

Supporting information

Tuned Depositing Ag clusters on ZrO₂ Nanocrystals from Silver

Mirror Reaction of Silver-Dodecylamine Complexes

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Experimental Section

Chemicals

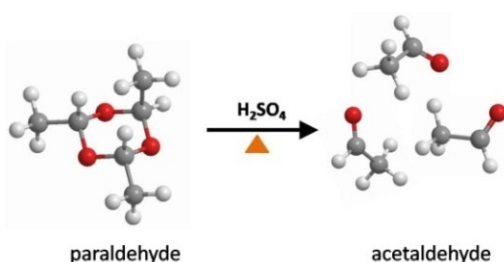
Paraldehyde ($\geq 98.0\%$) and 1-Dodecylamin (98%) and zirconium n-propoxide (IV) (70% w/w in n-propanol) were all obtained from Aladdin Chemical Corporation. Tert-butylamine was purchased from Sinopharm Chemical Reagent Corporation. Silver nitrate (AgNO₃, $\geq 99.8\%$), oleic acid (OLA), p-nitrophenol (4-NP), sodium borohydride (NaBH₄) and toluene were all obtained from Tianjin Damao Chemical Reagent Factory. All reagents (analytical grade) were used without further purification.

Synthesis of ZrO₂ nanocrystals

The synthesis of ZrO₂ nanocrystals has been reported previously by a two-phase hydrothermal method. In a synthesis of ZrO₂ nanocrystals, 560 mL water containing 40 mL *tert*-butylamine was transferred to a 1 L Teflon-lined stainless-steel autoclave. Subsequently, 40 mL oleic acid, and 12 mL zirconium (IV) n-propoxide were added to 150 mL toluene and the solution was transferred to the autoclave without stirring. The autoclave was sealed and maintained at 180 °C for 72 h, and then cooled to room temperature naturally. The obtained crude solution was centrifugated at 6000 rpm/min to remove the solid impurities, and then the upper supernatant solution containing ZrO₂ nanoparticles was precipitated by the addition of ethanol and further isolated by centrifugation. The purified ZrO₂ nanocrystals were re-dispersed in toluene.

Preparation of acetaldehyde (CH₃CHO) toluene solution

CH₃CHO toluene solution was prepared by depolymerization of paraldehyde and followed was collected by toluene (Scheme S1). About 25 mL of paraldehyde was added to a 50 mL three-neck round bottom flask, dropping two drops of sulfuric acid. Subsequently, the flask was transferred to an oil bath of 90 °C, and depolymerization of paraldehyde was started with H₂SO₄ as the catalyst. As a result, the condensed CH₃CHO generated by depolymerization of paraldehyde was collected by 50 mL of toluene. The molar concentration of the obtained CH₃CHO toluene solution was about 8 mol/L.



Scheme S1 Strategy for preparation of CH₃CHO toluene solution

Synthesis of Ag/ZrO₂-x nanocomposites

A stock solution of Ag precursor (silver-dodecylamine complexes solution, 0.1M) was firstly prepared by adding 2 mmol AgNO₃ and 1 g 1-Dodecylamin (98%) to 20 ml mixture solution of toluene and ethanol (volume ratio=3:1) under vigorous stirring at room temperature. In the synthesis of nanocomposites, 0.5 mL ZrO₂ nanocrystals (~200 mg/mL, 100 mg) toluene solution was added to 30 mL toluene in a 100 mL three-neck round bottom flask. Next, 0.5 mL Ag precursor solution (~5.4mg Ag) was added to the above solution followed by CH₃CHO toluene solution (~8 mol/L, 0.25 mL). Then the three-neck round bottom flask was transferred to a water bath of 50 °C. During the reduction, 0.25 mL of the sample solution was taken and diluted into 3 mL toluene for UV-vis spectroscopy characterization. The resultant solution was precipitated by the addition of ethanol and submitted to a cycle of centrifugation, re-dispersion, and precipitation. This procedure was repeated three times to obtained the purified nanocomposites, designated as Ag/ZrO₂-5 (about 5.4 mg are all deposited on 100 mg ZrO₂). Other Ag/ZrO₂ nanocomposites with different Ag loadings were synthesized by varying the amount of Ag precursor.

