Supporting Information

Magnetic Double-Shell Microsphere as a Highly Efficient Reusable Catalyst for Catalytic Application

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1. Experimental section

1.1. Materials Synthesis

1.1.1. Synthesis of Fe₃O₄ microspheres

The Fe₃O₄ micrspheres were synthesized following a reported method with slightly modification.¹ FeCl₃· $6H_2O$ (0.675 g, 2.5 mmol), NH₄Ac (1.927 g, 25 mmol), and trisodium citrate (0.2 g, 0.68 mmol) were dissolved in ethylene glycol (35 mL). The mixture was stirred vigorously for 1 h to form a homogeneous yellow solution, and then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 200 °C for 16 h. The reaction system was then cooled to room temperature naturally, and the resulting black product was collected with

the help of a magnet and washed with absolute ethanol three times. The final product was dispersed in absolute ethanol for further use.

1.1.2. Synthesis of Fe₃O₄@TiO₂ microspheres

The above-prepared magnetic Fe_3O_4 microspheres were dispersed in a mixed solvent containing 250 mL of absolute ethanol and 90 mL of acetonitrile. The mixture was ultrasonicated for 15 min, and then 1.5 mL of NH₃·H₂O solution (25 wt.%) was added. After the continuous mechanical stirring for 30 min, 3 mL of tetrabutyl titanate (TBOT) previously dissolved in 20 mL of absolute ethanol was introduced dropwise to the above suspension under the continuous mechanical stirring at 30 °C. The reaction system was kept under mechanical stirring for 1.5 h to obtain Fe₃O₄@TiO₂ core/shell microspheres. The product was collected by magnetic separation and washed with absolute ethanol three times. The final product was dispersed in deionized water for further use.

1.1.3. Synthesis of Fe₃O₄@TiO₂/Au microspheres

25 mL of HAuCl₄·3H₂O aqueous solution (1 g/L), 1.45 mL of 1 wt.% polyvinyl alcohol (PVA) aqueous solution and 170 mL of deionized water were mixed in a beaker under continuous magnetic stirring for 30 min. Then, 2.3 mL of freshly prepared NaBH₄ aqueous solution (0.1 M) was added to form a red color sol. After 30 min of sol generation, the colloid was immobilized by adding the above-prepared Fe₃O₄@TiO₂ core/shell microspheres (acidified to pH 1 by sulfuric acid) under vigorous mechanical stirring at 30 °C. The reaction system was kept under mechanical stirring for 2 h to obtain Fe₃O₄@TiO₂/Au microspheres.² The product was magnetically separated from the solution and rinsed with deionized water. The final product was dispersed in absolute ethanol for further use.

1.1.4. Synthesis of Fe₃O₄@TiO₂/Au@SiO₂ microspheres

The above-prepared Fe₃O₄@TiO₂/Au microspheres were dispersed in a mixture of 260 mL of absolute ethanol, 70 mL of deionized water and 5 mL of NH₃·H₂O solution (25 wt.%). After the continuous ultrasonication for 15 min and stirring for 15 min, a solution of tetraethyl orthosilicate (TEOS) prepared by dissolving 4 mL of TEOS in 20 mL of ethanol was subsequently added into the dispersion and the reaction was allowed to proceed for 12 h under continuously mechanical stirring.³ The resultant Fe₃O₄@TiO₂/Au@SiO₂ microspheres were collected with a magnet and washed with absolute ethanol three times. The final product was dispersed in absolute ethanol for further use.

1.1.5. Synthesis of Fe₃O₄@TiO₂/Au@SiO₂/Pd microspheres

The above-prepared Fe₃O₄@TiO₂/Au@SiO₂ microspheres were dispersed in 100 mL of absolute ethanol under continuous ultrasonication for 15 min. Then, 2 mL of 3-aminopropyl-triethoxysi-lane (APTES) was added into the dispersion and the dispersion was heated to 70 °C under mild mechanical stirring and reflux conditions for 6 h to functionalize the silicate surface with amino groups. Finally, with the help of a magnet, the APTES-modified Fe₃O₄@TiO₂/Au@SiO₂ microspheres were harvested and washed with absolute ethanol. Subsequently, 10 mL of PdCl₂ aqueous solution (1 g/L), 0.7 mL of PVA aqueous solution (1 wt.%) and 87 mL of deionized water were mixed in a beaker under continuously magnetic stirring for 30 min. Then, 2 mL of freshly prepared NaBH₄ aqueous solution (0.1 M) was added to form a brown color sol. After 30 min of sol generation, the colloid immobilized adding the above-prepared **APTES-modified** was by Fe₃O₄@TiO₂/Au@SiO₂ microspheres under vigorously mechanical stirring at 30 °C. The

reaction system was kept under mechanical stirring for 12 h to obtain $Fe_3O_4@TiO_2/Au@SiO_2/Pd$ microspheres.^{2,3} The product was magnetically separated from the solution and rinsed by deionized water. The final product was dispersed in deionized water for further use.

