Supporting Information

Facile one-pot synthesis of mulberry-shape silver nanoparticles-doped porphyrin nanoassembly with self-promoted electrochemiluminescence

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S1. Apparatus

The materials were characterized by scanning electron microscope (SEM) (Zeiss, Germany), transmission electron microscopy (TEM) (Hitachi-7650, Japan), energy dispersive spectroscopy (EDS)-mapping (Talos F200X, Thermo Fisher Scientific), X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250Xi) with Al Kα radiation as the X-ray source), Fourier transform infrared spectrophotometer (FT-IR spectrophotometer, EQUINX55, Broker, Germany) and UV-visible (UV-vis) absorption spectrophotometer (Agilent 8453, USA).

Electrochemiluminescence (ECL) experiments were carried out using a homemade ECL system, including an H-type electrochemical cell, a CHI 760D electrochemistry workstation (Chenhua, China) and an RFL-1 luminometer (Ruimai, China) equipped with a CR-105 photomultiplier tube (PMT) (Bingsong, China). ECL spectra were obtained with a homemade ECL spectrum acquiring system consisting of a CHI 760D electrochemical workstation (Chenhua, China), a spectrometer (SpectraPro HRS-300, Teledyne Princeton Instruments, USA) and an EMCCD (Newton, Andor Technology, UK). Electrochemical impedance spectroscopy (EIS) experiments were carried out by a CHI 760D electrochemistry workstation (Chenhua, China).

S2. Size distribution of AgNPs in AgNPs@TCPP nanoassembly

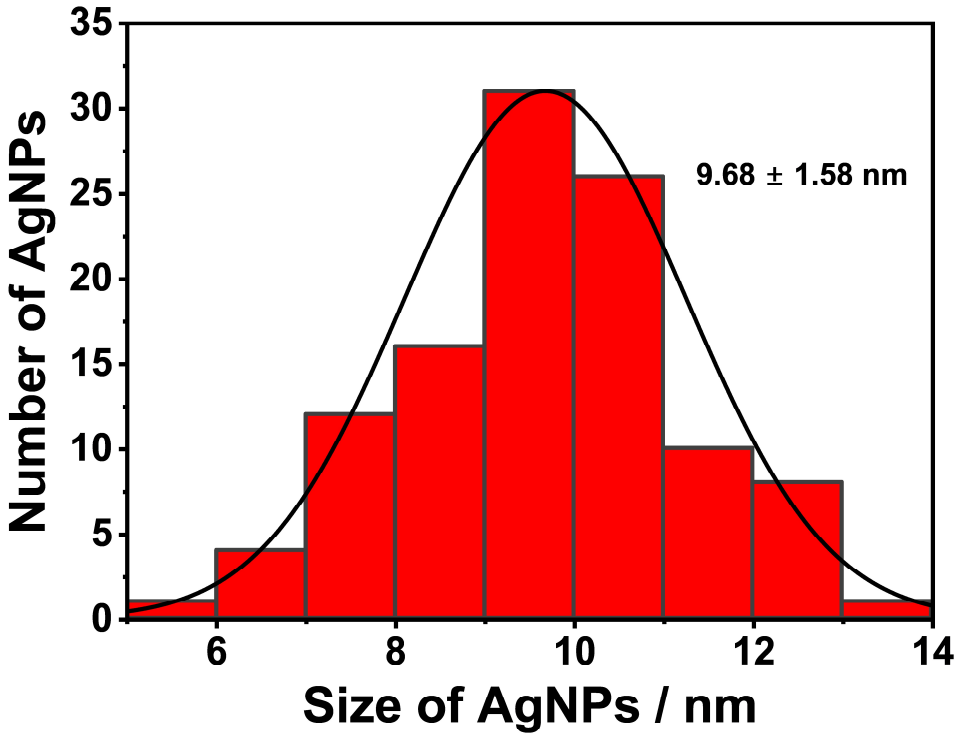

Figure S1. Size distribution of AgNPs in AgNPs@TCPP nanoassembly.

