NPs. Open-source Mieplot v4400 program was utilized for the calculation by specifying (a) the diameter (3.8 nm) and the refractive index of surrounding medium (n = 1.33, water) for Ag NPs, and (b) the diameter (12.0 nm) and the refractive index (n = 1.59, PS block) for Au NPs.

Dark-field microscope image

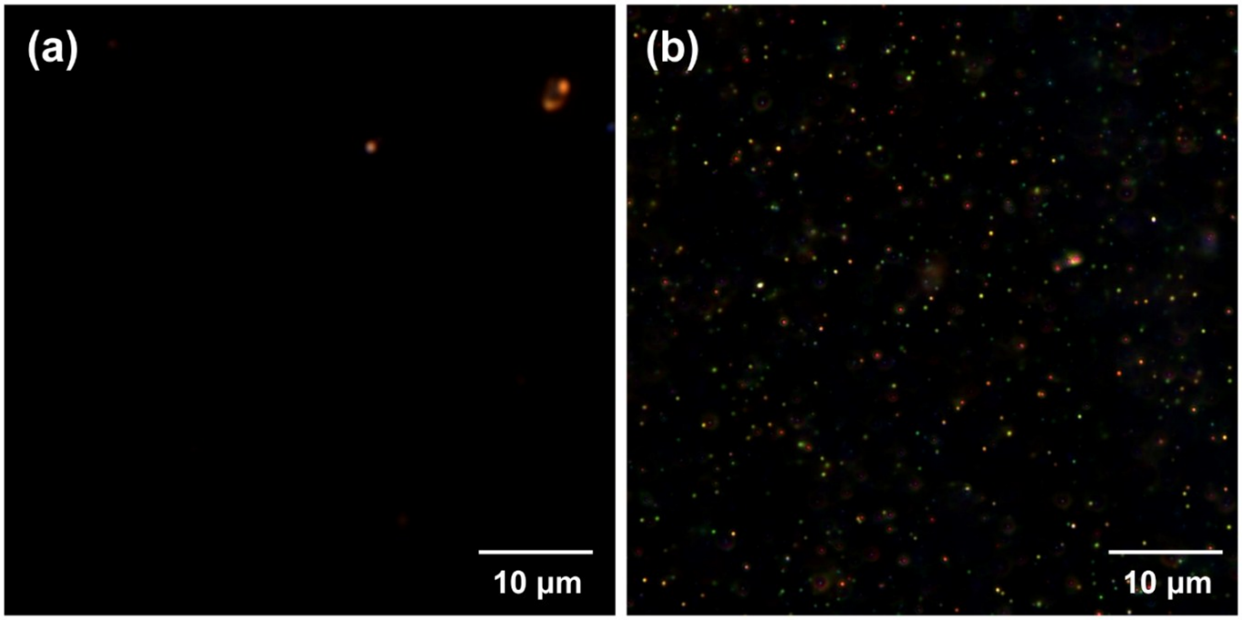

Figure S9. Dark-field images from bulk films Au@PS-PAA (a) and Au@PS-PAA@Ag (b) assemblies in the enlarged areas.

