Supporting Information

Interface modulation of bacteriogenic Ag/AgCl nanoparticles by Co^{2+} boosting up the catalytic activity for reduction reactions

Hao Zhou[a]*, Lin Che[a], Xuyun Guo[b], Xue Wang[a], Jingjing Zhan[a], Minghuo Wu[a], Yufeng Hu[a], Xianliang Yi[a], Xuwang Zhang[a], Lifen Liu[a]

[a]Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Food and Environment, Dalian University of Technology, 124221, Panjin, China.

[b]Department of Chemistry, The Hong Kong University of Science and Technology. Clear Water Bay, Kowloon, Hong Kong SAR, People's Republic of China, Hongkong, China.

*Corresponding authors. E-mail: zhouhao@dlut.edu.cn (H. Zhou)

S1. Materials

Sodium borohydride ($NaBH_4$, 98%), *m*-nitrophenol (99.0%), *o*-nitrophenol (99.0%) and *p*-nitrophenol (99.5%) were purchased from Aladdin (Shanghai, China). Silver nitrate ($AgNO_3$, 99.8%), methyl orange (MO, 99.5%), rhodamine B (RhB, 99.5%), cobalt chloride ($CoCl_2 \cdot 6H_2O$, 99.5%) and cobalt acetate ($Co(Ac)_2 \cdot 4H_2O$, 99.5%) were purchased from Damao Chemical reagent factory (Tianjin, China). All of the reagents were used without further purification.

S2. Preparation of biogenic Ag/AgCl NPs and their derivatives

The bacterium, i.e. strain *Bacillus* sp. CC-1, was incubated in an incubator at 150 rpm, 30^{o}C for 48h using TSB medium. Then, 5 mM $AgNO_3$ was added into the cultures, and further incubated for 12h. The intracellularly biogenic Ag/AgCl NPs was released by sterilization at 121 ^{o}C and 17 psi for 20 min. The as-obtained biogenic nanoparticles dispersions were stored at room temperature for catalytic performance determination. For the derivatives, 100 μM of various metal ions ($NiCl_2$, $MgCl_2$, $CaCl_2$, $CoCl_2$, $CdCl_2$ and $CuCl_2$) were added into 3 mL diluted Ag/AgCl NPs (OD_{416nm}~0.5), and incubated for 1h.

S3. Characterization of the as-synthesized NPs

For characterization, the as-synthesized NPs were collected by centrifugation (20000 rpm, 40min), and washed using ultrapure water three times. Then, the precipitates were lyophilized overnight. The crystal structure and purity of the as-synthesized biogenic NPs were determined by X-ray diffractometer (Shimadzu, XRD-7000S) using Cu Kα as a radiation source at a scan rate of 5^{o} min^{-1}. Cobalt and silver quantitative analysis was performed using a ICP-OES (Thermo ICAP-QC). A FEI NanoSEM450 SEM was used to examine the sample morphology. HAADF-STEM and element mapping of Ag/AgCl NPs and Co-Ag/AgCl NPs were carried out in FEI Titan Themis 200 TEM equipped with EDX (Bruker super-X). Chemical compositions and elemental chemical states were ensured through XPS spectra (Thermofisher 250XI). UV-vis spectra were obtained by ultraviolet and visible spectrophotometer (PerkinElmer LAMBDA 950).

S4. Details for catalytic reduction of *p*-nitrophenol and other substrates

For evaluating the catalytic performance of biogenic Ag/AgCl NPs and its derivatives,

the reduction of *p*-nitrophenol (PNP) into *p*-aminophenol was chosen as the model reaction. In brief, the reaction was performed at ambient temperature (25 ± 2 ^{o}C). 30 μL stock solution of 10 mM PNP was diluted to 3 mL using ultrapure water, thus the final concentration was 0.1 mM. Then 30 μL of $NaBH_4$ (1 M) was added to convert PNP into *p*-nitrophenolate ion, thus the concentration of PNP could be determined using time-course function (with a time interval of 1s) of visible spectrophotometer (λ_{max}=400 nm). The reduction reaction was initiated by adding different volume of biogenic NPs dispersions (generally from 30 μL to 200 μL). For the reaction mechanism investigation, the PNP concentration was varied at a range of 0.05 to 0.15 mM, while the concentration of $NaBH_4$ was kept constant (10 mM). In order to exclude the possible active species other than Co-Ag/AgCl NPs, the following control experiments were done:

(1) 30 μL Co^{2+} plus ultrapure water was added into 3 mL liquid contained 0.1 mM PNP and 10 mM $NaBH_4$, the final Co^{2+} concentration was 1.5 μM. This assay was used to exclude the effect of Co-Co_2B on the PNP reduction. This system showed no detectable PNP reduction activity.

