Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Interfacial electron transfer promotes photo-catalytic reduction of *4*-nitrophenol by Au/Ag2O nanoparticles confined in dendritic mesoporous silica nanospheres

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Experiment section:

Synthesis of mesoporous silica supports

Four kind of mesoporous silica material were synthesized as supports. DMSNs,[1-3] MCM-41[4, 5] and SBA-15[6] free of micropores were synthesized according to the literature report. DMSNs-D3 (DMSNs without 3 nm mesopores) was fabricated by following procedure: 1.64 g of CTATos, 0.31 g of $TEAH_3$ and 87 ml of deionized H_2O were mixed and stirred at 80 °C for 30 min. Then 12.52 g of TEOS was added into the mixed system quickly and stirred for 2 h. After adding 2.83 g of TMABr, the solution was transferred into a stainless-steel autoclave and maintained at 100 °C for 48 h. The synthesized DMSNS-D3s were filtrated, washed and dried in the oven at 80 °C overnight. The mother liquid molar ratio is 1.0 SiO_2: 0.06 CTATos: 0.026 $TEAH_3$: 80 H_2O: 0.3 TMABr.

Synthesis of mesoporous silica nanopaticles loaded with metal nanoparticles using an in-situ nanocrystal seeding-induced-growth (SIG) strategy

The DMSNSs were treated by HCl and then functionalized by aminopropyl before grafting metal nanopaticles. In a typical process, 2 g of DMSNSs, 3.36 mL of 1 M HCl and 80 mL of EtOH were added into a round-bottom flask, the mixture was refluxed with stirring at 60 °C for 1 h. The solid was dried at 80 °C after filtered. Then, 1.5 g of HCl washed DMSNSs, 2.61 g of APTMS and 60 mL EtOH were introduced into a round-bottom flask and maintained at 80 °C for 12 h in an oil bath with stirring under reflux condition. The solution was filtered and the solid was dried at 80 °C. In a 200 mL beaker, 1g of amino-functionalized DMSNs was suspended in 80 mL EtOH, and subsequently 20.8 mL of 4.85 mM $HAuCl_4$ ethanol solution was added. After being stirred at room temperature for 12 h, excess of $NaBH_4$ was added at once. The obtained product was filtered and washed repeatedly with deionized H_2O and ethanol and dried overnight at 80 °C. The products were denoted as 2%Au-DMSNs, where 2% represents the weight percentage content of metal and Au represents the metal element type contained. Unless otherwise indicated, all loading amounts in the experiments described below refer to weight percentage of metal elements. The other products which contain different kind of metal element (Ag, Pt), different metal content (0.25%, 0.5%, 1%, 5%, 10%) or use different silica support (MCM-41, SBA-15, DMSNs-D3) were synthesized and labeled in the same way.

The preparation method of 1%Ag/1%Au-DMSNs is shown as follow: 0.5 g of 1%Au-DMSNs was ultrasonically dispersed in 50 mL deionized H_2O. Then 0.47 mL of 50 mM $AgNO_3$ was added and stirred at room temperature for 3 h in dark. The mixture was stirred unceasingly for 30 min after adding excess $NaBH_4$. The product was obtained by filtration, washed repeatedly with deionized H_2O, and dried overnight at 80 ℃. To get 1%Ag_2O/1%Au-DMSNs, 5 mL of 1 M NaOH was added instead of excess $NaBH_4$. Other bimetallic catalysts were fabricated in a similar process.

Reduction of *4*-Nitrophenol

Aqueous solutions of *4*-NP (0.2 mL, 2.5 mM) and $NaBH_4$ (0.4 mL, 250 mM) were added into a quartz cuvette under stirring. Subsequently, a certain amount (30 μL) of aqueous solution of catalyst (5 mg/mL) was added. As the reaction progressed, the bright yellow solution gradually faded. The reaction was scanned by UV-vis spectrum repeatedly from 500 nm to 250 nm over the whole course to record the changes.

Scale-up experiments were carried out in a stainless-steel vessel of 50 mL. Typically, 1.5 mL of *4*-NP solution, 5 mL of $NaBH_4$ solution and 22 mL of H_2O were mixed and stirred at 250 r/min and maintained at room temperature. The whole reaction system was under irradiation of a Xenon lamp (300 W, $350nm<\lambda<780nm$) or in totally dark. After adding 0.3 mL of aqueous solution of catalyst, 0.5 mL of the products was taken per 5 minutes and diluted to 3 mL by H_2O. The diluted sample was also scanned by UV-vis spectrum to detect the concentration of *4*-NP.

