Electronic Supplementary Information (ESI)

CO_2-switchable Polymer-hybrid Silver Nanoparticles and Their Gas-tunable Catalytic Activity

Zanru Guo,[a]* Hongjian Gu,[a] Wei Ma,[a] Qiang Chen,[a] Zhanfeng He,[b]* Jiali Zhang,[a] Yongxin Liu,[a] Longzhen Zheng [a] and Yujun Feng[c]*

[a]Department of Polymer Materials and Chemical Engineering, School of Materials Science and Engineering, East China Jiao tong University, Nanchang, Jiangxi 330013, P. R. China. E-mail addresses: guozanru@ecjtu.edu.cn (Z. Guo)

[b]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation Southwest Petroleum University, Chengdu 610500, P. R. China. E-mail addresses: he_zhanfeng2008@126.com (Z He)

[c]Polymer Research Institute, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, P. R. China. E-mail addresses: yjfeng@scu.edu.cn (Y. Feng)

Characterizations

Fig. S1 was the ^{1}H NMR spectrum of trithioester terminated PDEAMA in $CDCl_3$: The signals at 0.9 ppm, 1.00 ppm, 1.2 ppm, 2.15 ppm are attributed to the protons in terminal $-CH_2$ and $-CH_3$, $-NCH_2CH_3$, side group $-CH_3$, $-CH_2-$ of main chain, respectively. 2.5 ppm and 2.6 ppm are the chemical shift of the protons in CH_3CH_2N- and $-OCH_2CH_2N-$, respectively. 4.0 ppm is the signal of the protons in $-OCH_2CH_2N-$. The characteristic signals of the polymer were assigned, indicating that the PDEAMA-CTA was obtained successfully.

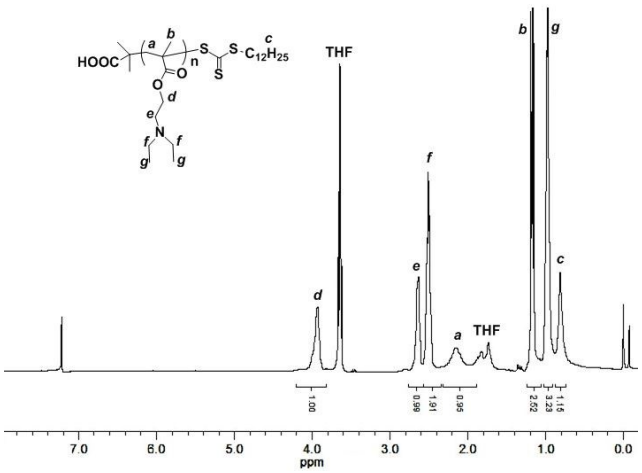


Fig. S1 ^{1}H NMR spectrum of PDEAEMA in $CDCl_3$.

Fig. S2 is the GPC chromatogram for PDEAEMA. The average number molecule weight (M_n) and polydispersity index (PDI, M_w/M_n) is 9,250 g mol^{-1} and 1.25, respectively.

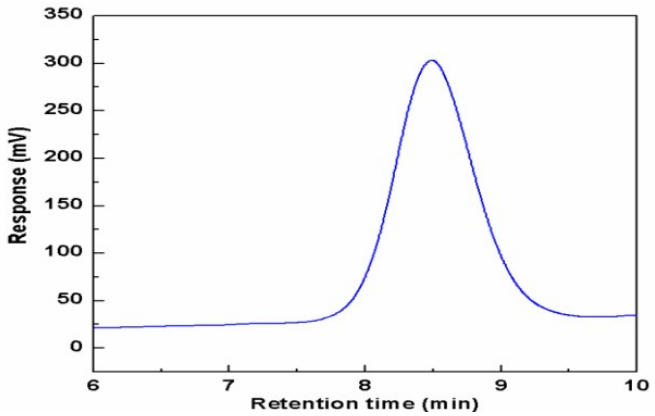


Fig. S2 GPCspectrum of PDEAEMA

Fig.S3 shows XRD pattern of Ag–NPs shows characteristic diffraction peaks for metallic silver [111], [200], [220] and [311] facets, indicative of the formation of pure Ag.