(2) 30 μL Co^{2+} plus the sterilization product of bacteria without Ag/AgCl NPs. The final Co^{2+} concentration was the same with (1). This assay was used to exclude the effect of Co^{2+}-biomolecules on the PNP reduction. This system showed no detectable PNP reduction activity.

(3) 30 μL Co^{2+} (in the form of cobalt acetate) instead of cobalt chloride. The final Co^{2+} concentration was the same with (1). This assay was used to exclude the effect of anion on the PNP reduction. The PNP reduction performance of $Co(Ac)_2$-Ag/AgCl NPs was shown in Table S1.

(4) Using the Co NPs obtained by $NaBH_4$ pre-reduced Co^{2+}. 150 μM Co^{2+} was firstly reduced by excess $NaBH_4$, and the as-synthesized Co NPs was mixed with 3 mL biogenic Ag/AgCl NPs. The catalytic performance was shown in Table S1.

(5) 30 μL Co^{2+} plus chemogenic Ag NPs. The chemogenic Ag NPs were synthesized through sodium citrate/ascorbic acid mediated Ag^{+} reduction.[1] For comparison, the Co^{2+} (150 μM) was pre-reduced by excess $NaBH_4$ to form Co NPs, then Co NPs were

mixed with chemogenic Ag NPs and then added into the PNP solution. The PNP reduction performance was shown in Table S1.

(6) 30 μL Co^{2+} plus biogenic Ag NPs. The biogenic Ag NPs were synthesized by the same strain, i.e. *Bacillus* sp. CC-1 using NaCl excluded LB media.[2] For comparison, the Co^{2+} (150 μM) was pre-reduced by excess $NaBH_4$ to form Co NPs, then Co NPs were mixed with biogenic Ag NPs and then added into the PNP solution the PNP reduction performance was shown in Table S1.

For the other substrates, the following final concentration was used: *m*-nitrophenol, 0.1 mM, *o*-nitrophenol, 0.1 mM, MO, 10 mg/L, RhB, 10 mg/L. The other details and catalytic performance of Ag/AgCl NPs and Co-Ag/AgCl NPs were listed in Table S2.

S5. Details for catalytic parameter κ calculation

Taken the PNP reduction by Co-Ag/AgCl NPs as an example. the catalytic parameter κ was calculated as follows:

The catalysts amount was obtained by centrifuging a large volume of Ag/AgCl dispersion (250 mL, OD_{416nm}~0.5), and lyophilized to collect the powders. In a common experiment, the powders' weight was about 10 mg. Therefore, we can calculate the catalysts amount used in PNP reduction. For example, 30 μL Co-Ag/AgCl NPs dispersion contains 0.0012 mg catalysts (although most of the catalysts were biomolecules according to the result of XPS). The apparent rate constant k_{app} was calculated using the linear part with the pseudo first order kinetic model:[3]

$$\ln(A_t/A_0) = -k_{app}t$$

where A_t and A_0 are absorbance of *p*-nitrophenol at time t and 0 s, which are proportional to their concentration. Then, the catalytic parameter κ was defined as the ratio of k_{app} (s^{-1}) and catalysts amount (g).