S3. SAED ring pattern

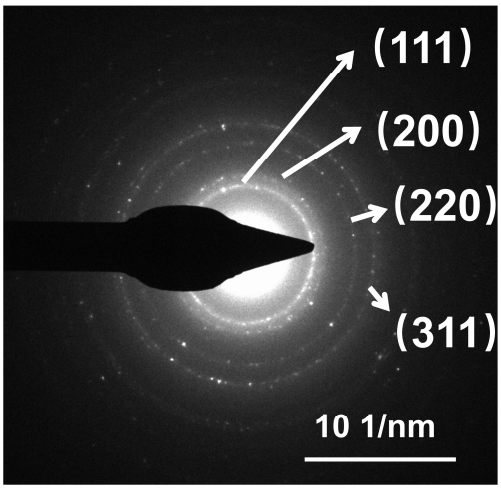

Figure S2. Selected area electron diffraction (SAED) ring pattern of AgNPs in AgNPs@TCPP nanoassembly.

S4. Deconvolution XPS spectra of N 1s in TCPP and AgNPs@TCPP nanoassembly

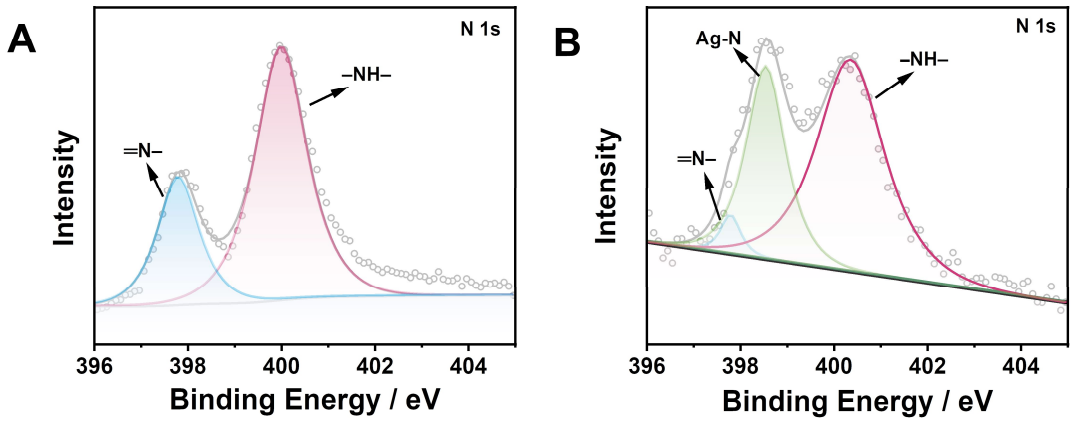

Figure S3. Deconvolution XPS spectra of N 1s in (A) TCPP and (B) AgNPs@TCPP nanoassembly.

