Electronic Supplementary Material (ESI) for Chemical Science.

Galvanic Replacement Synthesis of $Ag_xAu_{1-x}@CeO_2$ ($0 \leqslant x \leqslant 1$) Core@Shell Nanospheres with Greatly Enhanced Catalytic Performance

Dapeng Liu,[a] Wang Li,[a] Xilan Feng,[a] and Yu Zhang*[ab]

[a]*Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University, Beijing 100191, China,*

[b]*International Research Institute for Multidisciplinary Science, Beihang University, Beijing 100191 , P. R. China*

Email: jade@buaa.edu.cn

Experimental section

Synthesis of $Ag@CeO_2$ core@shell nanospheres:

2 mmol of $AgNO_3$ and 2 mmol of $Ce(NO_3)_3$ were dissolved in 10 mL H_2O. Then 0.84 mL of ammonia (25 %) were added with vigorously stirring. 30 min later, the products were purified by centrifugation and washed with water for three times.

Synthesis of $Ag_xAu_{1-x}@CeO_2$ core@shell nanospheres:

1g of NaCl was dissolved in 10 mL of H_2O first. Then 2 mL of the as-obtained $Ag@CeO_2$ aqueous dispersion were added. The $HAuCl_4$ aqueous solution was prepared by diluting a certain amount of $HAuCl_4$ (0.02 mM) aqueous solution in 50 mL of H_2O. The replacement reaction is triggered by dropping this $HAuCl_4$ aqueous solution very slowly. Four hours later, the product was purified by centrifugation with the help of ammonia (25 %).

Different usage of $HAuCl_4$ caused the structural evolution as well as the different composites. For examples, 1 mL of $HAuCl_4$ (0.02 mM) aqueous solution can induce the formation of $Ag_{0.64}Au_{0.36}@CeO_2$ core@shell nanospheres while 2 mL for $Ag_{0.41}Au_{0.59}@CeO_2$. Additionally, if excess $HAuCl_4$ was added in the reaction solution, $Au@CeO_2$ core@shell nanospheres could be obtained.

Characterization:

The X-ray diffraction patterns of the products were collected on a Rigaku-D/max 2500 V X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å), with an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopic (TEM) images were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. XPS measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with Al K_α X-ray radiation as the X-ray source for excitation.

Catalytic test:

Chemical Reduction of 4-NP by AB:

The catalytic test was carried out in a quartz curette in the UV/vis/NIR spectrophotometer. The aqueous solution of 4-NP ions (0.01 M) was prepared by pre-mixing 4-NP and NaOH together with the molar ratio of 1/1. In addition, AB (0.2 mmol/mL) aqueous solution was also freshly prepared. Typically 0.04 mL of 4-NP and 0.05 mL of AB aqueous solution were mixed in 3 mL of H_2O. Then 20 μL of catalysts were quickly added. The intensity of the absorption peak at 400 nm was monitored by UV−vis spectroscopy along with time.

Catalytic CO oxidation:

10 mg of catalysts were mixed with 20 mg of SiO_2 powders. The mixture was put in a stainless steel reaction tube. The experiment was carried out under a flow of reactant gas mixture (1 % CO, 20 % O_2, balance N_2) at a rate of 30 mL/min. The composition of the gas was monitored on-line by gas chromatography (GC 9800).

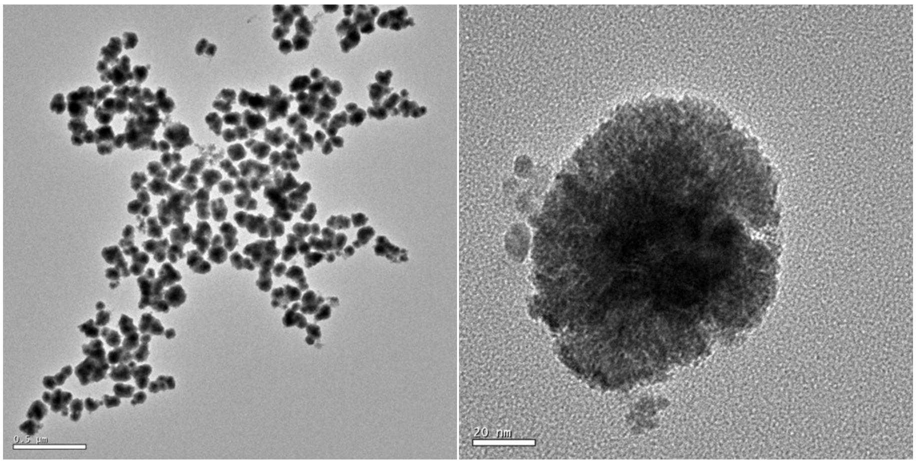

Figure S1. TEM images of Ag@CeO_2 core@shell nanospheres.