Stability test of the 1%Ag_2O/1.0%Au-DMSNs catalyst

Stability test was carried out in a beaker of 250 mL. Typically, 3.75 mL of *4*-NP solution (25 mM), 12 mL of $NaBH_4$ solution (1 M) and 200 mL of H_2O were mixed and stirred at 250 r/min and maintained at room temperature. After adding 5 mL of aqueous solution of catalyst (15 mg/mL), 0.3 mL of the products was taken per 1.5 minutes and diluted to 3 mL by H_2O. Progress of the reaction was monitored by measuring the UV–Vis absorption spectra of the reaction mixture. After the completion of the reduction reactions, 1%Ag2O/1.0%Au-DMSNs catalyst was recovered by centrifugation and then washed with water and dried in vacuum at room temperature for the next catalytic run. The aforementioned procedure was repeated six times.

Experiment results:

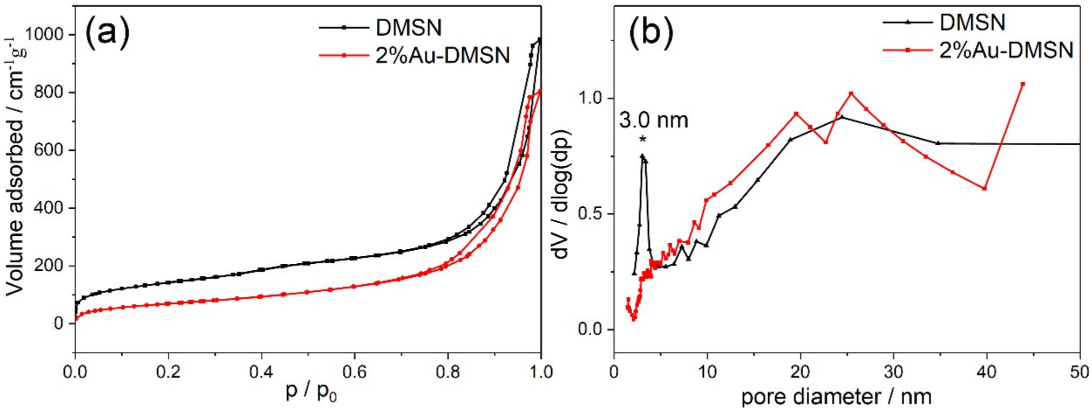

Fig. S1 (a) N_2 adsorption–desorption isotherms of DMSNs and 2%Au-DMSNs and (b) their corresponding pore size distribution curves calculated by the BJH method.

Table S1 Textural Characteristics of DMSNs and 2%Au-DMSNs.

Sample	**S_{BET} [a] (m^2/g)**	**V_{total} [b] (mL/g)**	**V_{inter} [c] (mL/g)**
DMSNs	485	1.38	0.41
2%Au-DMSNs	256	1.18	0.33

[a] Specific surface area measured from N_2 physisorption.

[b] Total pore volume measured at P/P_0= 0.99.

[c] Internal pore volume measured at P/P_0 = 0.80.