S5. UV-vis absorption spectra of TCPP and AgNPs@TCPP nanoassembly

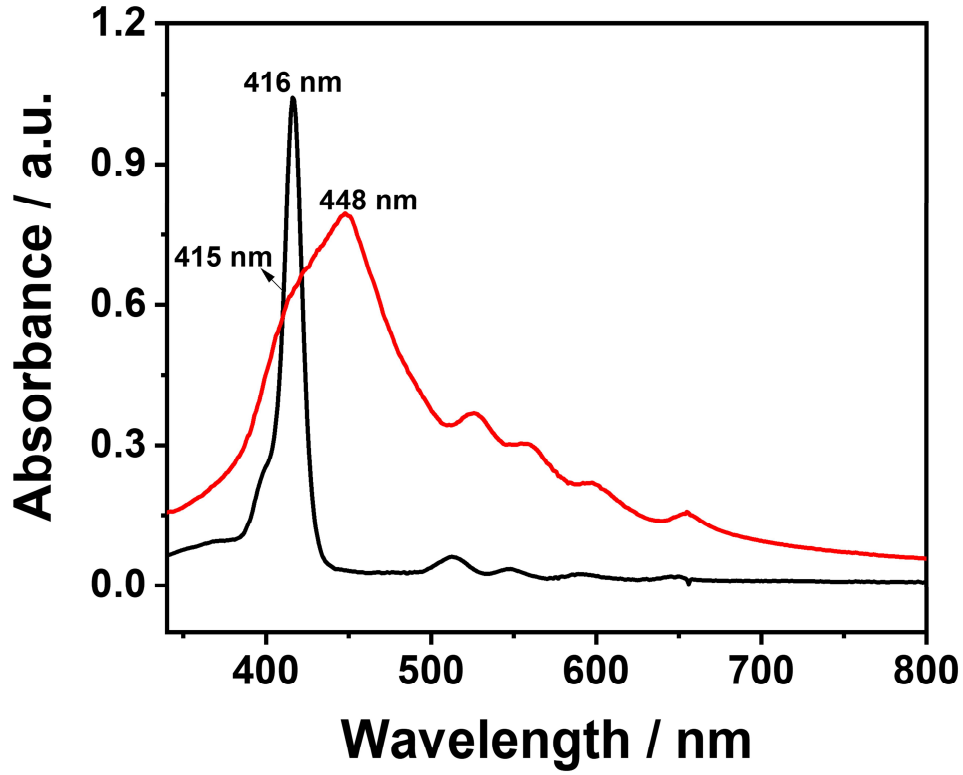

Figure S4. UV-vis absorption spectra of TCPP (black curve) and AgNPs@TCPP nanoassembly (red curve).

S6. UV-vis absorption spectrum of Ag nanoseeds

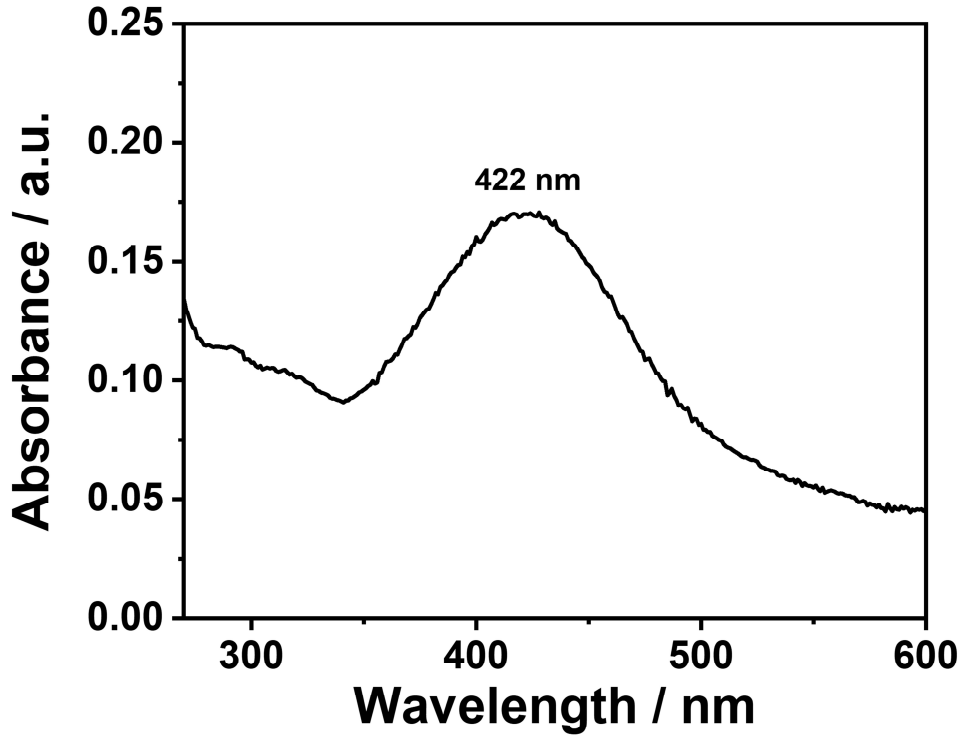

Figure S5. UV-vis absorption spectrum of Ag nanoseeds.