Characterization

UV-vis spectra were recorded in the range from 200 nm to 800 nm using a Shimadzu UV-1780 spectrometer. Ultra-HRSEM studies were done with a HITACHI S-5500 microscope operated at 100 kV by dropping the sample dispersions on carbon-coated copper grids. TEM images were obtained with a Philips Tecnai G² Spirit microscope

operated at 120 kV accelerating voltage. HRTEM analyses were performed using a FEI Tecnai G² F30 Spirit microscope operated at 300 kV accelerating voltage. Powder XRD patterns were obtained with a Rigaku D/Max2500V/PC diffractometer. FT-IR spectra were recorded with a Bruker Tensor 27 Infrared spectrometer. XPS spectra were obtained with a VG ESCALAB MK2 spectrometer

Catalytic study

The aqueous solutions of 4-NP (7.4 mM) and NaBH₄ (2.4 M) were freshly prepared. To investigate the catalytic activity, 300 mL of an aqueous solution containing Ag nanocrystals or Ag/ZrO₂ nanocomposites was transferred to a glass reactor at a constant PH value of 10. Then, the solution was purged prior to the run with N₂ in order to remove O₂. Under magnetic stirring, 6 mL of 4-NP solution and 6 mL of NaBH₄ solution were added into the above reactor in succession to start the reaction at 298 K. The intensity of the absorption peak at 400 nm for 4-NP was monitored by UV-vis spectroscopy along with time. After each cycle of reaction, another 12 mL of an aqueous solution containing 4-NP (3.7 mM) and NaBH₄ (1.2 M) was added to the reaction solution for the next reaction cycle. This step was repeated several times to study the stability of catalysts.

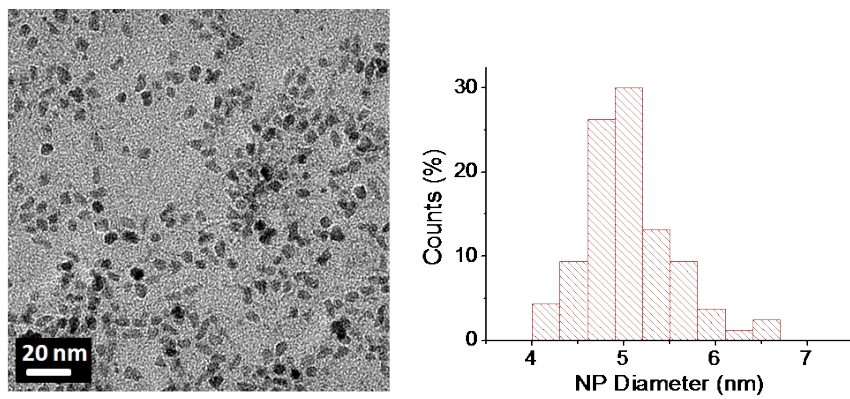


Fig. S1 TEM image of the as-synthesized ZrO_2 nanocrystals, together with its size distribution.

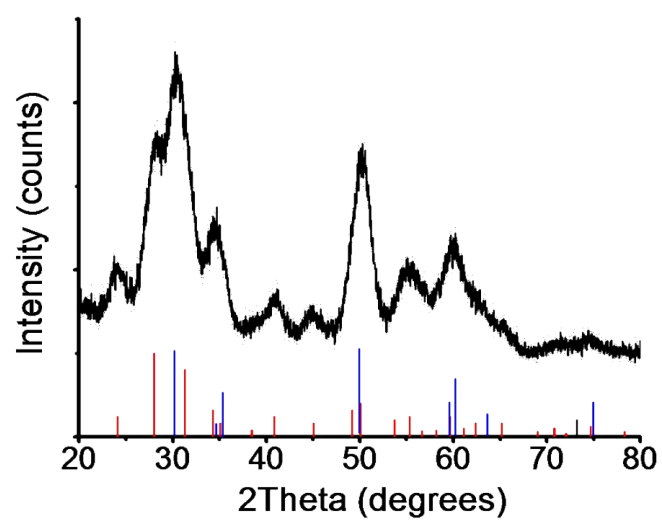


Fig. S2 XRD pattern of ZrO₂ nanocrystals. The blue and red vertical bars represent monoclinic and tetragonal structures, respectively.

