Electronic Supplementary Information (ESI)

Micromotor Based on Polymer Single Crystal and Nanoparticle: Toward Functional Versatility

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Experimental Section

Materials: $AuCl_3$, ε-caprolactone, 2-mercaptoethanol, Candida antarctica lipase B (CALB), silver enhancer kit, lipase from Pseudomonas cepacia, 1-butanol, pentyl acetate, Rhodamine B isothiocyanate, Rhodamine 6G (R6G), 10 nm iron oxide nanoparticle (Fe_3O_4NP) and hydrogen peroxide were obtained from Sigma Aldrich Company. Thiol end-functionalized polycaprolactone (PCL-SH) and 6 nm AuNP were synthesized following literature methods.[1,2]

Fabrication Methods: Polymer single crystals were prepared using a self-seeding technique.[3] In brief, PCL-SH (9 mg) was first dissolved in 1-butanol (30 g) at 60 °C for 10 min, after which, the solution was cooled to 5 °C and isothermally crystallized at 5 °C for 2 h. The crystal seeds were obtained by re-heating the solution to 46 °C for 10 min. Polymer single crystals were formed by allowing the above solution to crystallize at 22 °C for 24 h. Uncrystallized polymers were removed by isothermal filtration. To attach 6 nm AuNP, the solvent for polymer single crystal was first exchanged from 1-butanol to pentyl acetate by centrifugation method. Then, AuNP solution was mixed with polymer single crystal's pentyl acetate solution with 1 to 5 weight ratio and stirred for 24 h. Free AuNPs were removed by centrifugation. Ag-PCL was obtained by treating this AuNP-decorated polymer single crystal with silver enhancer kit.[4,5] Centrifugation was utilized to remove free AgNP in water. The final Ag-PCL is dispersed in water or PBS buffer for further micromotor study. To attach Fe_3O_4NP, Fe_3O_4NP's toluene solution was mixed with Ag-PCL's pentyl acetate solution with 1 to 10 weight ratio for 24 hrs. Excess Fe_3O_4NPs were removed by centrifugation. The introduction of RhBITC onto Ag-PCL surface was achieved by mixing Ag-PCL with 2 mM RhBITC aqueous solution for 12 h.[6] Un-attached RhBITC molecules were removed by centrifugation process. The enzymatic disassembly is done by mixing Ag-PCL or Ag-PCL-RhBITC

with lipase from Pseudomonas cepacia in PBS buffer at 37 °C.[7,8] After different periods of time, Ag-PCL or Ag-PCL-RhBITC is sampled and analyzed using TEM or fluorescence microscopy.

Characterizations: UV-Vis spectra were carried out on a Lambda 750 Spectrometer. TEM experiments were performed on a FEI Tecnai-F20 TEM operated at an acceleration voltage of 200 kV. TEM sample was prepared by drop-casting single crystal suspension on a carbon-coated nickel grid. Solvent was allowed to evaporate before TEM examination. For micromotor study, Ag-PCL is first placed in water or PBS buffer containing H_2O_2. The motion is then observed and recorded by a Nikon Eclipse 80i microscope. The motion analysis for the captured video is done using PhysVis software. The remote control under magnetic field is realized by placing a neodymium (NdFeB) magnet 5 cm far from the sample. Fluorescent images were captured using a Leica DM4000M fluorescence microscope. AFM image was obtained on a Bruker Dimension Scanning Probe Microscope. SERS experiment was performed on a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer. The 633 nm excitation laser was focused on Ag-PCL dispersed in solutions containing different concentrations of R6G through a long working distance 50× objective to a spot size of approximately 2 μm. The acquisition time for all spectra was 1 s.

Video S1: An individual Ag-PCL micromotor moving autonomously in circles.

Video S2: Large area view of the movement of Ag-PCL in 10% H_2O_2 aqueous solution.

Video S3: Autonomous movement of Ag-PCL in 1× PBS buffer containing 10% H_2O_2.

Video S4: Remote control of Ag-PCL with attached Fe_3O_4NP by applying an external magnetic field.

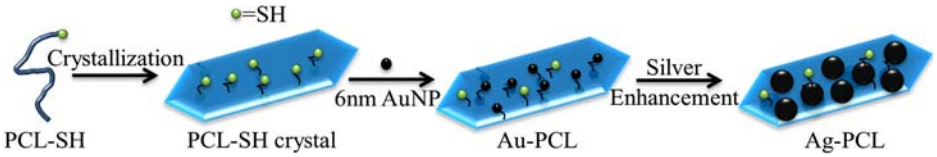

Fig. S1 Schematic illustration showing the fabrication process of Ag-PCL.