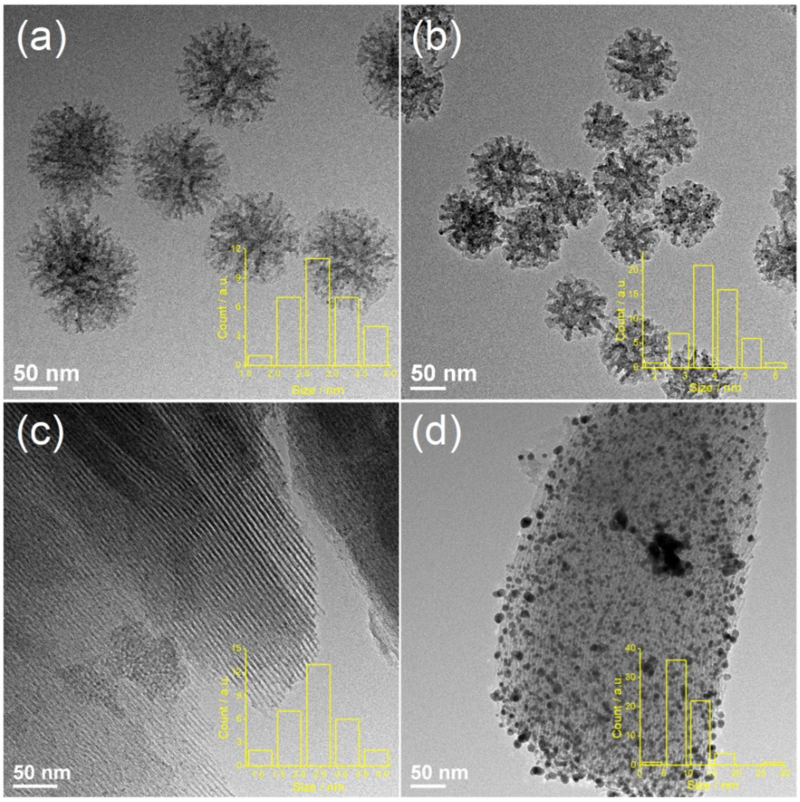

Fig. S2 TEM images of (a) 2%Au-DMSNs, (b) 2%Au-DMSNs-D3, (c) 2%Au-MCM-41, (d) 2%Au-SBA-15.

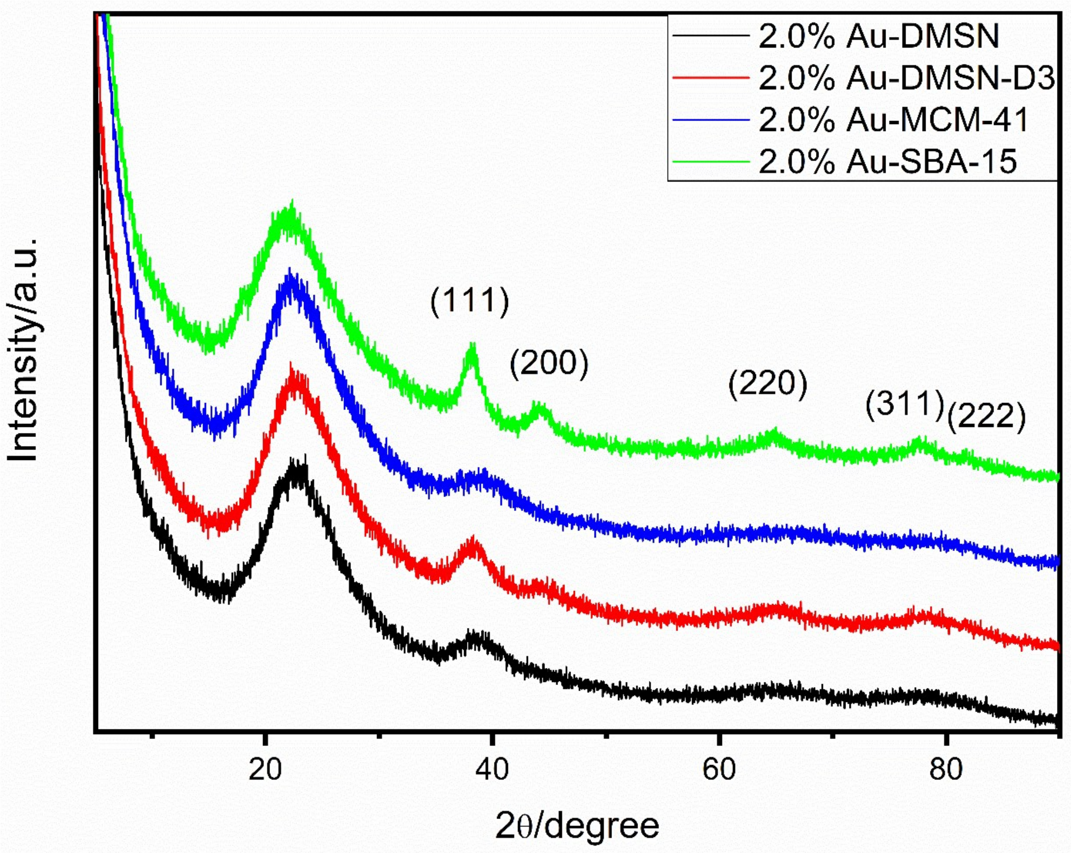

Fig. S3 XRD patterns of 2%Au NPs loaded on different kinds of mesoporous silica supporters.