SEM images of bulk films of Au@PS-PAA@Ag assemblies

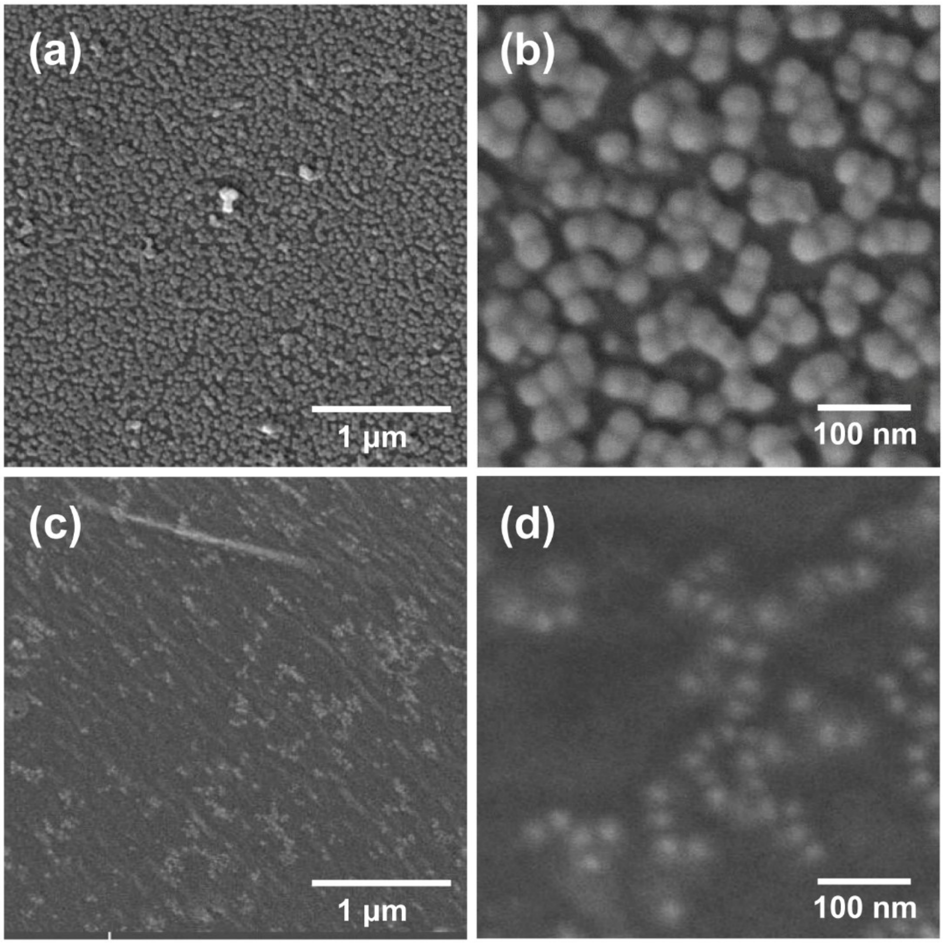

Figure S10. SEM images of bulk films of Au@PS-PAA@Ag assemblies in different magnifications. (a, b) without the addition of PVP homopolymer; (c, d) with the addition of PVP homopolymer.

Measurement of scattered light

The measurement of scattered light was conducted as described in the literature.[7] As shown in Figure S11a, the experimental setup was mainly composed of a light source (He-Cd laser, wavelength = 442 nm), a spectrograph (Andor Shamrock SR-303i-A), and a CCD camera (DV420A-OE). In this experiment, we adjusted the laser intensity via attenuating lens having different transmittance, and measured scattered lights from Au@PS-PAA@Ag assemblies (Figure S11b), Au@PS-PAA micelles (Figure S11c), and pure water (Figure S11d) from the perpendicular direction to the incident laser. The maximum intensities from each solution were re-presented in the Main Text (Figure 3e)