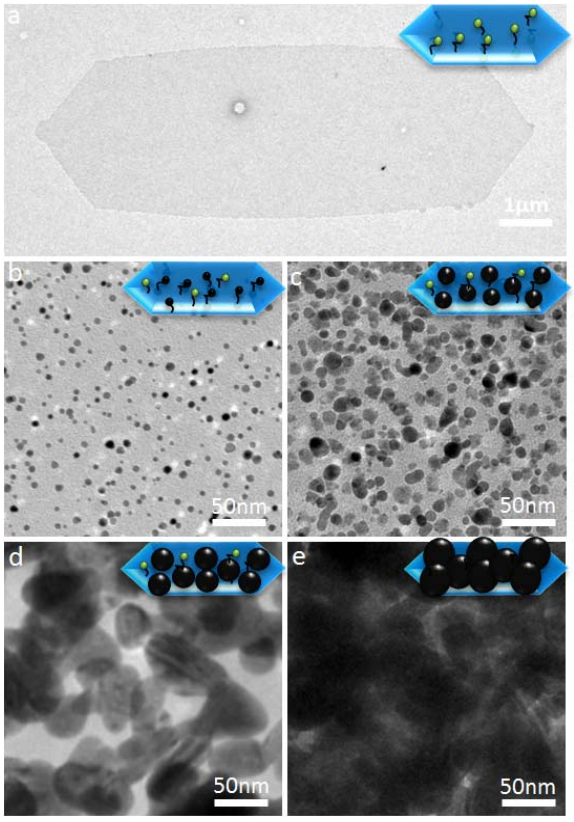

Fig. S2 TEM images of PCL-SH single crystal before (a) and after (b) AuNP decoration. TEM images of AuNP decorated PCL-SH after (c) 1 min, (d) 3 min and (e) 5 min silver enhancement.

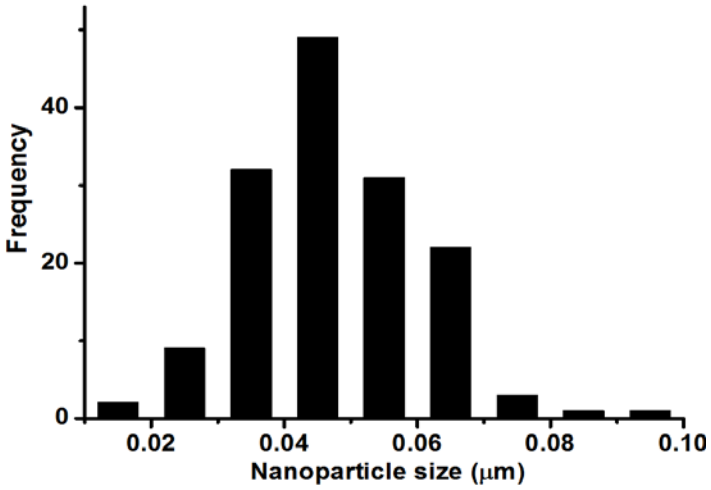

Fig. S3 Size distribution histogram of AgNPs measured from Fig. 1b in the main text.

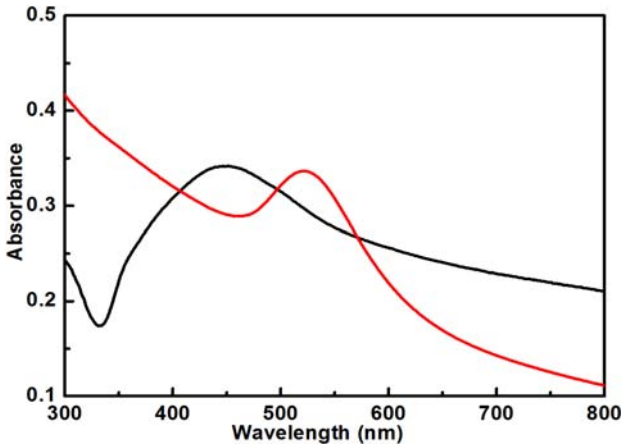

Fig. S4 UV-Vis spectra of AuNP decorated PCL-SH (red curve) and AuNP decorated PCL-SH after 3 min silver enhancement (black curve).

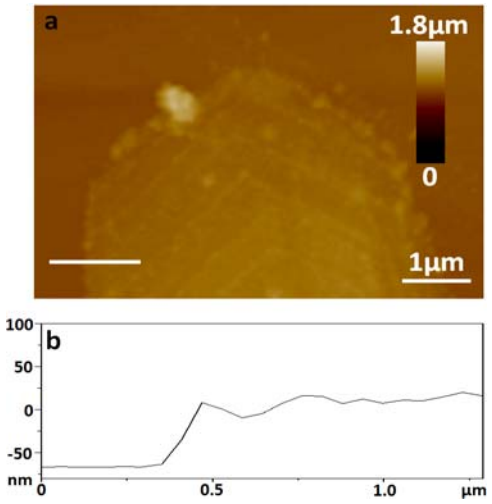

Fig. S5 (a) AFM image of Ag-PCL. (b) AFM cross section analysis of (a).