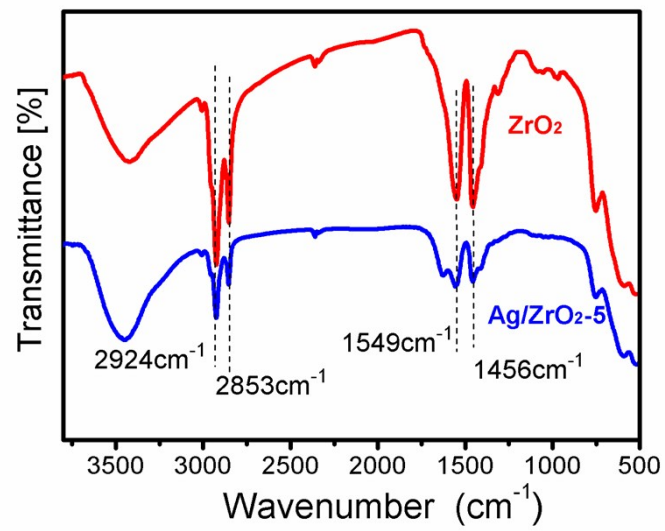


Fig. S3 FT-IR spectra of ZrO₂ nanocrystals and Ag/ZrO₂-5 nanocomposite. The bands at 2924 and 2853 cm⁻¹ are the C-H antisymmetric and symmetric stretching vibrations, and the bands at 1549 and 1456 cm⁻¹ are the COO- antisymmetric and symmetric stretching vibrations.

The silver mirror phenomenon in toluene

3 mL silver precursor solution (0.1 mmol/mL) was added to 30 mL toluene in a 100 mL test tube. Then, a certain amount of CH_3CHO toluene solution (~ 8 mol/L, 0.5 mL) was added to the reaction solution and the test tube was transferred to a water bath of 50 °C without stirring. After 1 h, the test tube was taken out and the product solution was removed. It appeared reflective mirrors on tube wall, indicating the occurrence of an obvious silver mirror reaction in toluene.



Fig. S4 Photograph of the test tube for reduction of silver-dodecylamine complexes by acetaldehyde in toluene.

