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## **Supplementary Information for**

Continuous synthesis of size-tunable silver nanoparticles by green

electrolysis method and multi-electrode design for high yield

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Fig. S1 Photo of electrolytic synthesis reactor for the continuous system



Fig. S2 XPS spectra of silver nanoparticles (a) XPS of silver nanoparticles, (b) XPS of Ag 3d, (c) XPS of O 1s, (d) XPS of C 1s, (d) XPS of N 1s

Fig. S2 (a) shows the XPS spectrum of the surface of silver nanoparticles capping with PVP. The elements of Ag, O, C and N were detected, as shown in Fig. S2 (b)-(e). We also measured these elements' atomic concentration: C is 75.67%, N is 7.59%, O is 16.49%, Ag is 0.25%. It is worth noting that the atomic concentration of O is slightly higher than that of PVP, and the atomic concentration of N is lower than that of PVP, but the atomic concentration of silver is fairly low. It indicates silver nanoparticles were protected well by PVP. It can be observed that two peaks of Ag occurred at 367.2 eV and 373.6 eV, which correspond to Ag 3d<sub>5/2</sub> and 3d<sub>3/2</sub> binding energies, respectively. In comparison with Ag<sup>0</sup> (368.3 eV and 374.3 eV), the peaks were shifted to lower binding energies, indicating that the chemical environment around Ag atoms was changed. PVP has the structure of a polyvinyl skeleton with polar groups. So it maybe indicates silver atoms interact with N or O of PVP.



Fig. S3 HRTEM image of silver nanoparticles

The size of the silver nanoparticle is about 18.5 nm. In the HRTEM image, the facet having

fringe spacing of 0.237 nm corresponds to (111) of silver.



Fig. S4 Photos of improved multi-electrode electrolytic reactor

The multi-electrode electrolytic synthesis process is as follows: Firstly, two groups of silver electrodes were polished, washed, and fitted on the cover of the reactor, and 5mg/ml PVP aqueous solution was prepared. Secondly, the multi-electrode electrolytic reactor was laid in 70°C water bath, and two tubules were connected with the inlet and outlet of the reactor, respectively. A DC power source was connected with the two groups of parallel electrodes through the control device "Alternating Polarity Controller", and the alternating time of anodes and cathodes was set at one

minute. When preparing colloidal AgNPs, the voltage of 7V was applied to silver electrodes under a magnetic stirring condition, and simultaneously the PVP solution was continuously pumped into the reactor with a peristaltic pump at the flow rate of 540mL/h, 380mL/h and 220mL/h, respectively. Finally, the AgNPs solution flowed out of the tube and was collected.



Fig. S5 Photo of colloidal AgNPs that synthesized by multi-electrode electrolysis



Fig. S6 TEM images and size distributions of AgNPs that synthesized by multielectrode electrolytic reactor with different flow velocity: (a) 540mL/h, (b) 380mL/h, (c) 220mL/h