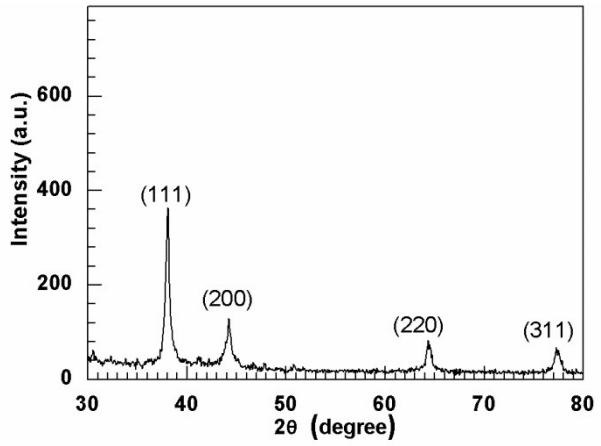


Fig. S3 XRD pattern of Ag-P1

Fig. S4 is the FT-IR spectra of the nanoparticles and the PDEAEMA.

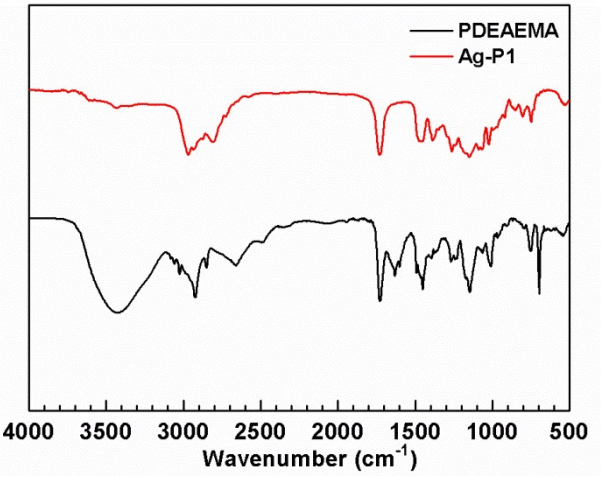


Fig. S4 IR spectrum of Ag-P1 and PDEAEMA (KBr pellet method).

Fig. S5 is the UV-vis spectra of Ag-P1measured with the same concentration at different times. There is no obvious difference in the shape, position, and symmetry of the absorption peak during 12 months, indicative of the long-term stability of hybrids.

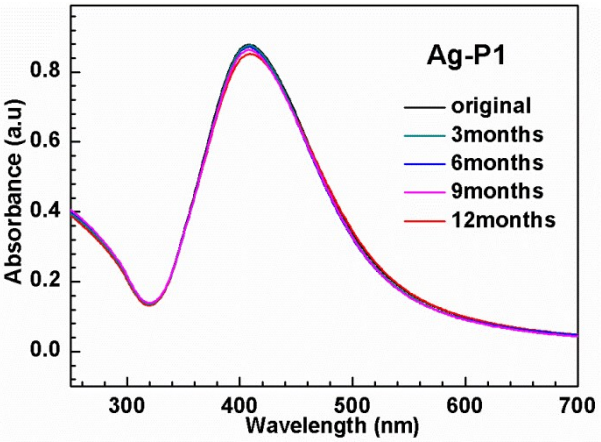


Fig. S5 The stability analysis for Ag-P1 (0.1mg·mL^{-1}) in water after bubbling CO_2 at 25℃ by UV-

vis spectra.

Fig. S6 is TEM of Ag-P1 in water after bubbling N_2 at 25°C.An obvious aggregation state of the AgNPs hybrids can be observed.