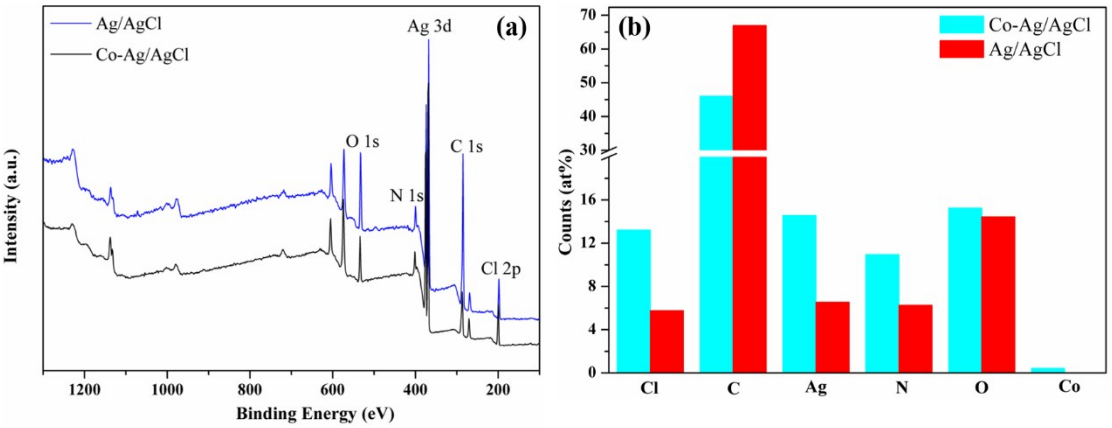

Figure S1. (a) XPS survey scan of Ag/AgCl NPs and Co-Ag/AgCl NPs. (b) Element composition of Ag/AgCl NPs and Co-Ag/AgCl NPs. The Co content was obtained by ICP-OES, while the contents of the other elements were extracted from the results of XPS.

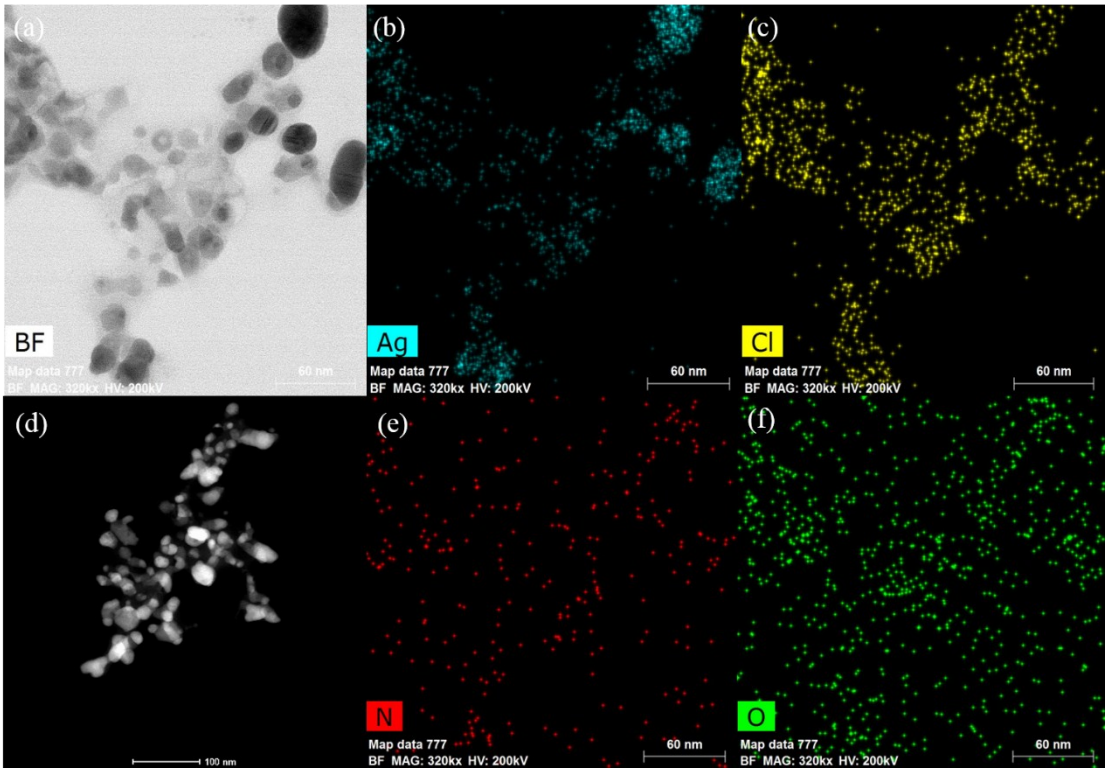

Figure S2. HAADF-STEM image of Ag/AgCl NPs. (a) Bright field image of the as-synthesized NPs. (b) Ag mapping. (c) Cl mapping. (d) Dark field image of the as-synthesized NPs. (e) N mapping. (f) O mapping.