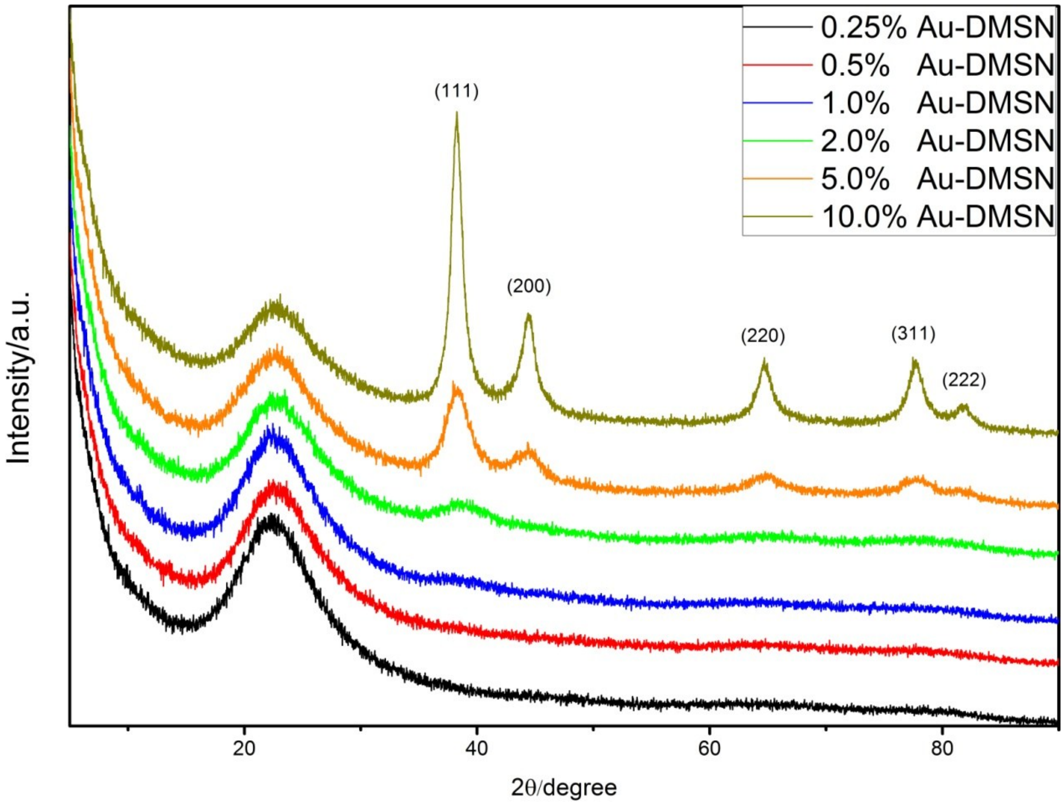

Fig. S4 XRD patterns of different content of Au loaded on DMSNs.

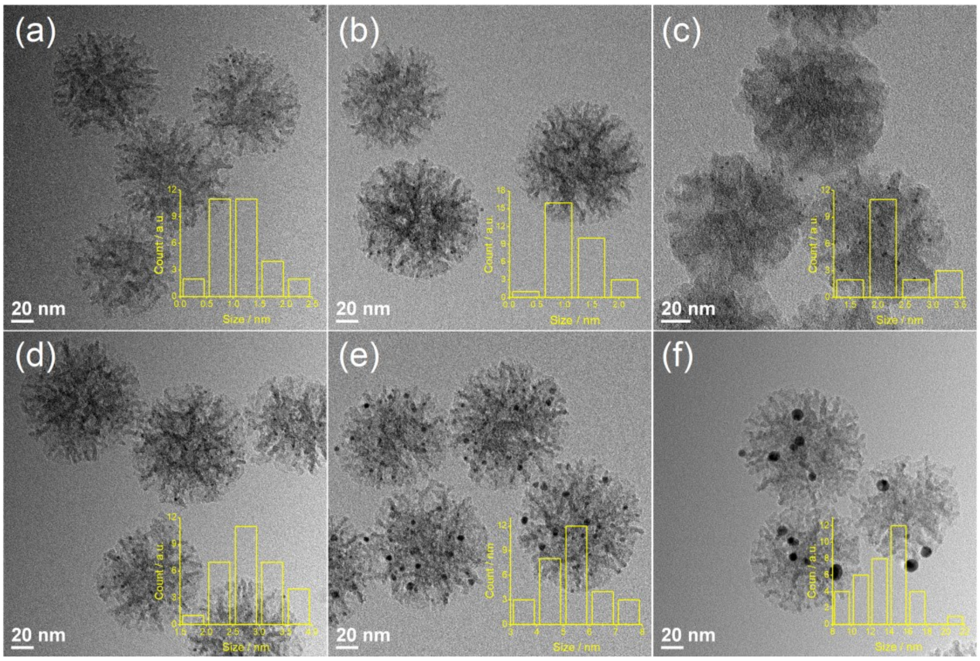

Fig. S5 Typical TEM images of catalysts: (a) 0.25%Au-DMSNs (b) 0.5%Au-DMSNs (c) 1.0%Au-DMSNs (d) 2.0%Au-DMSNs (e) 5.0%Au-DMSNs (f) 10.0%Au-DMSNs.