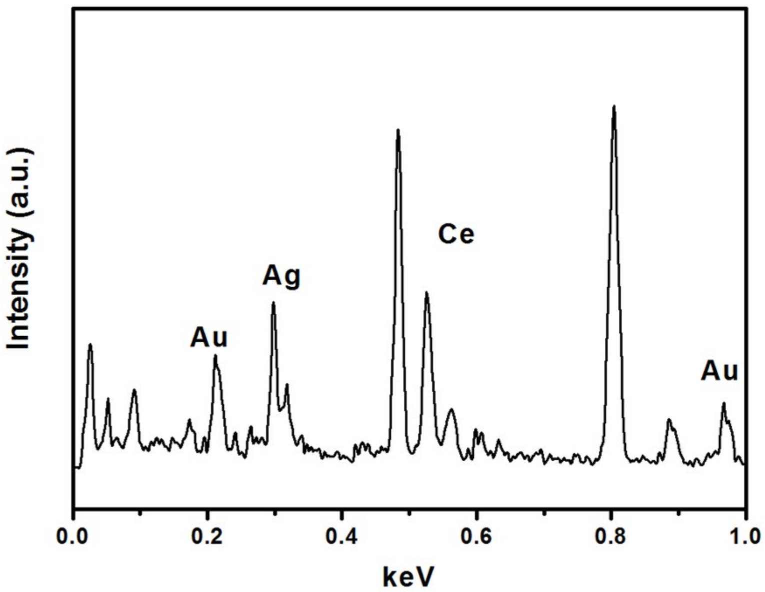

Figure S2. EDX spectrum of $Ag_{0.64}Au_{0.36}@CeO_2$

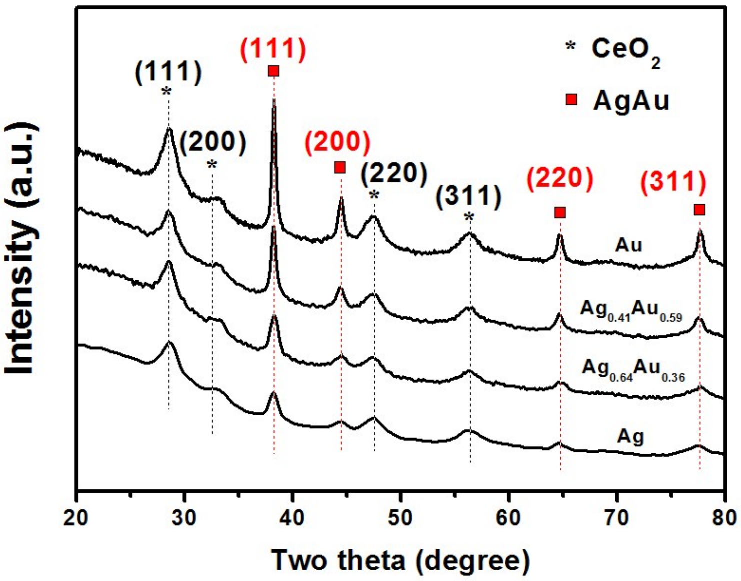

Figure S3. XRD patterns of Ag_xAu_{1-x}@CeO_2 core@shell nanospheres.