1.1.6. Synthesis of Fe₃O₄@TiO₂/Au@SiO₂/Pd@TiO₂ microspheres

The above-prepared Fe₃O₄@TiO₂/Au@SiO₂/Pd microspheres were dispersed in 30 mL of deionized water containing 0.4 g of hydroxypropyl cellulose (HPC) under continuous ultrasonication for 30 min. After the continuously mechanical stirring for 12 h, the HPC-modified Fe₃O₄@TiO₂/Au@SiO₂/Pd microspheres were separated and collected with a magnet, and washed with absolute ethanol. Then, the above-prepared HPC-modified Fe₃O₄@TiO₂/Au@SiO₂/Pd microspheres were dispersed in a mixed solvent containing 95 mL of absolute ethanol and 0.4 mL of deionized water. After the continuous ultrasonication for 30 min, 4 mL of TBOT previously dissolved in 20 mL of absolute ethanol was slowly introduced into the dispersion using a syringe pump (0.5 mL·min⁻¹) under continuous mechanical stirring at 30 °C, following the dispersion was refluxed at 85 °C for 100 min. The product was collected by magnetic separation, washed with absolute ethanol and dried at 60 °C for 2 h.⁴ The obtained product was subsequently calcined at 500 °C for 2 h in Ar atmosphere.

1.1.7. Synthesis of magnetic double-shell $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ microspheres

Alkaline etching method SiO₂ obtain the was used to remove to Fe_3O_4 (a) TiO_2/Au (a) Pd (a) TiO_2 microspheres. Typically, 0.2 of g Fe₃O₄@TiO₂/Au@SiO₂/Pd@TiO₂ microspheres were dispersed in 40 mL of NaOH solution (0.125 M) and kept for 24 h. Then, the alkaline solution was exchanged with a fresh one and kept for another 24 h. After separated with magnet, the solution was discarded and the magnetic double-shell Fe₃O₄@TiO₂/Au@Pd@TiO₂microspheres were washed with deionized water three times and dried at 60 °C overnight.⁵

1.2. Catalyst characterization

TEM characterization was performed on a Hitachi H-800 system operated at an acceleration voltage of 200 kV to evaluate the structure, size, and Au and Pd distribution on the samples. Samples for TEM analysis were prepared by drying a drop of microspheres dispersion on an amorphous carbon coated copper grid for the observation. XRD was used to characterize the phase structure of the samples. Measurements were performed using a PuXi AXS-D8 diffractometer (China) operated at 36 kV and 20 mA with a slit of 1/2 at a scanning rate of $4^{\circ} \cdot \min^{-1}$ in a scanning range of $2\theta = 10 - 80^{\circ}$, using Cu Ka radiation (k = 0.15406 nm). Samples for XRD were prepared by gently crushing the obtained products with a mortar and pestle and were placed in a quartz glass holder for characterization. Surface area measurements were performed on an ASAP 2010 BET analyzer. The magnetization curve of the samples was measured with a vibrating sample magnetometer (LAKE SHORE, 7407). Actual Au and Pd contents in the samples were tested by ICPS-8100 ICP-AES spectrometer (SPECORD 50 PC UV-VIS Spectrophotometer).

1.3. Catalytic tests

1.3.1. Catalytic tests of reduction of 4-nitrophenol to 4-aminophenol

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH₄ was chosen as a model reaction under an ambient temperature of about 25 °C to quantitatively examine the catalytic activity and recyclability of Fe₃O₄(*a*)TiO₂/Au, Fe₃O₄(*a*)TiO₂/Au(*a*)SiO₂/Pd and Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres stabilized in water. A typical reduction procedure was carried out as follows: 40 mL of aqueous solution of catalyst (1 mg) was placed in a beaker. Then, freshly prepared NaBH₄ aqueous solution (0.5 M, 0.5 mL) and 4-NP aqueous solution (12 mM, 0.25 mL) were subsequently added into the above solution under stirring. After the reaction takes place for different times, the mixture was immediately transferred into a quartz cuvette with an optical path length of 1 cm. The catalytic activity was monitored by a UV-vis spectrometer with the wavelength in the range 250-700 nm and a decrease of the intensity of the peak around 400 nm attributed to the typical absorption of 4-NP occurs. The color of the solution changes gradually from yellow to transparent as the reaction proceeds. After each cycle of reaction, another 0.5 mL of NaBH₄ and 0.25 mL of 4-nitrophenol were added to the reaction solution to evaluate the recyclability of the catalysts. This step was repeated ten times to study the stability of the catalysts. For the ten successive cycles of reduction of 4-NP with $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ microspheres as catalysts, the reaction time is about 4 min.