Table S2 The metal contents of different samples with different dosage of $HAuCl_4$ determined by ICP-OES analysis.

sample	**Au（wt%）**
DMSNs-H-NH_2-0.5%Au	0.25
DMSNs-H-NH_2-1%Au	0.35
DMSNs-H-NH_2-2%Au	1.16
DMSNs-H-NH_2-5%Au	4.62

It should be noted that, considering the very low chemical activity of Au catalyst with 10.0 % loading, the Au loading was not measured.

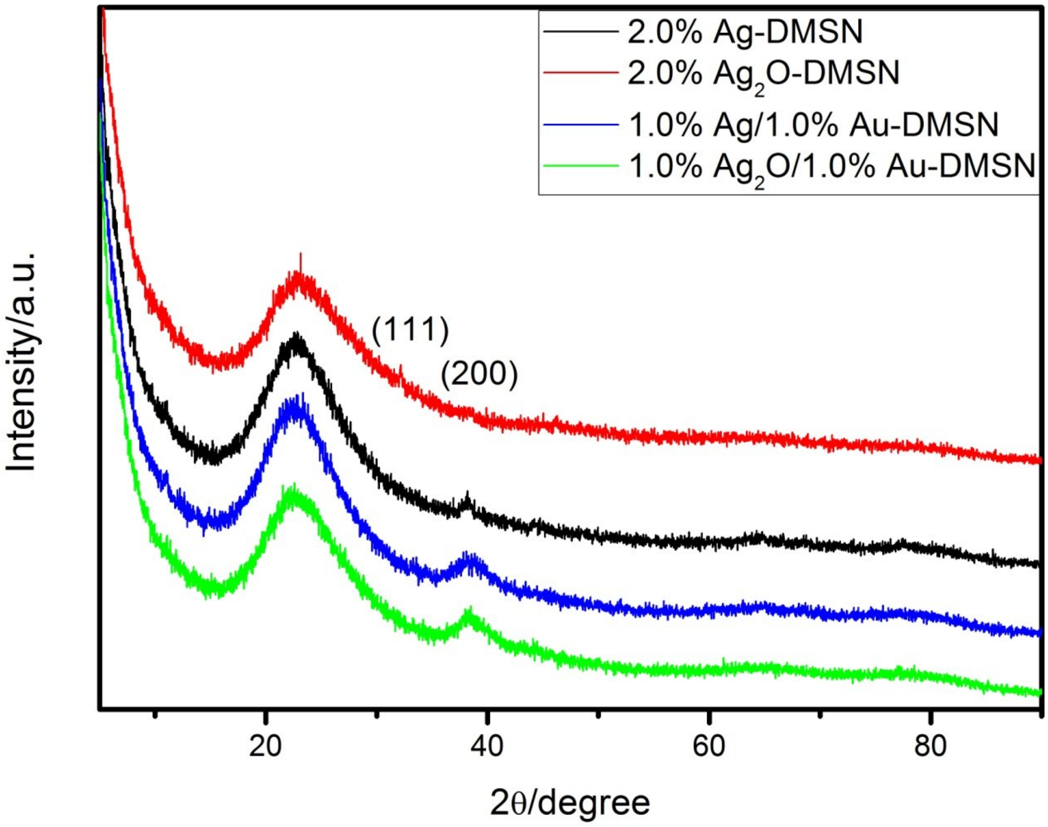

Fig. S6. XRD patterns of different composition of metal loaded on DMSNs.