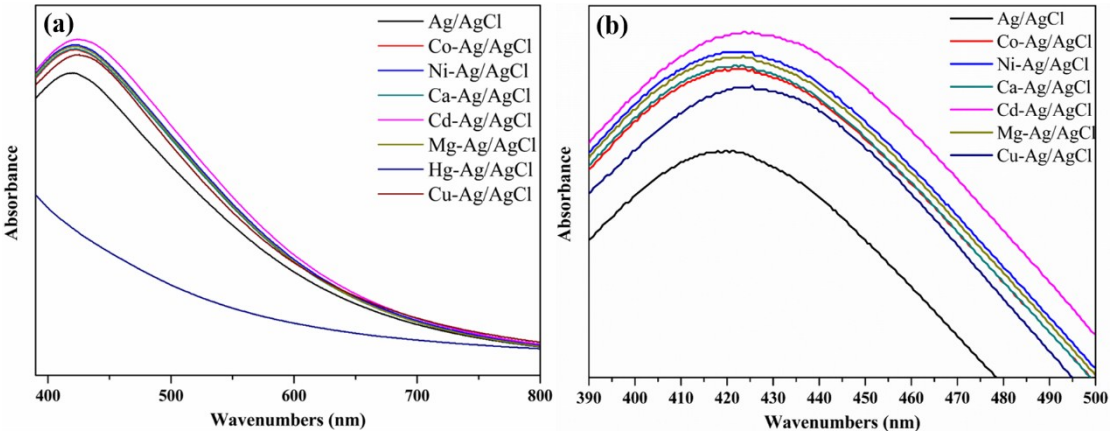

Figure S3. (a) UV-vis spectra of various M^{2+}-Ag/AgCl NPs dispersion (M=Co, Ni, Ca, Cd, Mg, Hg and Cu). (b) Enlarged UV-vis spectra (390 nm to 500 nm) of various M^{2+}-Ag/AgCl NPs dispersion except Hg-Ag/AgCl NPs.

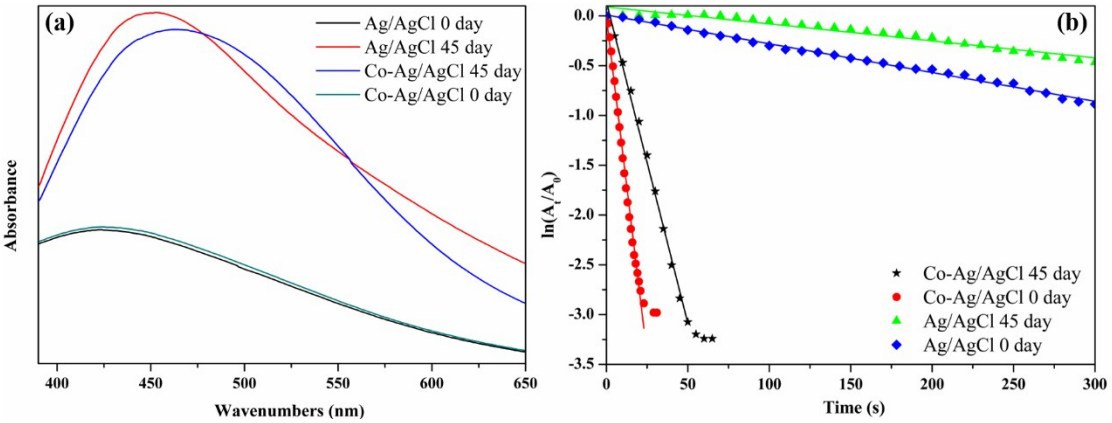

Figure S4. (a) UV-vis spectra of Ag/AgCl NPs and Co-Ag/AgCl NPs which were freshly prepared and stored at room temperature for 45 days. (b) Plot of $ln(At/A_0)$ versus reaction times for pseudo-first-order reduction kinetics of *p*-nitrophenol in the presence of excess $NaBH_4$.