1.3.2. Catalytic tests of Suzuki-Miyaura coupling reaction of aryl iodides

The Suzuki–Miyaura coupling reaction of aryl iodides was carried out in three-port flask (50 mL) with a reflux condensing tube. All reactions and manipulations were run under air atmosphere. Typically, a reaction tube was charged with aryl iodide (0.5 mmol), aryl boronic acid (1 mmol), Au sol (2 μ mol) or Pd sol (2 μ mol) or Fe₃O₄@TiO₂/Au@Pd@TiO₂

microsphere catalyst (20 mg), K_2CO_3 (1 mmol) and absolute ethanol (10 mL). The mixture was mechanically stirred at 80 °C, and monitored by High Performance Liquid Chromatography (HPLC) at specific time. The crude product was characterized by HPLC analysis (HITACHI, D 2000 with a 25 cm Lachrom C18 column, and UV-visible detector with measurement wavelength at 254 nm).

Catalyst	$\begin{array}{c} \textbf{BET} \\ (\textbf{m}^2 \cdot \textbf{g}^{-1}) \end{array}$	Pore diameter ^a (nm)	Pore volume ^b (cm ³ ·g ⁻¹)
Fe ₃ O ₄ @TiO ₂ /Au	168.8	0.16	6.01
Fe_3O_4 (@TiO_2/Au (@SiO_2/Pd)	68.40	0.074	12.2
Fe_3O_4 (@TiO_2/Au (@Pd (@TiO_2))	134.4	0.25	6.92

Table 1. Physical properties of different catalysts.

^a BJH desorption cumulative volume of pores.

^b BJH desorption average pore diameter.

Table 2. Actual Au and Pd contents in Fe $_3O_4$ @TiO $_2$ /Au, Fe $_3O_4$ @TiO $_2$ /Au@SiO $_2$ /Pd and

Fe ₃ O ₄ (<i>a</i>)TiO ₂ /Au(<i>a</i>)Pd(<i>a</i>)TiO ₂ micros	pheres.
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Nanocatalysts	Actual Au content (wt.%)	Actual Pd content (wt.%)	TOF (h ⁻¹) ^a
Fe ₃ O ₄ @TiO ₂ /Au	5.01		142
Fe ₃ O ₄ @TiO ₂ /Au@SiO ₂ /Pd	0.50	0.23	321
Fe ₃ O ₄ @TiO ₂ /Au@Pd@TiO ₂	0.69	0.17	891

^a TOF is calculated by moles of product per molar Au and Pd per hour when the reduction

occurs in the initial 1 min.

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Nanocatalysts	Reaction Time(min)	Conversion(%) ^[b]	$TOF(h^{-1})^{[c]}$
Au sol	10	3.5	52.5
Pd sol	10	96	1438
Fe ₃ O ₄ @TiO ₂ /Au@Pd@TiO ₂	60	100	4152
(500°C)	00	100	1152

Catalyst EtOH, 80 °C

Table 3. Suzuki-Miyaura coupling reaction of aryl iodides over different catalysts.^[a]

B(OH)₂

^[a] Reaction conditions: 80 °C, ethanol (10 mL), iodobenzene (0.5 mmol), phenylboronic acid

(1 mmol), K_2CO_3 (1 mmol), Au sol (2 μ mol), Pd sol (2 μ mol), catalyst (20 mg).

^[b] Determined by HPLC using pentamethylbenzene as internal standard.

^[c] TOF is calculated by moles of product per molar Au or Pd per hour, when the reduction occurs in the initial 10 min.

Table 4. Actual Au and Pd contents in Au sol, Pd sol and Fe₃O₄@TiO₂/Au@Pd@TiO₂(700°C) microspheres.

Nanocatalysts	Actual Au content	Actual Pd content	TOF (h ⁻¹) ^a
Au sol	4.56×10 ⁻⁷ mol		197
Pd sol		5.64×10 ⁻⁸ mol	355
Fe ₃ O ₄ @TiO ₂ /Au@Pd@TiO ₂ (700 °C)	0.71 wt.%	0.16 wt.%	588

^a TOF is calculated by moles of product per molar Au and Pd per hour when the reduction occurs in the initial 1 min.