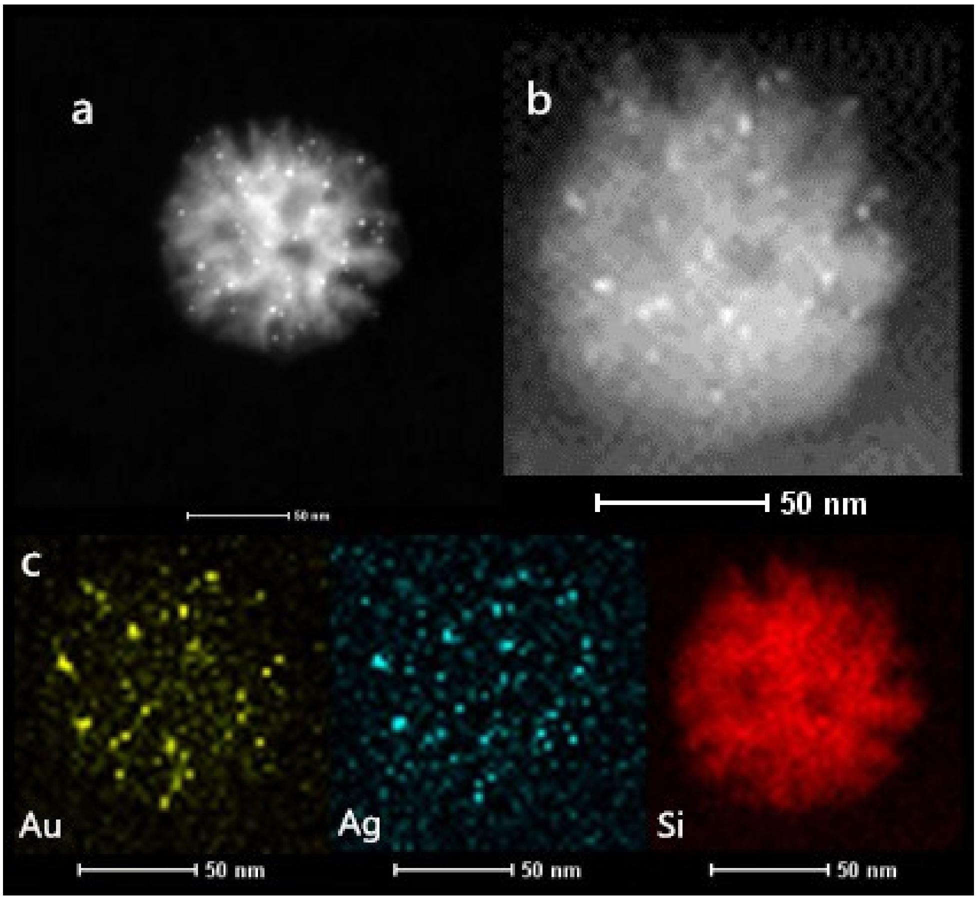

Fig. S7. (a) HAADF-STEM, (b) High-resolution HAADF-STEM and (c) STEM EDX mappings of 1%Ag/1%Au-DMSNs.

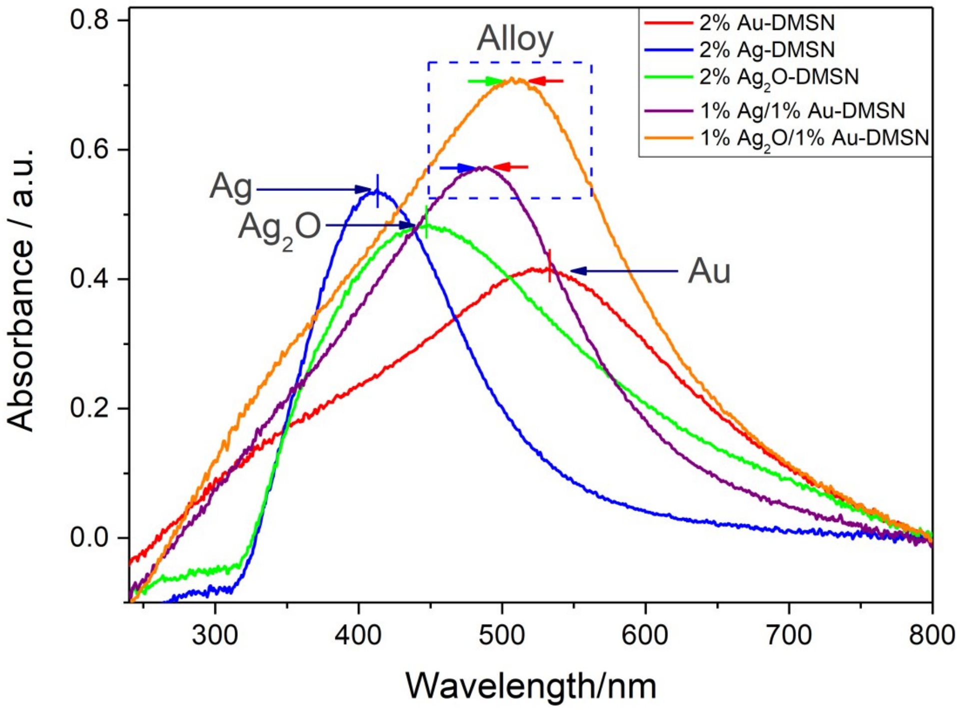

Fig. S8 UV-vis absorption spectra of DMSNs loaded with single metal component and bimetallic components.