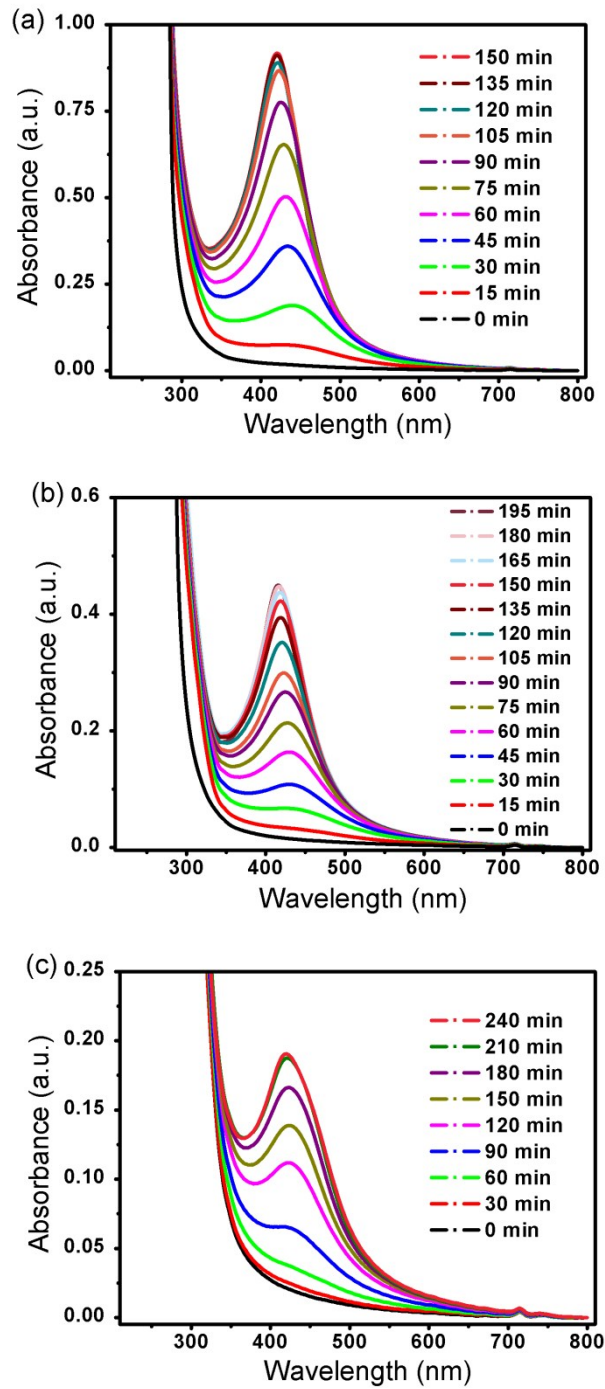


Fig. S5 UV-vis absorption spectra of Ag/ZrO₂-2.5 (a), Ag/ZrO₂-1.5 (b) and Ag/ZrO₂-0.75 (c) nanocomposite solutions taken at different reaction time.

Reduction of silver-dodecylamine complexes by acetaldehyde without ZrO_2 nanocrystals

In the reduction, 0.5 mL silver precursor solution (0.1 mmol/mL) was added to 30 mL toluene in a 100 mL three-neck round bottom flask. Then, a certain amount of CH_3CHO toluene solution (~ 8 mol/L, 0.25 mL) was added to the reaction solution and the three-neck round bottom flask was transferred to a water bath of 50 °C with stirring. During the reduction, 0.25 mL of the sample solution was taken and diluted into 3 mL toluene for UV-vis spectroscopy characterization. The resultant product is designated as Ag-5.

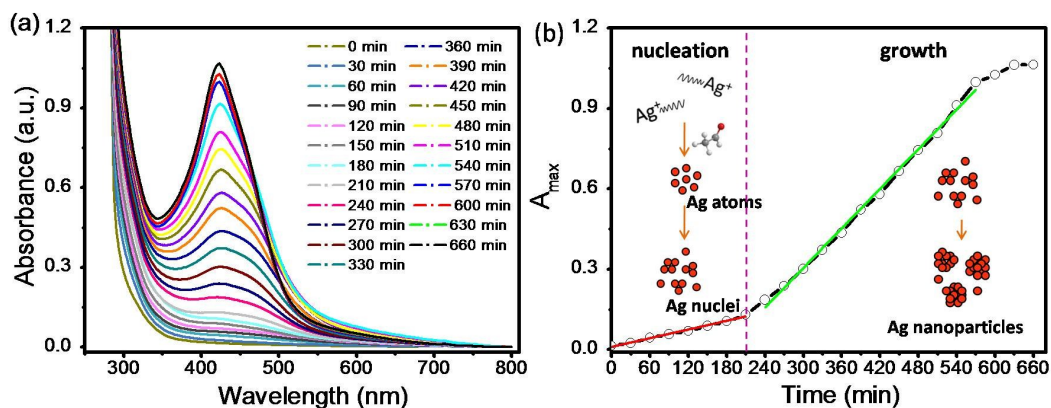


Fig. S6 (a) Time evolution of UV-vis absorption spectra for the synthesis of Ag-5 nanocrystals. (b) The corresponding plot of A_{max} against the reaction time for Ag-5 nanocrystals. There are two processes: nuclei formation, which refers to the accumulation of Ag atoms and self-nuclei when the concentration of Ag atoms reaches the critical concentration before 210 min; crystal growth, growth of nuclei into Ag nanocrystals in an accelerated way after 210 min.