2. Results and discussion

2.1 XRD

Figure S1 shows the XRD patterns of Fe₃O₄, Fe₃O₄@TiO₂, Fe₃O₄@TiO₂/Au, $Fe_3O_4(a)TiO_2/Au(a)SiO_2$, $Fe_3O_4(a)TiO_2/Au(a)SiO_2/Pd$, $Fe_3O_4(a)TiO_2/Au(a)SiO_2/Pd(a)TiO_2$, Fe₃O₄@TiO₂/Au@SiO₂/Pd@TiO₂(500 °C) and Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres. The typical diffraction peaks located at 30.10° , 35.42° , 43.05° , 53.39° , 56.94° , and 62.52° can be well indexed to the lattice planes of (220), (311), (400), (422), (511), and (440) of cubic phase spinel Fe₃O₄ (JCPDS 19-0629) (Figure S1a). After the coating of a TiO₂ layer, the XRD patterns show no much variation but with a broaden peak appeared around 20 at 12.84°, indicating the formation of amorphous TiO₂ layer (Figure S1b and 1f). Further loading of Au and Pd nanoparticles and coating of a SiO₂ layer have no much effect on XRD results (Figure S1c-1e). No characteristic diffraction peaks belonged to SiO₂ were detected, indicating the formation of amorphous SiO₂ shell on Fe₃O₄(a/TiO₂/Au. The cubic phase spinel structure of Fe_3O_4 was retained, but the intensity of the diffraction peaks were weakened slightly due to the influence of the coating of amorphous TiO₂ and SiO₂ layers. Because of the good dispersity of Au and Pd nanoparticles, the diffraction peaks of Au and Pd were invisible. After the Fe₃O₄@TiO₂/Au@SiO₂/Pd@TiO₂ microspheres were calcined at 500 °C for 2 h in Ar gas atmosphere, the representative peaks located at 25.37°, 38.00°, 48.16°, 54.05°, 55.20°, 62.86° , and 75.27° were clearly observed, which can be indexed to the lattice planes of (101), (004), (200), (105), (211),(204), and (215) lattice planes of anatase TiO₂ (JCPDS 73-1764)⁶, respectively (Figure 2g and h). The XRD results firmly prove the successful formation of Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres.

2.2. Surface area and porous structure

То estimate the surface porous structure $Fe_3O_4(a)TiO_2/Au$, area and of $Fe_3O_4(a)TiO_2/Au(a)SiO_2/Pd$, and $Fe_3O_4(a)TiO_2/Au(a)Pd(a)TiO_2$ microspheres, Brunauer-Emmett-Teller (BET) and BJH measurements were performed. Figure S2 shows the N_2 adsorption-desorption isotherms and pore size distribution of Fe₃O₄(a)TiO₂/Au, Fe₃O₄@TiO₂/Au@SiO₂/Pd, and Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres. It can be seen that both Fe₃O₄@TiO₂/Au and Fe₃O₄@TiO₂/Au@SiO₂/Pd microspheres exhibit a type IV isotherms with H4 hysteresis loop characteristics [Figure S2A (a and b)]⁷, suggesting the existence of mesoporous structure in the microspheres. While for Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres, a type-IV isotherm with the combination of H3 hysteresis loop characteristics was found [Figure S2A(c)], indicating the creation of mesoporous structure.⁸⁻¹⁰ However, for Fe₃O₄@TiO₂/Au microspheres, they exhibit only one narrow peak centered at ~ 2.8 -3.8 nm, which are ascribed to the existence of mesopores in TiO₂ shells of Fe₃O₄@TiO₂/Au microspheres and between the Fe₃O₄@TiO₂/Au microspheres.¹¹ The pore size distribution profile is somewhat varied for Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres, and they exhibit a typically double pore distribution centered at $\sim 2.8-4.4$ nm and 5.6-11.2 nm. The smaller pores are ascribed to the mesopores in the TiO₂ shells of Fe₃O₄(a)TiO₂/Au(a)Pd(a)TiO₂ microspheres and the mesopores between the Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres.¹¹ The larger mesopores are due to the space chamber between double TiO₂ shells of Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres. The Brunauer-Emmett-Teller (BET) surface areas of Fe₃O₄@TiO₂/Au, Fe₃O₄@TiO₂/Au@SiO₂/Pd, and Fe₃O₄@TiO₂/Au@Pd@TiO₂ catalysts are estimated to be 168.8, 68.4 and 134.4 m²·g⁻¹,