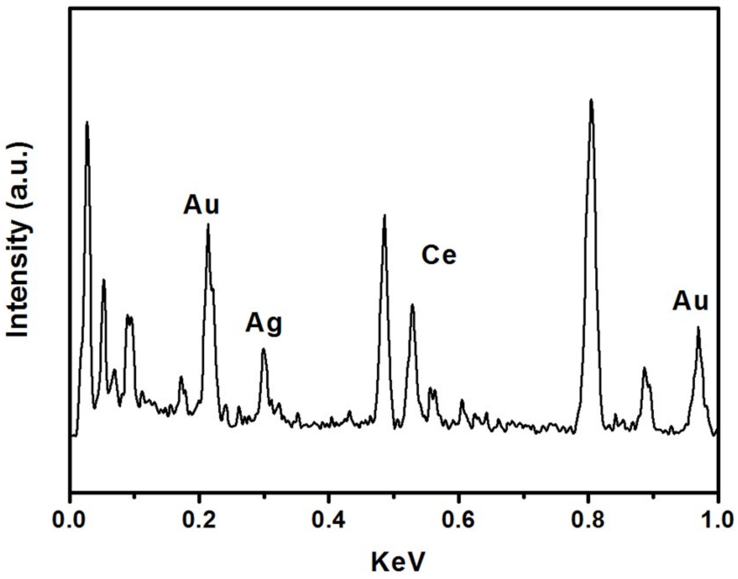

Figure S4. EDX spectrum of $Ag_{0.41}Au_{0.59}$@CeO_2.

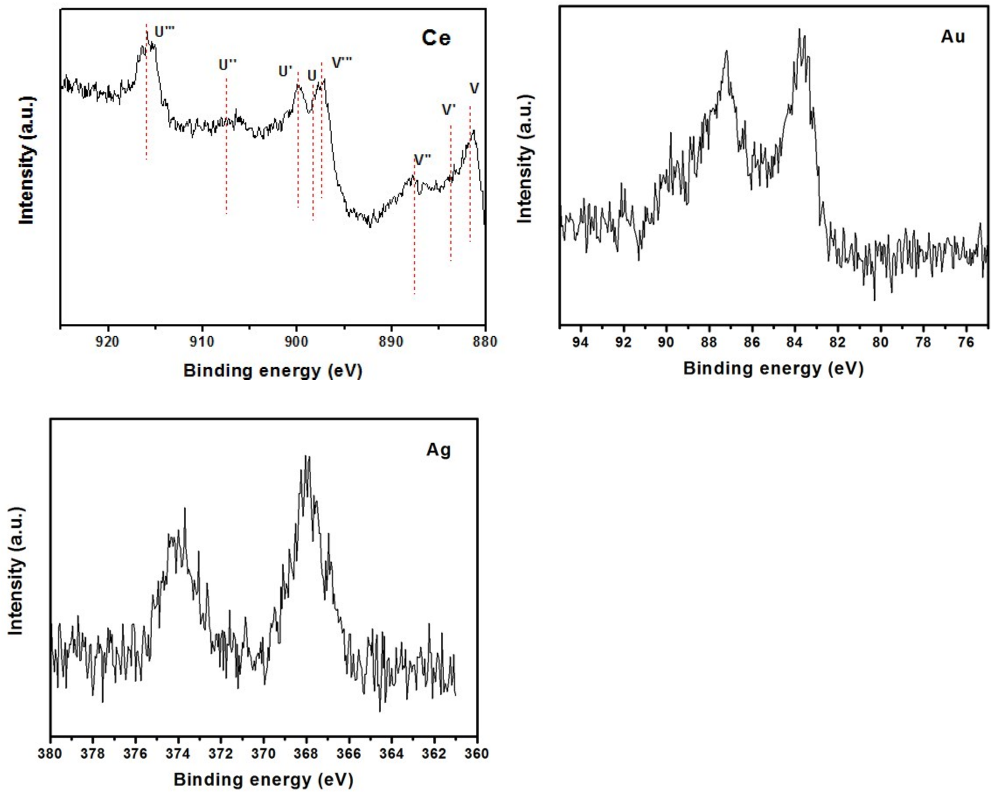

Figure S5. XPS spectra of $Ag_{0.64}Au_{0.36}@CeO_2$.

According to ref 7, the observed peaks can be assigned for CeO_2 (Ce^{4+}) as v, v'' and v''' for Ce $3d_{5/2}$, with the corresponding Ce $3d_{3/2}$ peaks labeled as u, u'' and u'''. An additional doublet is also observed due to the presence of Ce_2O_3 (Ce^{3+}) and is assigned as v' and u'. Due to the presence of both Ce^{4+} and Ce^{3+}, it implies that cerium is present at the surface in both 4+ and 3+ oxidation states.