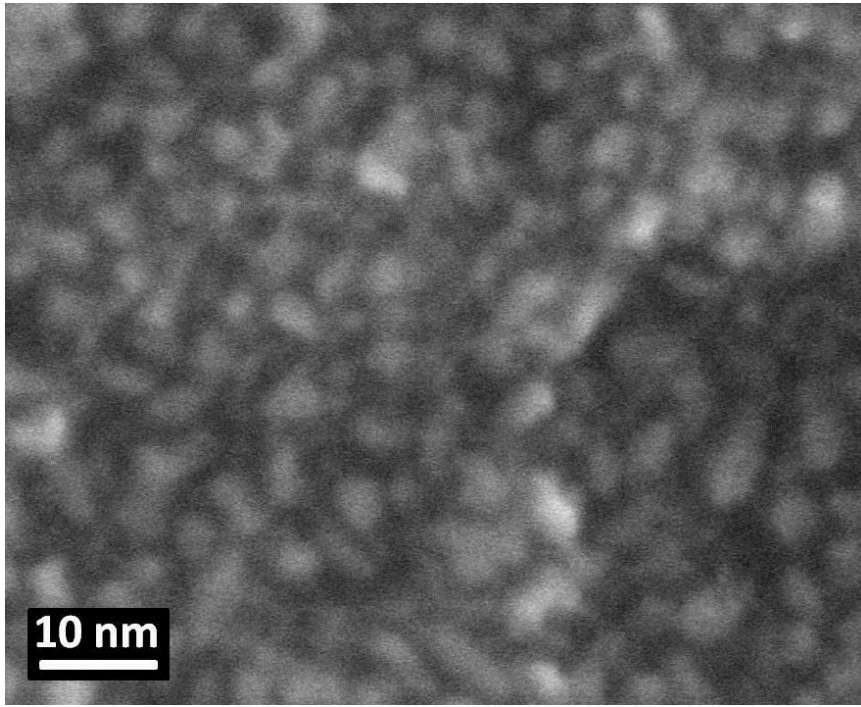


Fig. S7 Ultra-high resolution scanning electron microscopy (Ultra-HRSEM) image of Ag/ZrO₂-5 nanocomposite.

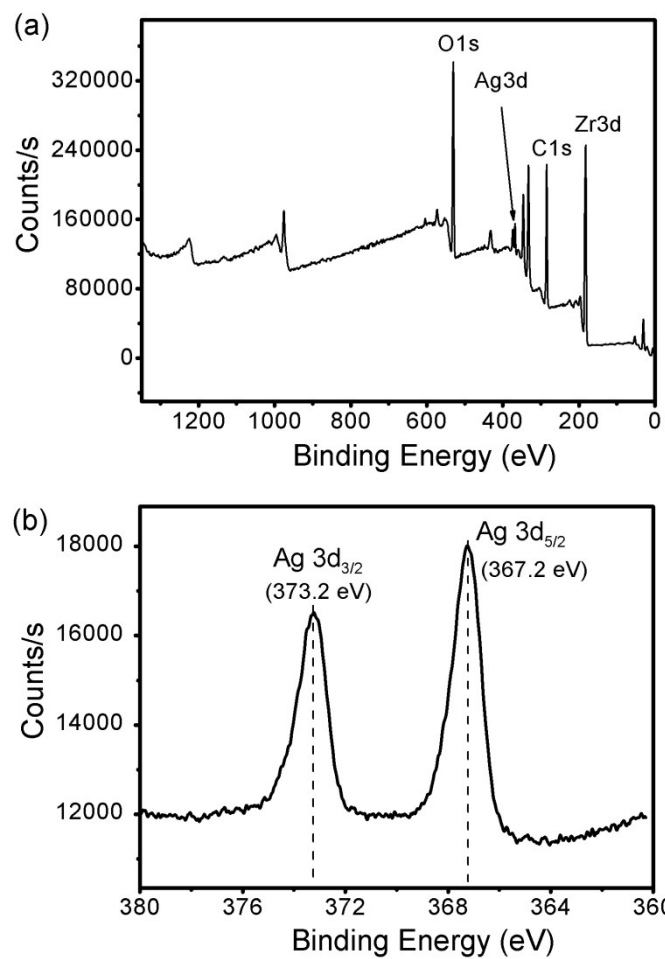


Fig. S8 (a) XPS full scanned spectrum of Ag/ZrO₂-5, (b) Ag 3d spectrum of Ag/ZrO₂-5.