S7. Effect of $AgNO_3$ amount on synthesis of AgNPs@TCPP nanoassembly

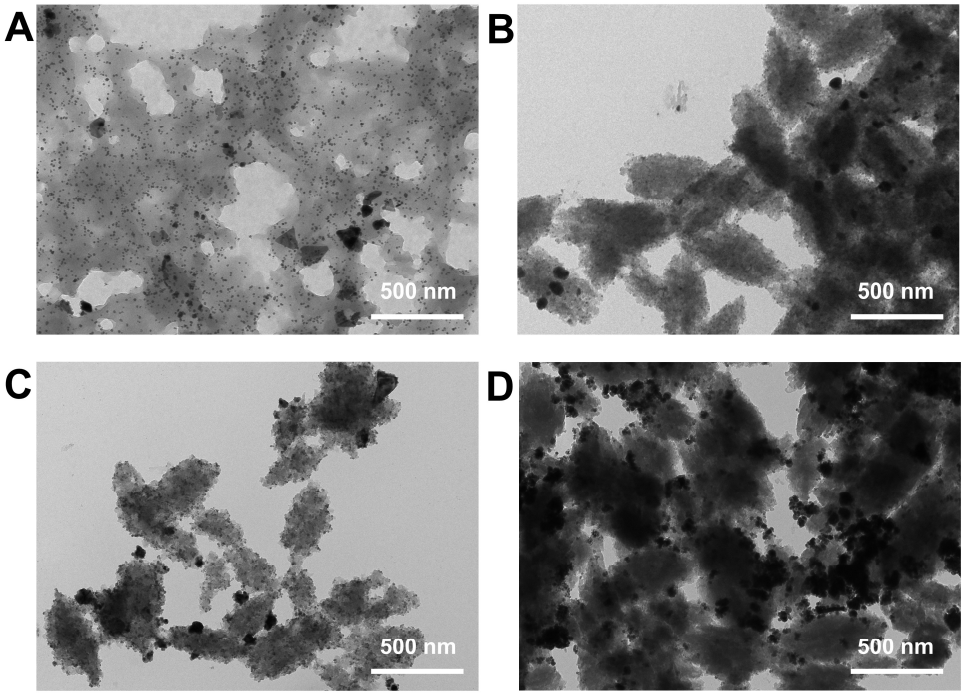

Figure S6. TEM images of AgNPs@TCPP nanoassembly with different amount of $AgNO_3$. (A) 2.5 mg, (B) 5 mg, (C) 10 mg and (D) 30 mg.