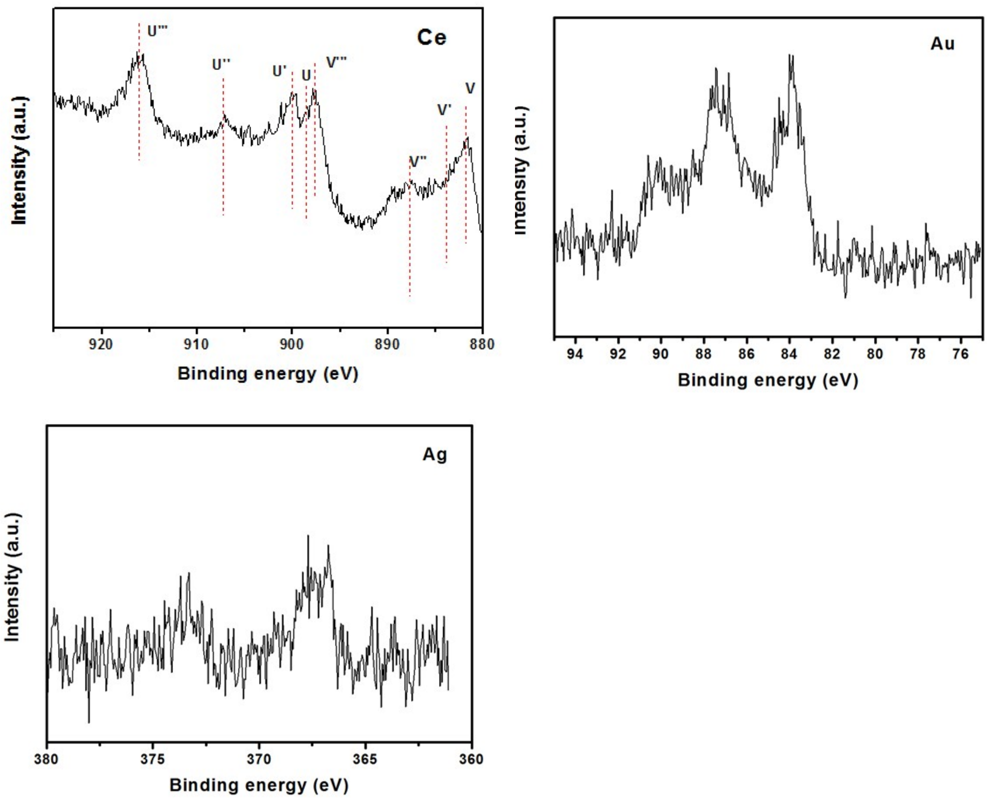

Figure S6. XPS spectra of $Ag_{0.41}Au_{0.59}@CeO_2$.