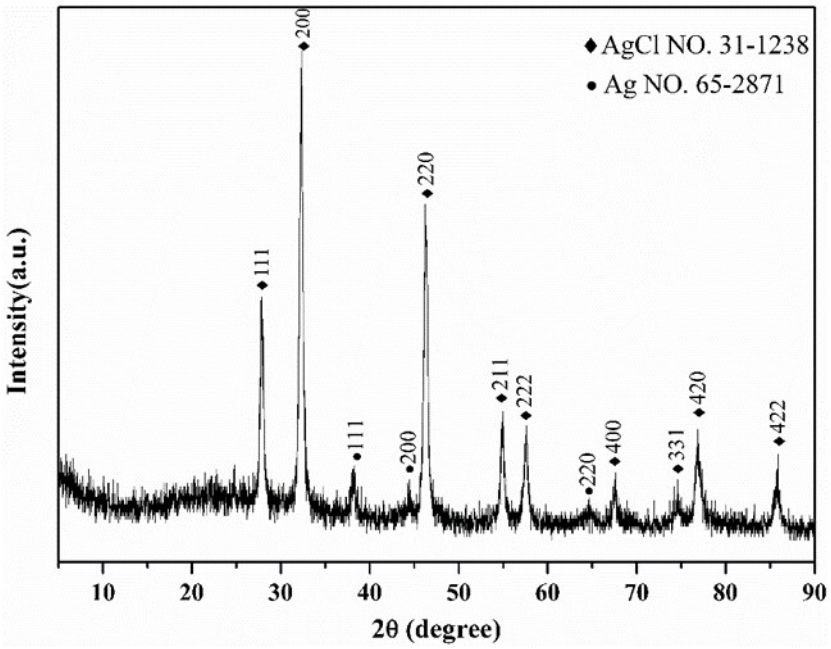

Figure S5. XRD pattern of the Co-Ag/AgCl NPs.

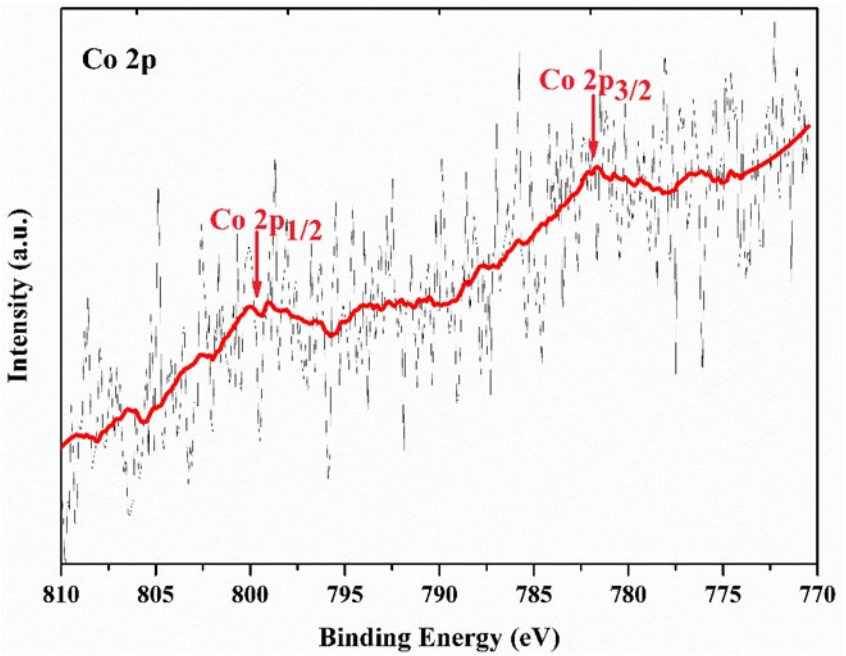

Figure S6. Co 2p XPS spectrum of Co-Ag/AgCl NPs.