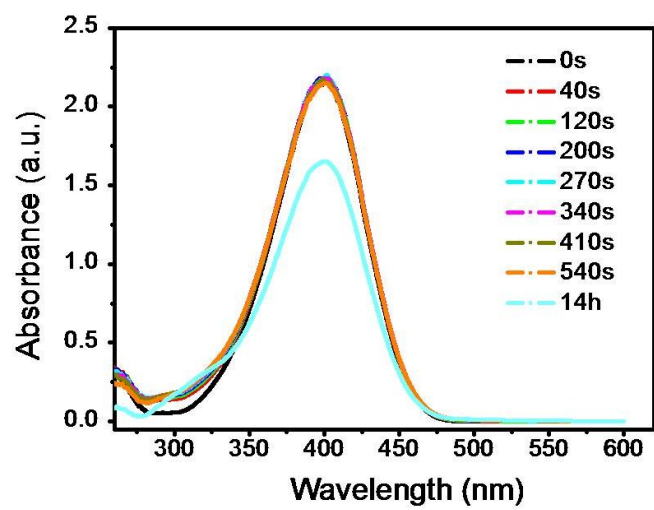


Fig. S9 UV-vis absorbance spectra for the catalytic reduction of 4-NP by NaBH₄ with the pure ZrO₂ nanocrystals.

Synthesis of pure Ag clusters

For comparison, we also synthesize pure Ag clusters without the presence of ZrO_2 . However, pure Ag clusters synthesized in toluene cannot be directly used in 4-NP reduction. So, pure Ag clusters are impregnated on fumed silica, which is then washed by ethanol to remove toluene and dispersed in water. In the synthesis of pure Ag clusters, 2 mL silver precursor solution (0.1 mmol/mL) was added to 30 mL toluene solution containing 0.2 mL oleic acid in a 100 mL three-neck round bottom flask. Then, a certain amount of CH_3CHO toluene solution (~ 8 mol/L, 0.75 mL) was added to the reaction solution and the three-neck round bottom flask was transferred to a water bath of 50 °C with stirring. After the reduction was finished, about 400 mg fumed silica was added to the resultant product, which was subsequently precipitated by the addition of ethanol and submitted to a cycle of centrifugation, re-dispersion, and precipitation for three times to remove the remaining oleic acid. The purified product was dispersed in water by sonication.

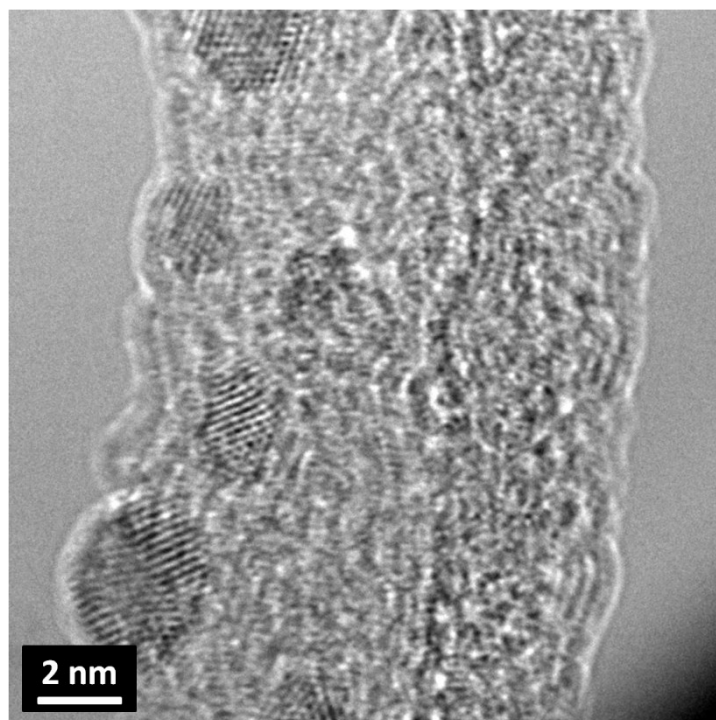


Fig. S10 HRTEM image of Ag clusters loaded on fumed silica.

