Electronic Supporting Information

Optical Tuning of Plasmon-Enhanced Photoluminescence

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1. Characterizations of the Au@Ppy NPs

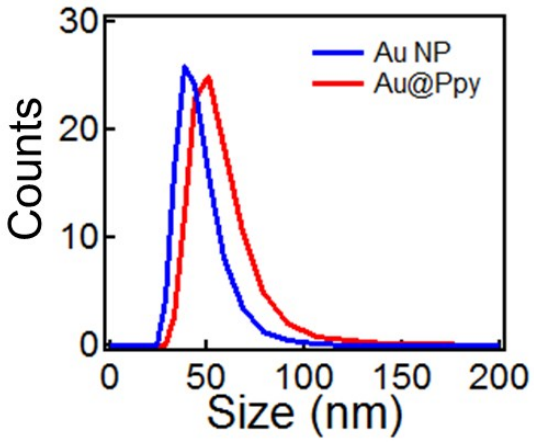


Fig. S1. Dynamic light scattering spectra of Au NPs and Au@Ppy NPs.

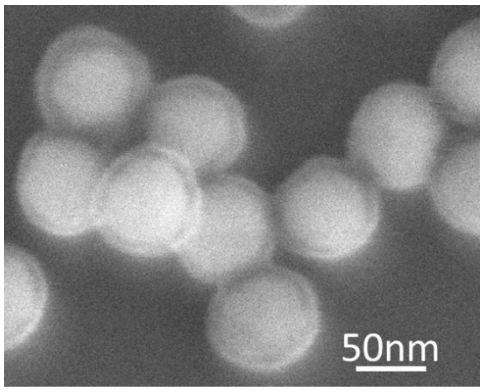


Fig. S2. SEM image of the Au@Ppy NPs (shell thickness: ~7 nm).

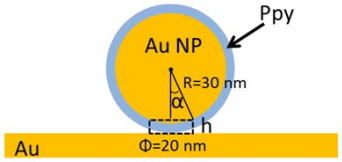
2. Enhancement factor (EF) calculation:

The EF is defined as

$$EF = \frac{I_{NP}/V_{NP}}{I_{Ppy}/V_{Ppy}} \quad (1),$$

where I_{NP} and I_{Ppy} are the PL intensities of Au@Ppy NPoM and Ppy particles at the peak wavelengths respectively, V_{NP} and V_{Ppy} are the volume of Ppy coatings in the gap and the spheres respectively.

For the values of I_{NP} and I_{Ppy}, they can be read directly from the spectra under same excited power of laser (350 μW). In our calculation, these values are extracted from the fitted peaks of the averaged spectra (Fig. 2g). For the volume of NPoM, we consider the major contribution of the PL intensity is coming from the nanogap region, which can be estimated as a cylinder (dash-framed in Scheme. S1) with diameter of ~20 nm (facet size of 60 nm Au NPs). The height (h) of the cylinder is equivalent to the shell thickness. For the volume of Ppy, it is based on the calculation from its SEM image (Fig.S4c), which is 1.336×10^{-3} μm^3.



Scheme S1. Geometry of Au@Ppy NPoM.

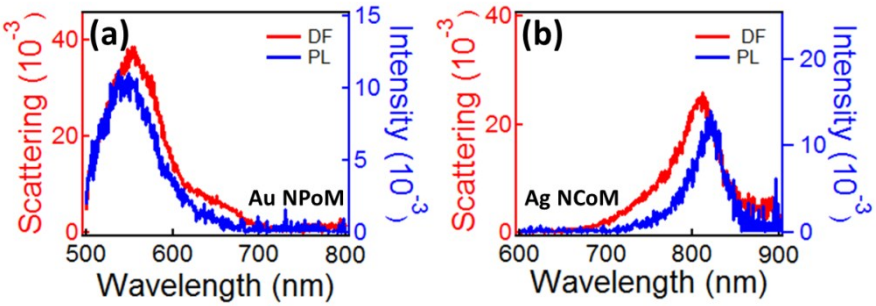


Fig. S3. DF and PL spectra of (a) 100 nm Au NPoM and (b) 100 nm Ag nanocube on mirror (NCoM).