S8. Effect of growth time on synthesis of AgNPs@TCPP nanoassembly

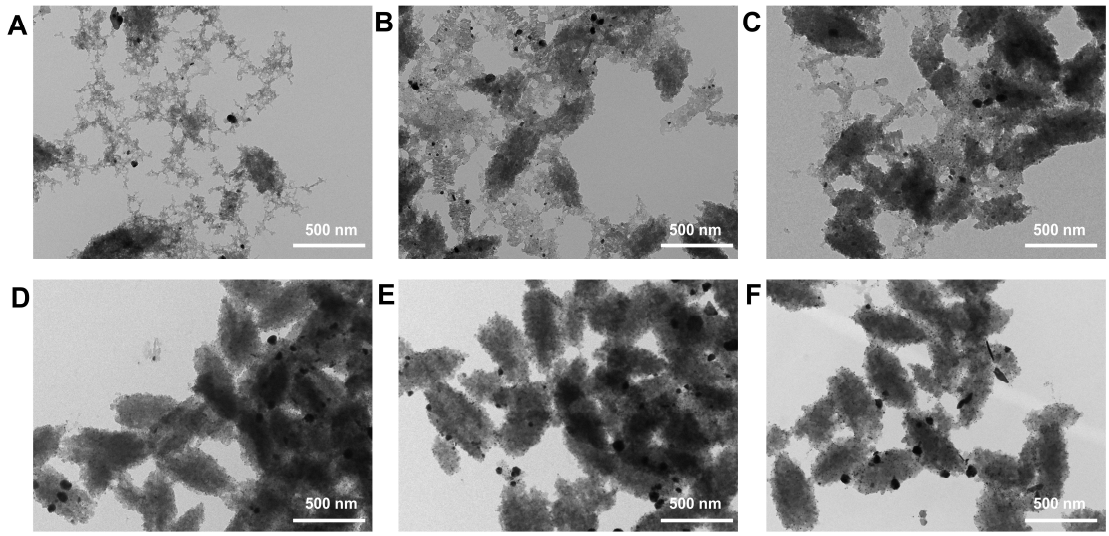

Figure S7. TEM images of AgNPs@TCPP nanoassembly with different growth times. (A) 2 min, (B) 7 min, (C) 11 min, (D) 16 min, (E) 20 min and (F) 25 min.

S9. Preparation of SDS-TCPP aggregate and CTAB-TCPP aggregate

The preparation of the surfactant-assisted TCPP aggregates was partially referred the previous reports.[1] Taking sodium dodecyl sulfate-assisted TCPP aggregate (SDS-TCPP aggregate) as an example, 4 mg of TCPP was dissolved in 0.5 mL of 0.2 M NaOH solution, and 0.01 M SDS was dissolved in 9.5 mL of 0.01 M HCl solution. Then, the TCPP solution was injected into the SDS solution and triggered the self-assembly of TCPP into ordered aggregates through noncovalent interactions including π-π stacking and hydrophobic-hydrophobic interactions. With continuous stirring for 48 h at room temperature, SDS-TCPP aggregate was obtained and purified by centrifugation. Using the same procedures, cetyltrimethylammonium bromide-assisted TCPP aggregate (CTAB-TCPP aggregate) was prepared.

S10. Characterization of SDS-TCPP aggregate and CTAB-TCPP aggregate

As displayed in Figure S8A, the TEM image of SDS-TCPP aggregate showed a uniform rod-like structure with 200 nm in length and 20 nm in width. The CTAB-TCPP aggregate (Figure S8B) exhibited a slightly larger rod-like structure of 350 nm in length and 50 nm in width. The results showed the successful synthesis of SDS-TCPP aggregate and CTAB-TCPP aggregate.

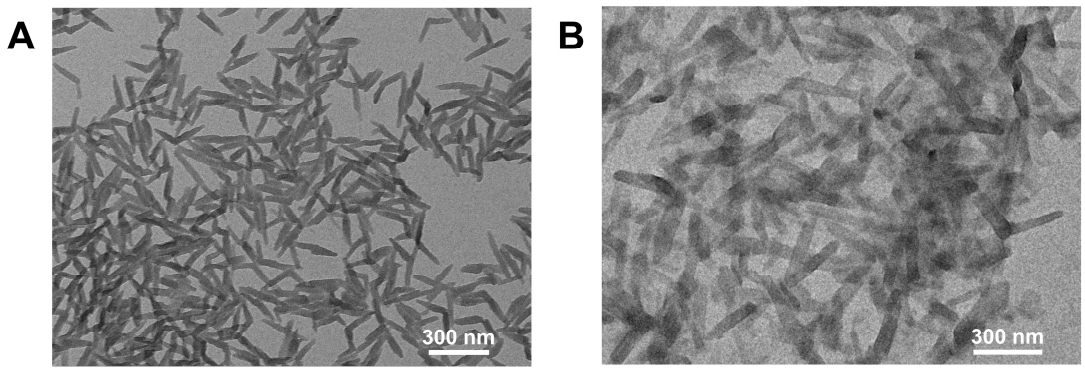

Figure S8. TEM images of (A) SDS-TCPP aggregate and (B) CTAB-TCPP aggregate.