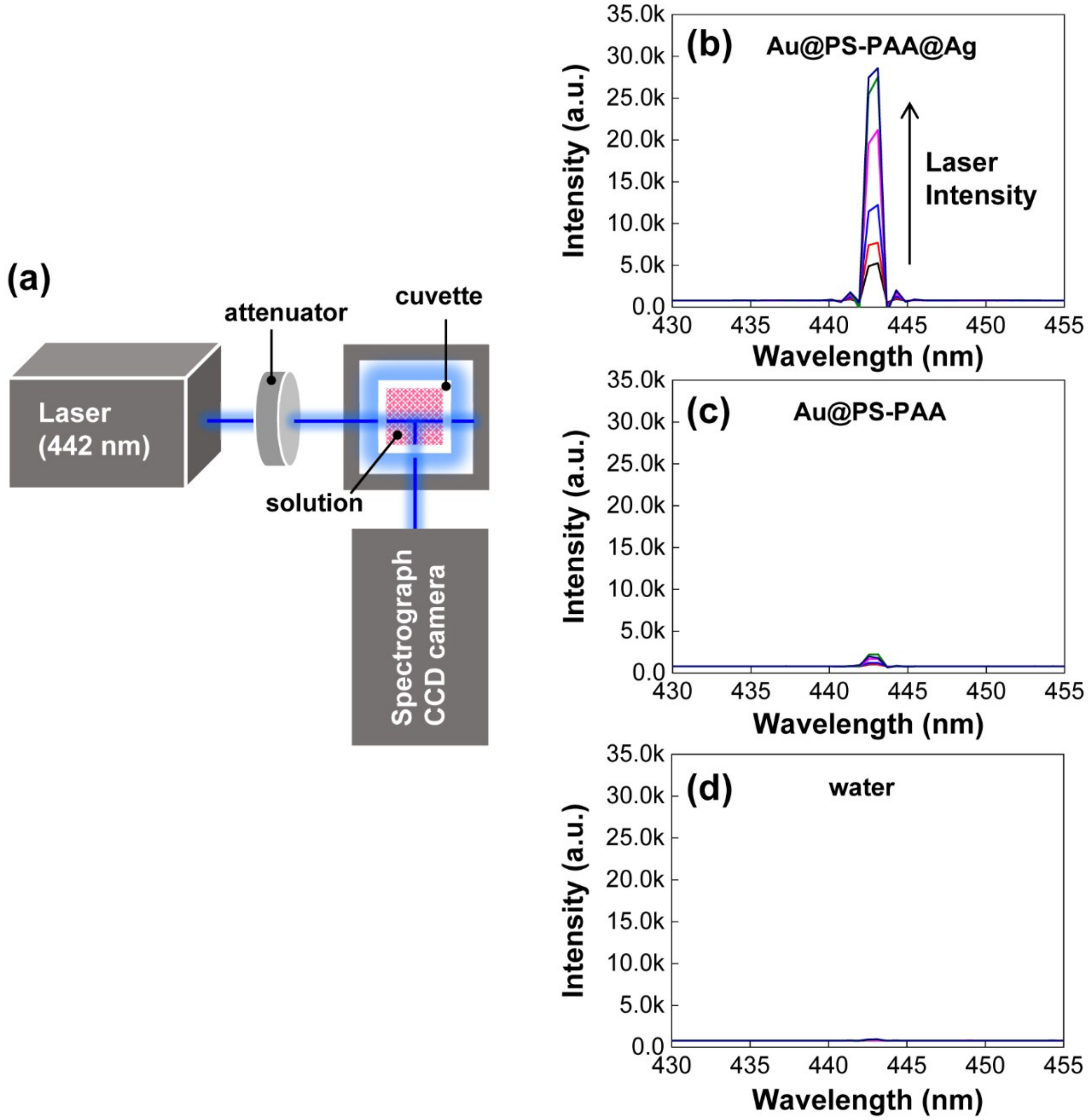

Figure S11. (a) Schematics for experimental setup, (b – d) The measurement of scattered lights from Au@PS-PAA@Ag assemblies (b), Au@PS-PAA micelles (c), and water (d).

Adjustment of concentration of Au@PS-PAA micelles and synthetic condition for Ag NPs

The molar extinct coefficient of Au NPs and diameter of Au NPs have linear relationship in logarithmic scale as [8]

$$\ln \varepsilon = k \ln D + a \text{ --------------- (S1)}$$

where ε is the molar extinction coefficient of Au NPs in $M^{-1}cm^{-1}$, D is the diameter of Au NPs in nm, k = 3.32111, and a = 10.80505, respectively. Therefore, by determining D from TEM images, the molar extinction coefficient of Au NPs can be determined from equation (S1), Once ε is known, the molar concentration of Au NPs (C) can be calculated by measuring absorbance (A) from Lambert-Beer law of $A = \varepsilon b C$, where, b is path length of the beam of light through the solution in cm.

Note, the equation (S1) has been found to be valid independent of capping agent on the NP surface and the solvent condition.[8] Hence, we applied the equation (S1) to calculate the molar extinction coefficient of Au NPs in the form of Au@PS-PAA micelles. Then, absorbance values of each solutions of Au@PS-PAA micelles were adjusted, so that the molar concentrations of all the Au@PS-PAA micelles with different-sized Au NPs can be identical as 0.162 nM; this corresponded to UV-Vis absorbance values of 0.03 (for the case of 12 nm Au NPs), 0.40 (for 26 nm Au NPs), 1.67 (for 40 nm Au NPs), and 3.50 (for 50 nm Au NPs).

It needs to be noted that, under the same molar concentration, the number of PS-PAA polymers for coating Au NPs in the form of Au@PS-PAA micelles increases with the NP diameter. Therefore, to compensate the increased number of PAA blocks in the synthesis of Ag NPs, we increased the amount of $AgNO_3$ (10 mM) and hydroquinone (10 mM) to 50 µL for Figure 4 (in the main text) without changing other experimental condition. Note, 30 µL solutions of $AgNO_3$ (10 mM) and hydroquinone (10 mM) were utilized to prepare Au@PS-PAA@Ag assemblies in Figure 1 – 3 (in the main text).

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