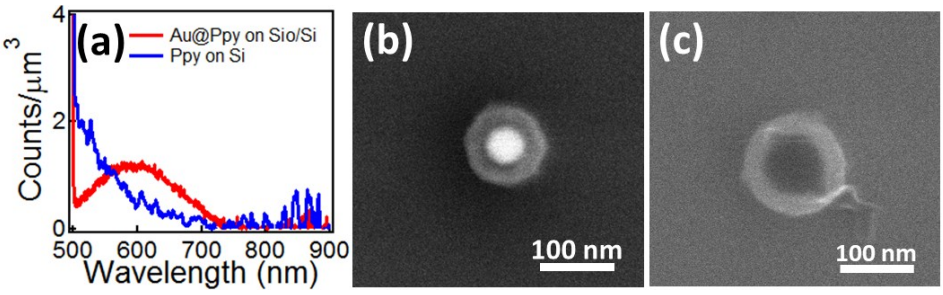


Fig. S4. (a) PL spectra of Au@Ppy NP and Ppy bead on Si substrate and (b, c) their corresponding SEM images. (b) Au@Ppy NP, (c) Ppy bead.

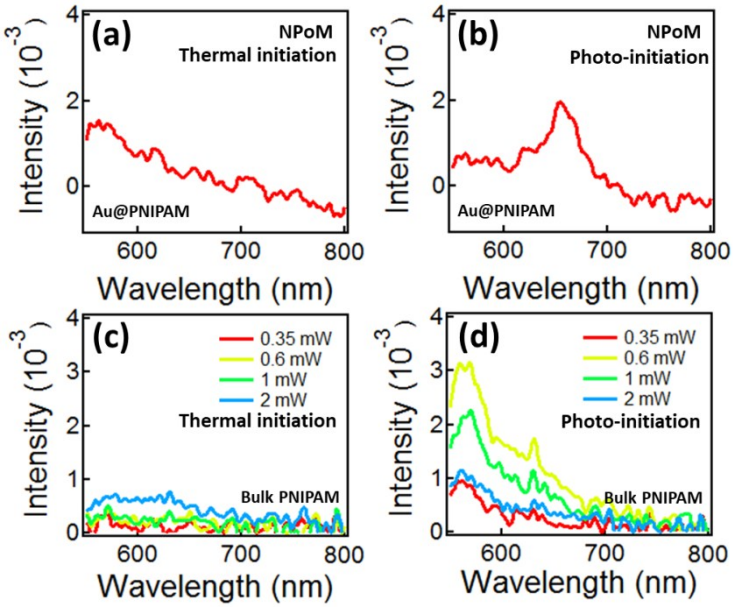


Fig. S5 PL spectra of (a, b) Au@PNIPAM NPoMs and (c, d) PNIPAM beads with (a, c) thermally initialized PNIPAM coatings ($K_2S_4O_8$ as the initiator) and (b, d) photo-initialized PNIPAM coatings (2-hydroxy-2-methylpropio-phenone as the photo-initiator). Clearly, the PL signals mainly come from the incorporated segment of photo-initiators but neither from the PNIPAM chains, nor from the plasmon gap emission.

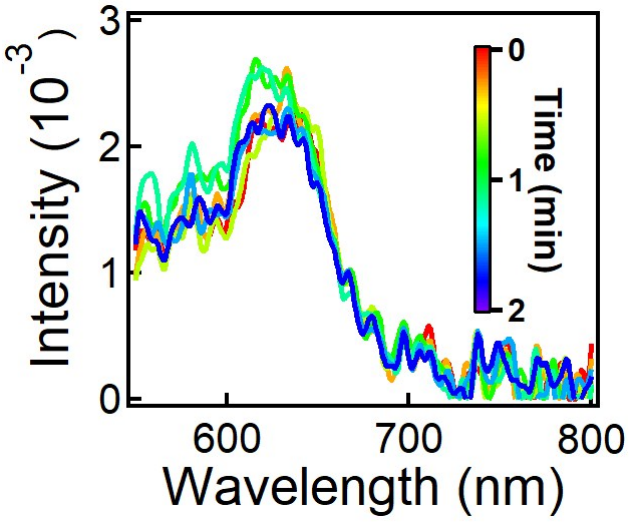


Fig. S6 Time-dependent PL spectra of Au@PNIPAM NPoM system under the irradiation of 532 nm laser (0.35 mW).