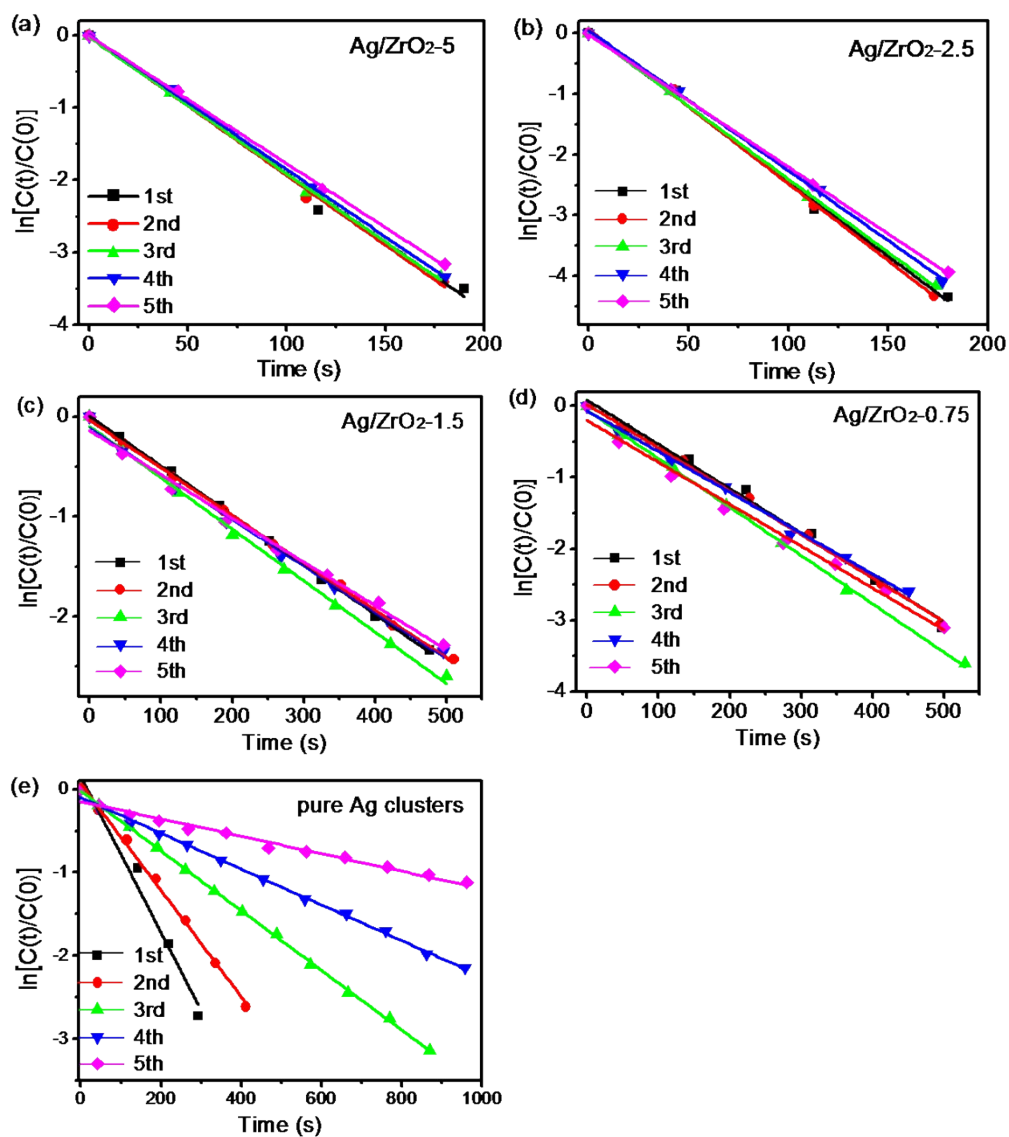


Fig. S11 Plot of $\ln[C(t)/C(0)]$ against the reaction time in five successive reduction of 4-NP by NaBH_4 . (a) Ag/ZrO_2-5 .

(b) $\text{Ag/ZrO}_2-2.5$. (c) $\text{Ag/ZrO}_2-1.5$. (d) $\text{Ag/ZrO}_2-0.75$. (e) Pure Ag clusters.