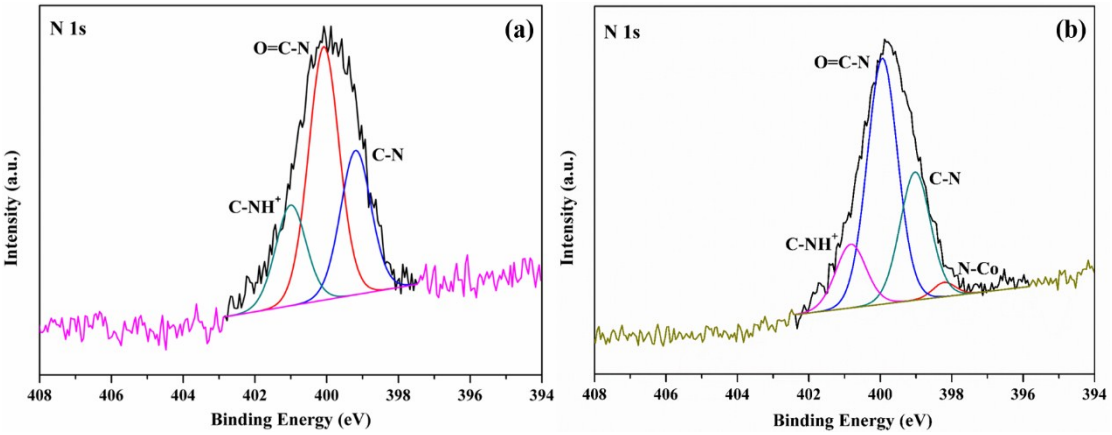

Figure S7. N 1s spectra of the Ag/AgCl NPs (a) and Co-Ag/AgCl NPs (b).

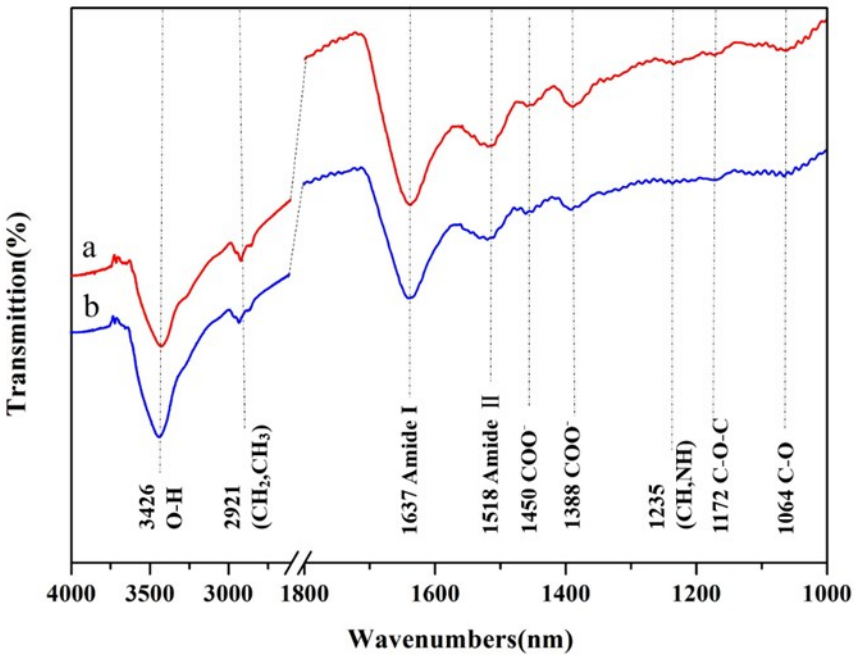

Figure S8. FTIR spectra of biogenic Ag/AgCl NPs (a) and Co-Ag/AgCl NPs (b).