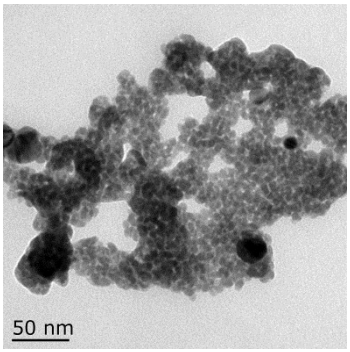
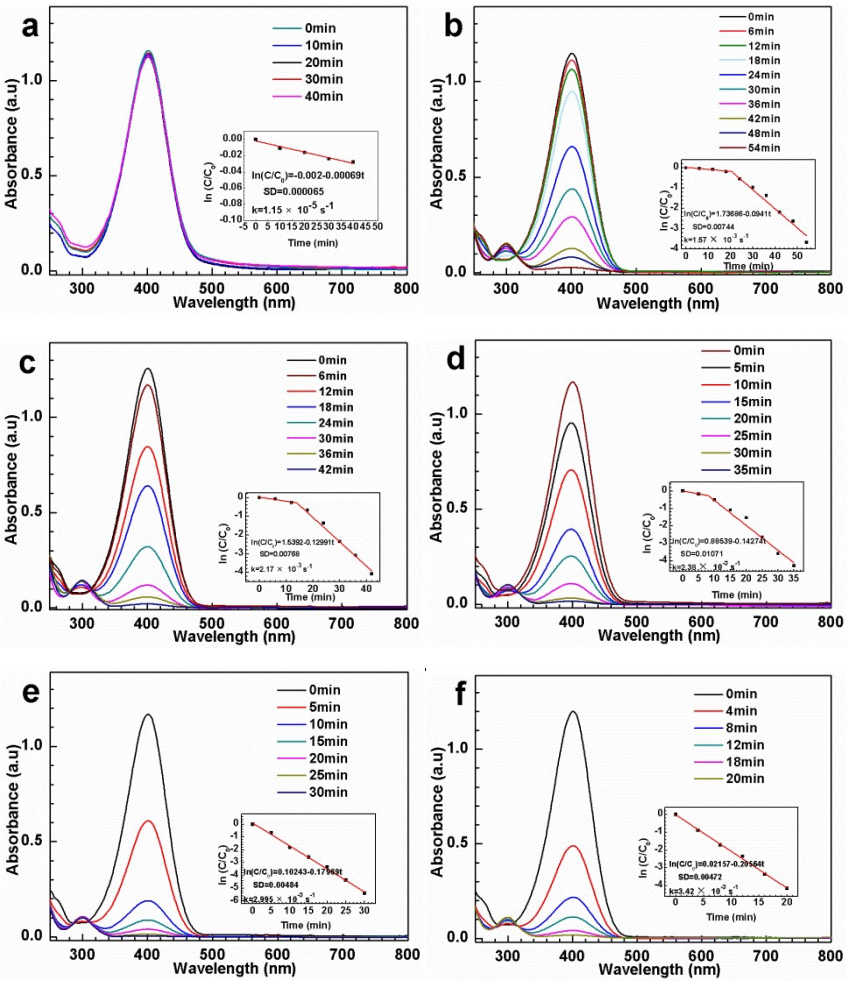


Fig. S6 TEM images of Ag-P1 in water after bubbling N_2 at 25℃.

Fig. S7 shows the time-dependent UV spectra for the reduction of 4-nitrophenol in presence of Ag-P1 hybrids at different CO_2 flow rate.



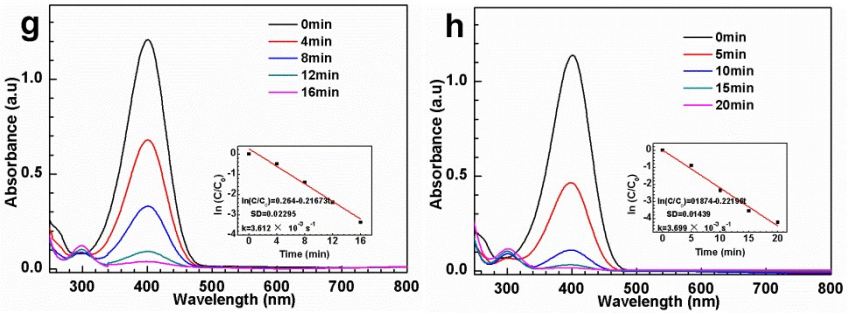


Fig. S7 Time-dependent UV-vis spectral changes of 4-nitrophenol catalyzed by Ag-P1 with different flow rate of CO_2 bubbling: (a) 0 mL·min^{-1}, (b) 10 mL·min^{-1}, (c) 15 mL·min^{-1}, (d) 20 mL·min^{-1}, (e) 25 mL·min^{-1}, (f) 30 mL·min^{-1}, (g) 40 mL·min^{-1} and (h) 50 mL·min^{-1}, respectively. The insert images of the plots of $In(C/C_0)$ versus the time t. The concentrations of 4-NP is 0.0139 mg·mL^{-1}, the concentrations of $NaBH_4$ is 0.38 mg·mL^{-1}and the concentrations of Ag-P1 is 2x10^{-3} mg·mL^{-1}.