Table S3 Surface compositions of catalysts determined by XPS.

Sample	Au component (%)			Ag component (%)		Ag/Au ratio
	Au^0	Au$^{\delta+}$	Au^{3+}	Ag^0	Ag$^+$	
2%Au-DMSNs	33.0	50.6	16.4	-	-	-
2%Ag-DMSNs	-	-	-	92.5	7.5	-
1%Ag/1%Au-DMSNs	47.1	32.6	20.3	82.9	17.1	2:1
1%Ag_2O/1%Au-DMSNs	54.8	26.3	18.9	51.3	48.7	2:1

a: The percentage of each species is only for this element itself.
b: The Ag/Au ratio is mole ratio.

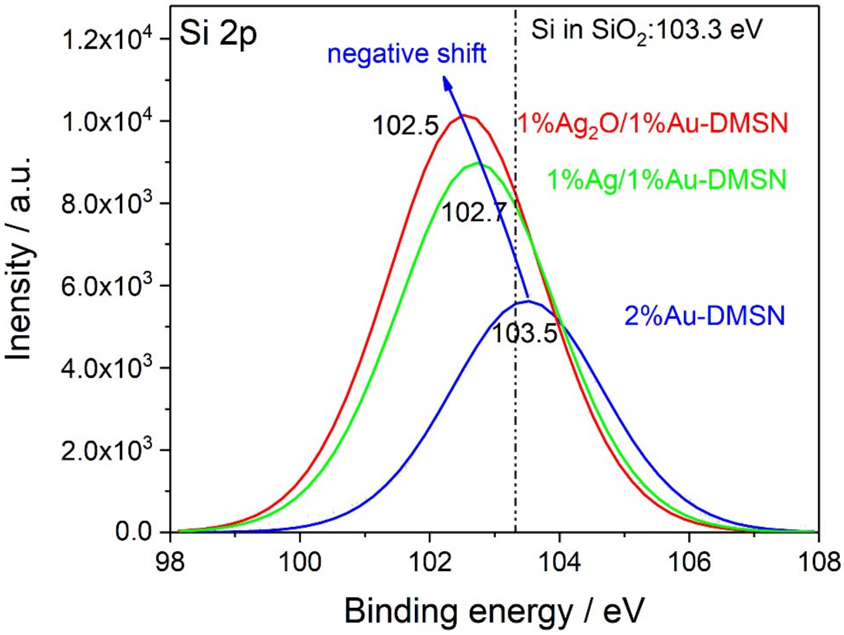

Fig. S9 Si 2p XPS spectra of 2%Au-DMSNs, 1%Ag/1%Au-DMSNs, and 1%Ag_2O/1%Au-DMSNs.

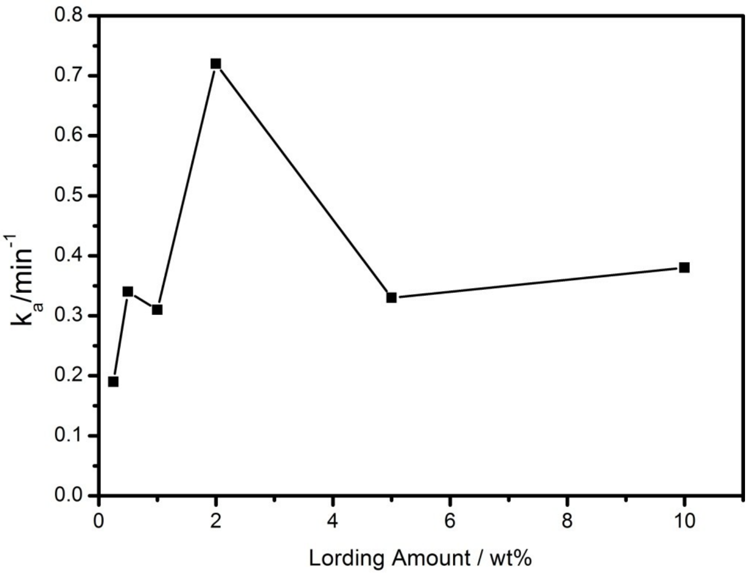

Fig. S10 The catalytic activity of Au-DMSNs with different Au loading amount for the reduction of *4*-NP.