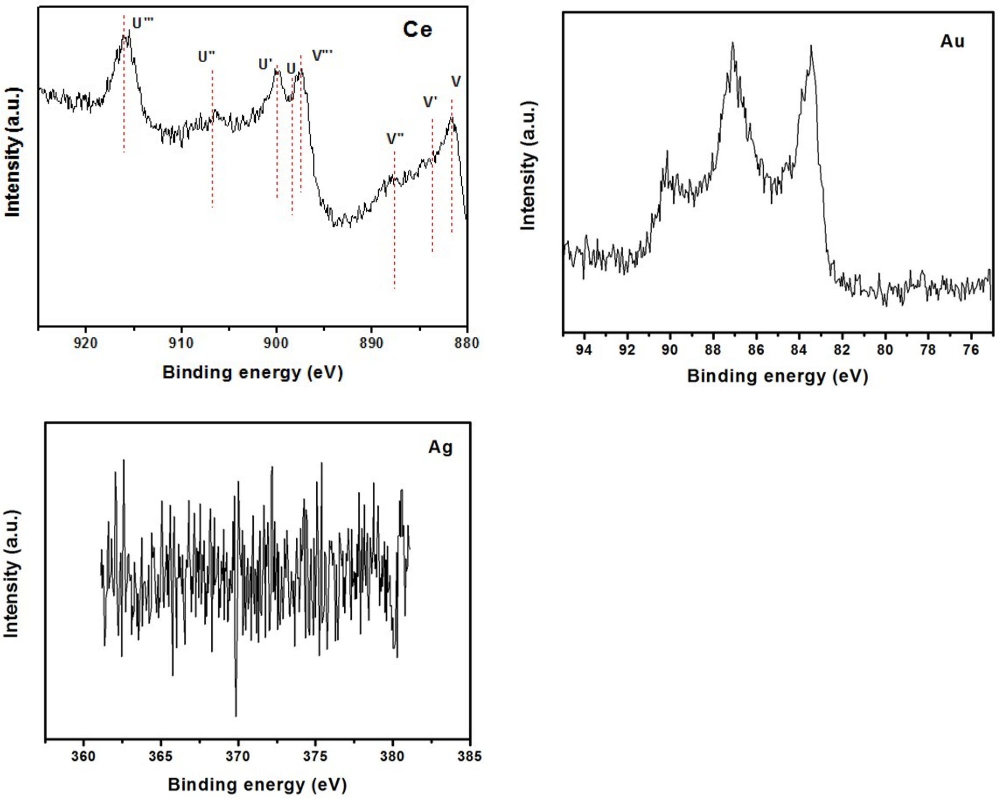

Figure S7. XPS spectra of Au@CeO_2.

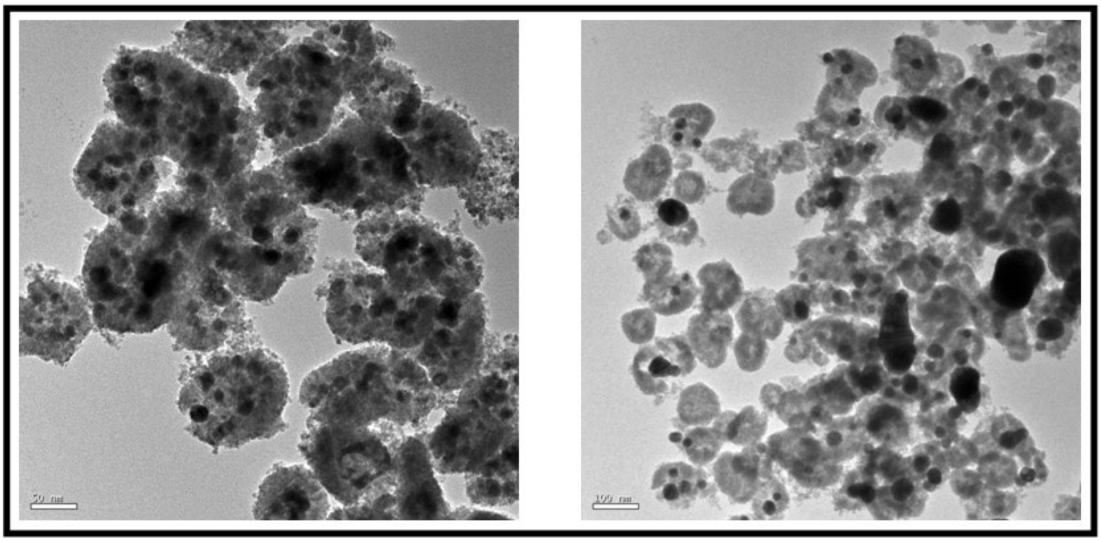

Figure S8. TEM images of the as-prepared Ag_xAu_{1-x}@CeO_2 ~~without~~ with addition of NaCl in the reaction solution.

Table S1. Catalytic data of the as-prepared Ag_xAu_{1-x}@CeO_2 catalysts with Pt@CeO_2.

Sample	**T_{100} (°C)**[a]	**TOF (min^{-1})**[b]	**Reference**
Ag@CeO_2	200	1.3	This work
$Ag_{0.64}Au_{0.36}$@CeO_2	120	3.5	This work
$Ag_{0.41}Au_{0.59}$@CeO_2	150	2.3	This work
Au@CeO_2	> 300	1.6	This work
Pt@CeO_2	140	1.4	Ref. 7

[a] Calculated TOF for catalytic reduction of 4-NP

[b] T_{100} for catalytic CO oxidation