S11. Calculation of ECL efficiency

To estimate the relative ECL efficiency ($\boldsymbol{Ø_{ECL}}$), the ECL intensity and current with potentiostatic method of AgNPs@TCPP nanoassembly, SDS-TCPP aggregate and CTAB-TCPP aggregate in the presence of 0.02 M $K_2S_2O_8$, were compared to that of 0.1 mM $Ru(bpy)_3^{2+}$ with the same coreactant. The electrode was applied with the potential of -1.5 V for 8 s. $\boldsymbol{Ø_{ECL}}$ was calculated with the following equation S1:

$$\Phi_{ECL} = \left\{\frac{\int ECL\, dt}{\int Current\, dt}\right\}_x \Big/ \left\{\frac{\int ECL\, dt}{\int Current\, dt}\right\}_{st} \times 100\% \quad \text{(S1)}$$

where "ECL" and "Current" represent ECL intensity and electrochemical current values, respectively, "st" refers to the $Ru(bpy)_3^{2+}/K_2S_2O_8$ standard and "x" refers to the AgNPs@TCPP nanoassembly, SDS-TCPP aggregate or CTAB-TCPP aggregate.

Table S1. ECL efficiency of TCPP luminophores.

	AgNPs@TCPP nanoassembly	SDS-TCPP aggregate	CTAB-TCPP aggregate
$\boldsymbol{Ø_{ECL}}$	217%	92.3%	57.5%

S12. EIS of TCPP and AgNPs@TCPP nanoassembly modified GCE

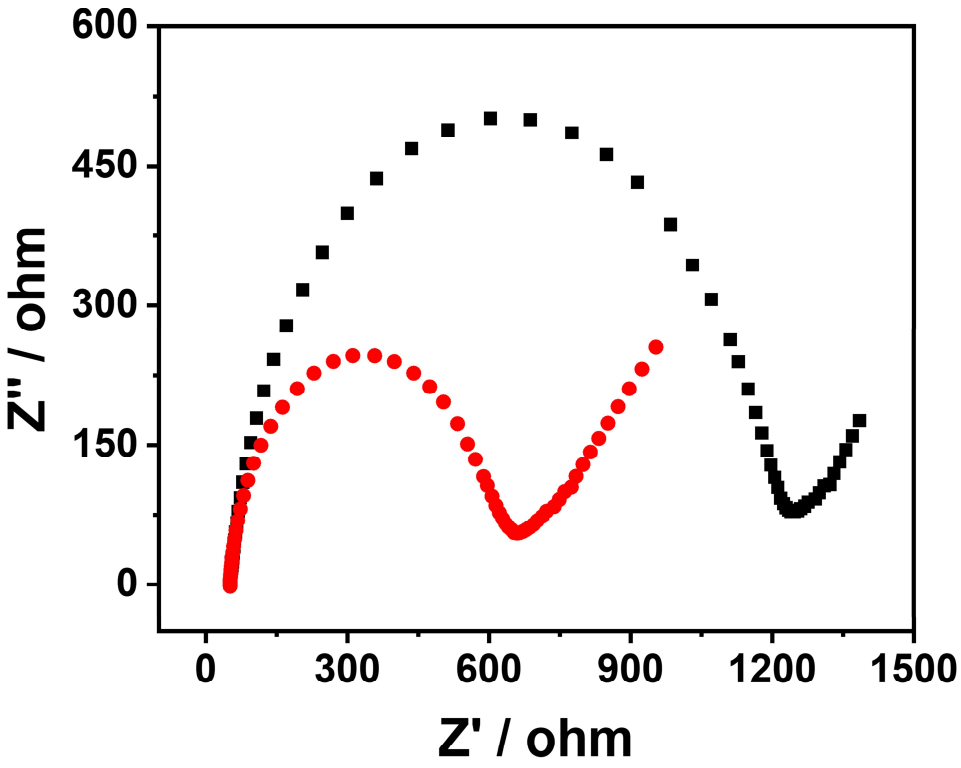

Figure S9. EIS of TCPP (black sign) and AgNPs@TCPP nanoassembly (red sign) modified GCE in 0.2 M KCl solution containing 5 mM $[Fe(CN)_6]^{4-/3-}$.

References

1. Q. Han,C. Wang,Z. Li,J. Wu,P. k. Liu,F. Mo and Y. Fu, *Analytical Chemistry,* 2020, **92**, 3324-3331.