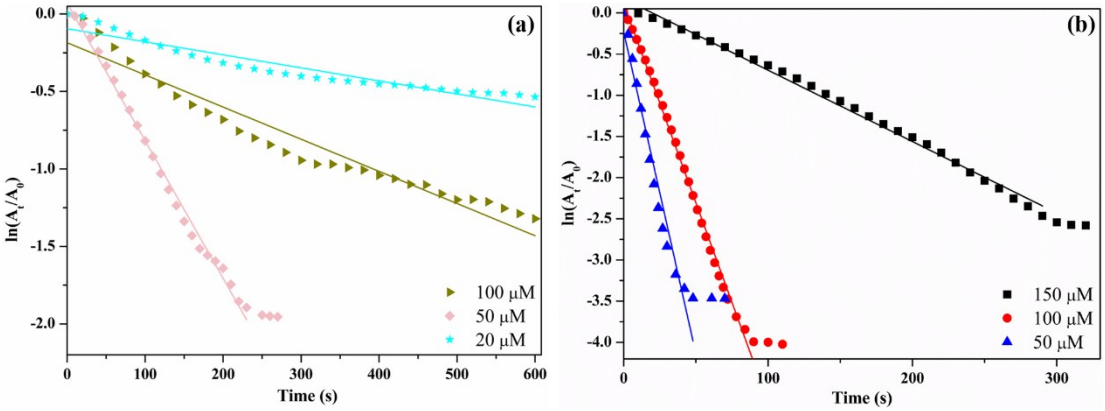

Figure S9. Plot of $ln(A_t/A_0)$ versus reaction times for pseudo-first-order reduction kinetics of *p*-nitrophenol in the presence of excess $NaBH_4$. (a) Ag/AgCl NPs with different concentration of PNP. (b) Co-Ag/AgCl NPs with different concentration of PNP.

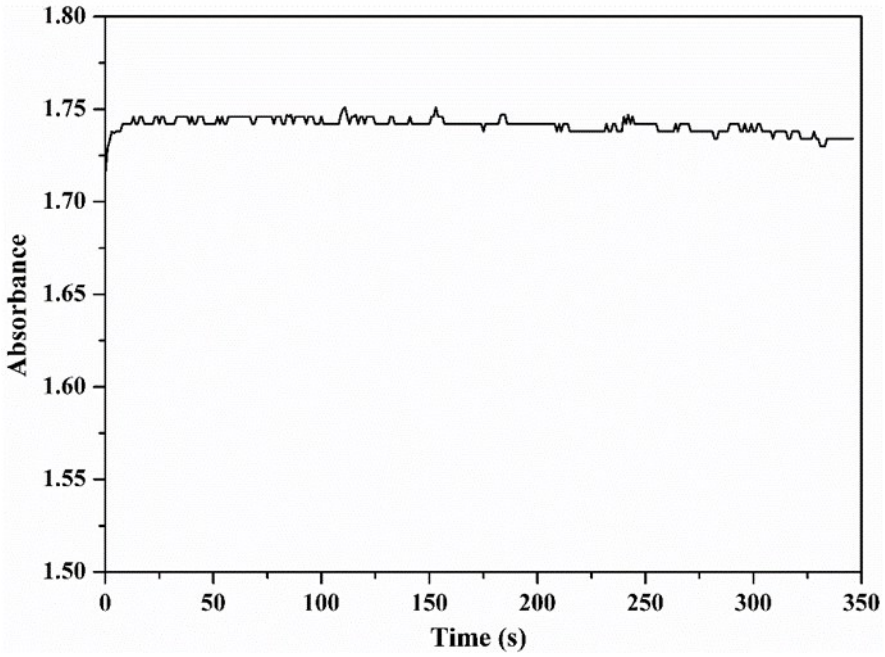

Figure S10. Time-course curve of adding 1.5 μM $CoCl_2$ into 0.1 mM PNP and 10 mM $NaBH_4$.