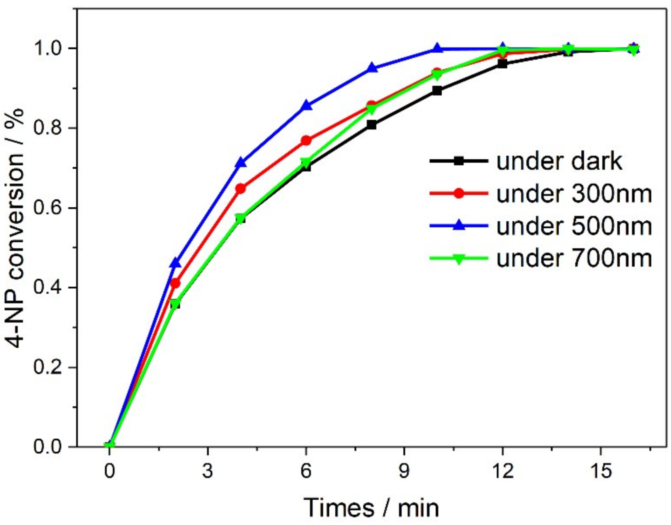

Fig. S11 Catalytic performance of 1%Ag_2O/1%Au-DMSNs under different wavelength irradiation.

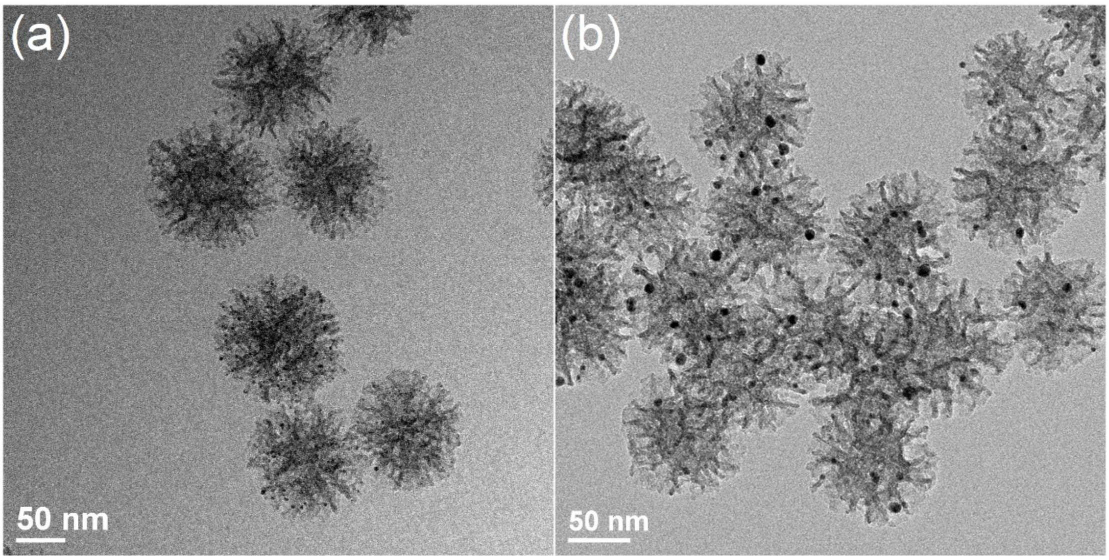

Fig. S12 Typical TEM images of 1%Ag_2O/1%Au-DMSNs catalyst before (a) and (b) after 6 times recycling runs for the reduction of *4*-NP with $NaBH_4$.

Table S4 Comparison of recent reports on noble metal-based catalysts catalyzed reduction of *4*-NP by $NaBH_4$. The comparisons for the chemical reactivity were done for the noble metal-based catalysts under the similar reaction conditions.

catalyst	Catalyst used (mg)	K^a (10^{-3} s^{-1})	K/M^b (s^{-1} g^{-1})	Ref.
Ag–NP/C pheres	1.0	1.69	1.69	7
TAC–Ag-1.0	4.0	5.19	1.30	8
Ag/SiNSs-1	10.0	18.05	1.81	9
Ag/C	2.0	5.32	2.66	10
Ag/SNTs	5.0	16.02	3.24	11
CNFs/Ag	1.0	4.60	4.60	12
Fe3O4@SiO2–Ag	1.0	7.67	7.67	13
Ag@SBA-15	0.9	12.70	14.10	14
Ag/KCC-1	0.2	10.00	50.00	15
1.0%Ag_2O1.0%Au-DMSNs	0.15	13.50	90.00	This work

[a] The reaction rate constant.

[b] The reaction rate constant per total weight of used catalyst.

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