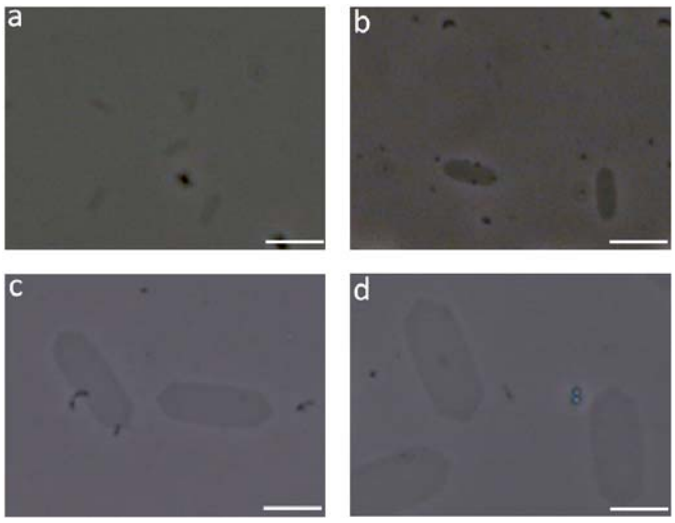

Fig. S6 Polymer single crystal grown at different seeding temperature (a) 44 °C (b) 45 °C (c) 46 °C (d) 47 °C. Scale bar: 5 µm.

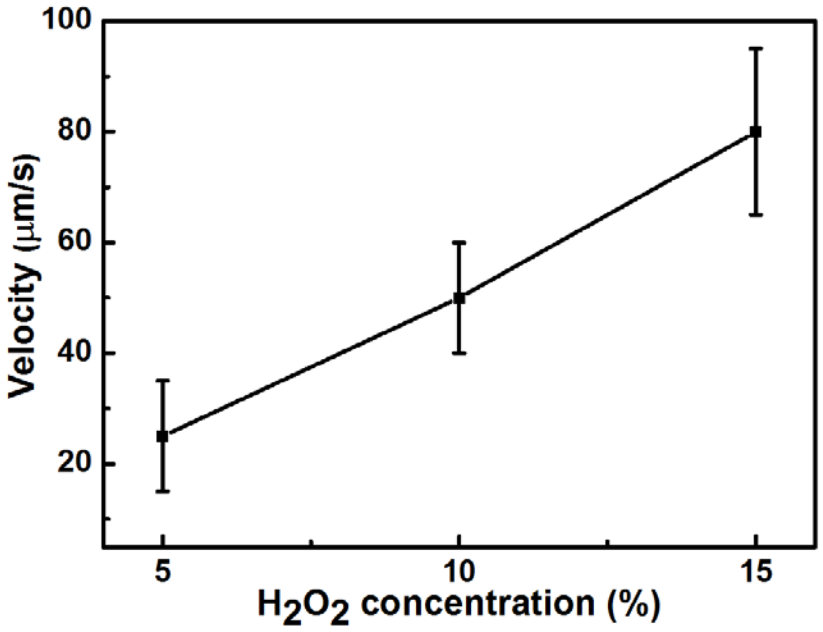

Fig. S7 Velocity of Ag-PCL micromotor at different H_2O_2 concentrations. Error bars indicate the standard deviation.

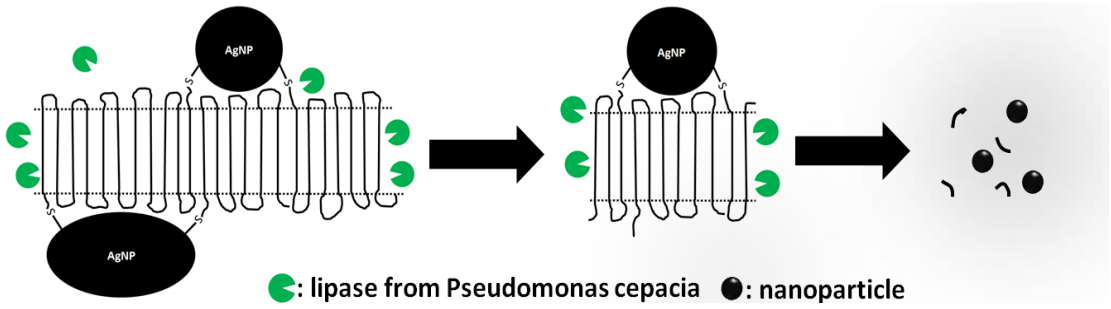

Fig. S8 Schematic illustration showing the enzymatic disassembly of Ag-PCL.

Supplementary References

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