Fig. S8 shows the time-dependent UV spectra for the reduction of 4-nitrophenol without Ag-P1 hybrids by bubbling CO_2.

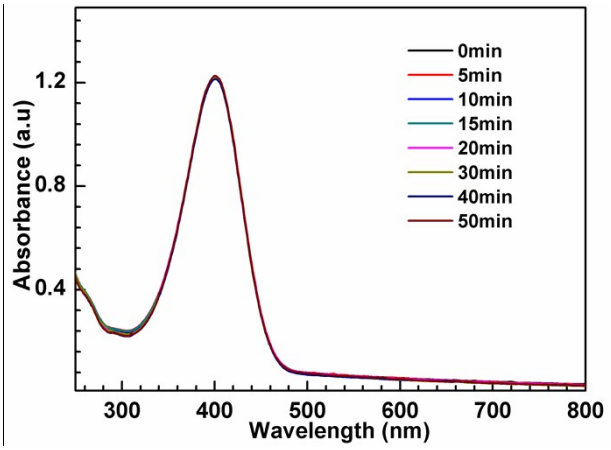


Fig. S8 The time-dependent UV spectra for the reduction of 4-nitrophenolin without Ag-P hybrids by bubbling CO_2. The flow rate of CO_2 is 30 mL·min^{-1}, and the concentrations of 4-NP is 0.0139 mg·mL^{-1}.

Fig. S9 shows pH value of the reaction solution at different flow rate of CO_2.

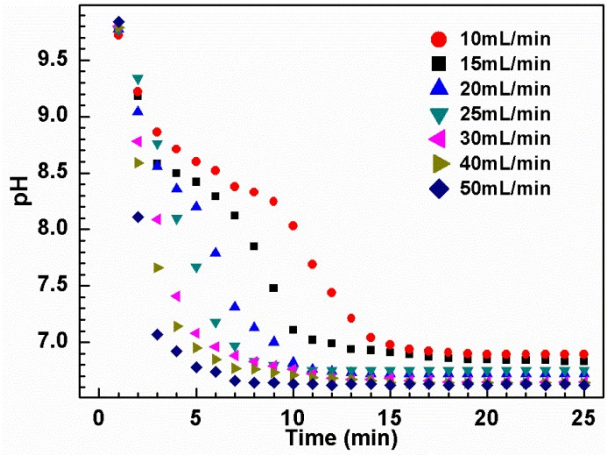


Fig. S9 The pH changes of the reaction solution at different flow rate of CO_2.

Calculation of the polymer content onto one nanoparticle

We assume that PDEAEMA-AgNPs hybrids is 1.0 g. Based on the TGA data, the weight of polymer ($W_{polymer}$) and Ag (W_{Ag}) can be known. Thus the average number of the polymer chains and silver nanoparticles in the hybrids can be calculated by dividing their average molecular weight. Then the average number (A) of polymer chains wrapped per silver nanoparticle can be calculated from Equation (1).

$$A = \frac{\frac{W_{polymer}}{M_{n(polymer)}} \times N_A}{\frac{w_{Ag}}{M_{Ag}}} \qquad (1)$$

Where N_A is Avogadro's number, $M_{n(polymer)}$ is the the molar mass of polymer and it can be obtained in CPC analysis, M_{Ag} is the weight of one silver nanoparticles

The density of the silver (ρ) is 10.53g·cm^{-3}. Thus the weight of one silver nanoparticles can be calculated using Equation (2).

$$M_{Ag} = \rho \times \mathbf{V} \qquad (2)$$

Where V is the volume of one silver nanoparticle. The volume of one silver nanoparticle can be calculated using equation (3).

$$V = \frac{4}{3}\pi(\frac{1}{2}D)^3 \qquad (3)$$

Where D is the diameter of the silver nanoparticle, which be obtained from TEM observation.

The weight ratio of polymer to silver for Ag-P1, Ag-P2 and Ag-P3 are 90:10, 84:16, 71:29 (w/w %), respectively; and the diameter of Ag-P1, Ag-P2 and Ag-P3 are 8.51 nm, 10.06 nm and 14.16 nm, respectively. So, we calculated that an average number of 2000, 1900 and 2470 polymer chains were coated onto one Ag-P1, Ag-P2 and Ag-P3, respectively.