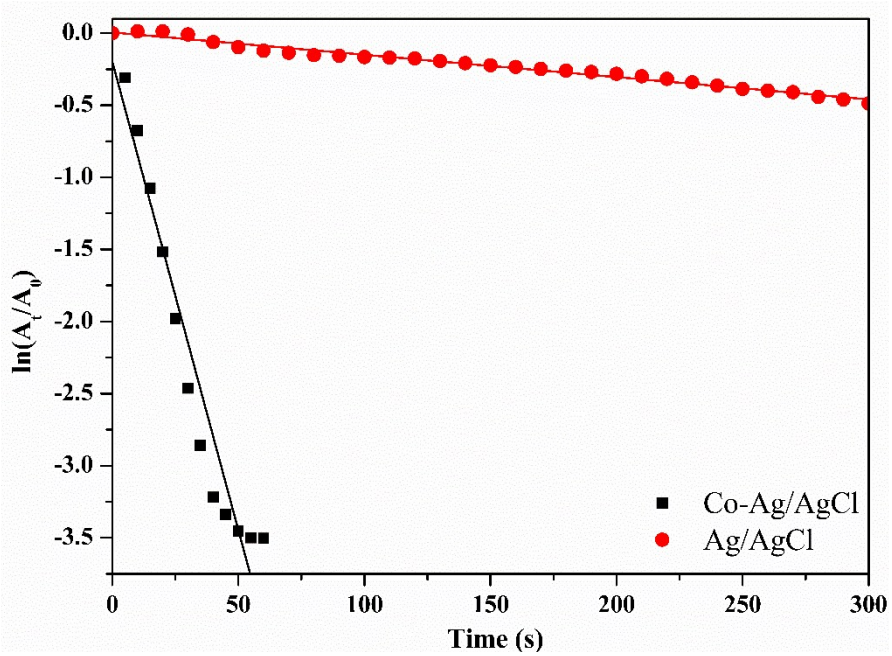

Figure S11. Plot of $ln(A_t/A_0)$ versus reaction times for pseudo-first-order reduction kinetics of *p*-nitrophenol by biogenic Ag/AgCl NPs and Co-Ag/AgCl NPs generated by *Bacillus* sp. YT-1 in the presence of excess $NaBH_4$.

Table S1. Comparison of the catalytic performance of Ag containing NPs

catalysts	amount (mg)	apparent rate constant k_{app} (s^{-1})	activity parameter *K* (s^{-1} g^{-1})	reference
$Ag_{0.6}Ni_{0.4}$	0.2	0.031	156	4
AgNP-PG-5K	0.004	0.0055	1375	5
TAC-Ag-1.0	4	0.00519	1.3	6
Fe_3O_4-@C@Ag-Au	0.01	0.0158	1580	7
Biogenic Ag/AgCl	0.008	0.0026	325	this work
Co-Ag/AgCl[a]	0.0012	0.0837	69750	this work
Co-Ag/AgCl[b]	0.0012	0.0897	74750	this work
Co NPs-Ag/AgCl	0.0012	0.0107	8917	this work
Ni-Ag/AgCl	0.0012	0.0149	12417	this work
Cd-Ag/AgCl	0.008	0.0123	1537	this work
Biogenic Ag	0.01	0.0027	270	this work
Chemogenic Ag	0.001	0.0006	600	this work
Co-biogenic Ag	0.01	0.041	4100	this work
Co-chemogenic Ag	0.001	0.0058	5800	this work
Co NPs-chemogenic Ag	0.001	0.0039	3900	this work
Co NPs-biogenic Ag	0.01	0.0084	840	this work

[a] The cobalt source was $CoCl_2$

[b] The cobalt source was $Co(Ac)_2$

Table S2. Catalytic performance of Ag/AgCl NPs and Co-Ag/AgCl NPs towards various substrates for hydrogenation reaction.

substrate	λ_{max} (nm)	catalyst	Catalyst amount (μg)	apparent rate constant k_{app} (s^{-1})	activity parameter *K* (s^{-1} g^{-1})
o-nitrophenol	415.5	Ag/AgCl	8	0.0037	462.5
		Co-Ag/AgCl	1.2	0.0255	21250
m-nitrophenol	401.5	Ag/AgCl	8	0.0193	2412.5
		Co-Ag/AgCl	1.2	0.0727	60583
methyl orange	465	Ag/AgCl	8	0.0262	3275
		Co-Ag/AgCl	1.2	0.2867	238916
rhodamine B	553.5	Ag/AgCl	8	0.0149	1863
		Co-Ag/AgCl	1.2	0.3548	295666

Reference

(1) Qin. Y.; Ji. X.; Jing J.; Liu H.; Wu H.; Yang W. Colliods Surf., A, 2010, 372, 172.
(2) Ramanathan. R.; O'Mullane. A. P.; Parikh. R. Y.; Smooker. P. M.; Bhargava, S. K.; Bansal. V. Langmuir, 2010, 27, 714.
(3) Begum, R.; Naseem, K.; Ahmed, E.; Sharif, A.; Farooqi, Z. H. Colliods Surf., A, 2016, 511, 17.
(4) Kumar, M.; Deka, S. *ACS Appl. Mater. Interfaces* **2014**, 6, 16071.
(5) Baruah, B.; Gabriel, G. J.; Akbashev, M. J.; Booher, M. E. *Langmuir* **2013**, 29, 4225.
(6) Rashid, M. H.; Mandal, T. K. *J. Phys. Chem. C* **2007**, 111, 16750.
(7) An, Q.; Yu, M.; Zhang, Y.; Ma, W.; Guo, J.; Wang, C. *J. Phys. Chem. C* **2012**, 116, 22432.