respectively. In comparison with the Fe₃O₄@TiO₂/Au@SiO₂/Pd microspheres, the coating of outer layers of mesoporous TiO₂ and removal of SiO₂ layers in Fe₃O₄@TiO₂/Au@/Pd@TiO₂ microspheres create larger specific surface Therefore, may area. the $Fe_3O_4(@TiO_2/Au(@/Pd(@TiO_2 microspheres have the larger surface area. However, as the$ average size of Fe₃O₄@/TiO₂/Au microspheres is much smaller and the coating of amorphous TiO_2 , the Fe₃O₄@TiO₂/Au microspheres possessed higher specific surface area in comparison with $Fe_3O_4(a)TiO_2/Au(a)/Pd(a)TiO_2$ microspheres. BJH desorption cumulative volume of pores for the Fe₃O₄@TiO₂/Au, Fe₃O₄@TiO₂/Au@SiO₂/Pd, and Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres are 6.01, 12.2 and 6.92 cm³·g¹, respectively (Table 1). The large specific surface area and pore volumes help to improve catalytic performance of the Fe₃O₄@TiO₂/Au@Pd@TiO₂ catalysts. The largest BJH desorption average pore diameter of 0.25 nm was obtained for Fe₃O₄@TiO₂/Au@/Pd@TiO₂ microspheres in comparison that of 0.16 and 0.074 nm for Fe₃O₄@TiO₂/Au and Fe₃O₄@TiO₂/Au@SiO₂/Pd microspheres (Table S1). The BET measurements further confirm the Fe₃O₄@TiO₂/Au@Pd@TiO₂ microspheres with mesoporous shells.¹²⁻¹⁴ The results of the pore diameter and pore volume measurements further prove the existence of space chamber between the double TiO₂ shells in $Fe_3O_4(@TiO_2/Au(@)/Pd(@TiO_2)$ microspheres after the alkaline etching removal of SiO_2. The hollow space chamber between double TiO₂ shells benefits the facile mass transportation of reactants and the contact of Au or Pd nanoparticles with reactants. These features may greatly improve their catalytic performance.

2.3. Thermal stability and catalytic activity after calcination

To study its thermal stability, the Fe₃O₄@TiO₂/Au@Pd@TiO₂ microsphere was calcined at 700 °C and 900 °C for 2 h under Ar atmosphere. The TEM images of Fe₃O₄@TiO₂/Au@Pd@TiO₂ microsphere calcined at 900 °C are shown Fig. S4. It is revealed by the TEM characterization that the double-shell geometry of Fe_3O_4 (@TiO₂/Au(@Pd(@TiO₂)) microsphere is partially destroyed after calcination at 900 °C (Fig. S3a), and the noble metal Au and Pd nanoparticles become larger with the increase of calcination temperature (~10 nm) (Fig. S3b). This may cause the decrease of catalytic activity. The catalytic performance of Fe₃O₄@TiO₂/Au@Pd@TiO₂ microsphere after calcination at 700 and 900 °C on reduction of 4-nitrophenol was also tested. It is found that the catalytic performance on reduction of 4-nitrophenol is largely changed after calcination. The TOF of the catalytic activity of Fe₃O₄@TiO₂/Au@Pd@TiO₂ microsphere calcined at 700 °C decreases to 588 h⁻¹, lower than that of Fe₃O₄@TiO₂/Au@Pd@TiO₂ microsphere (891 h⁻¹) before calcination (Table S4 and Fig. S4) When calcining the Fe₃O₄(a)TiO₂/Au(a)Pd(a)TiO₂ microsphere at 900 °C, the Fe₃O₄@TiO₂/Au@Pd@TiO₂ microsphere entirely lose the catalytic activity (Fig. S4). This may be due to the increase of the noble metal Au and Pd nanoparticles, as proven by the TEM characterization (Fig. S3b).

The XRD characterization of Fe_3O_4 @TiO₂/Au@Pd@TiO₂ microsphere calcined at 700 °C and 900 °C for 2 h under Ar atmosphere were also performed, as shown in Fig. S4. It was revealed that after calcination at 900 °C, the phase structure of double TiO₂ shells was almost changed into rutile from anatase.



Figure S1. XRD patterns of (a) Fe_3O_4 , (b) Fe_3O_4 @TiO₂, (c) Fe_3O_4 @TiO₂/Au, (d) Fe_3O_4 @TiO₂/Au@SiO₂, (e) Fe_3O_4 @TiO₂/Au@SiO₂/Pd, (f) Fe_3O_4 @TiO₂/Au@SiO₂/Pd@TiO₂, (g) Fe_3O_4 @TiO₂/Au@SiO₂/Pd@TiO₂ (500 °C), and (h) Fe_3O_4 @TiO₂/Au@Pd@TiO₂ microspheres.



Figure S2. (A) N_2 absorption-desorption isomers of (a) $Fe_3O_4@TiO_2/Au$, (b) $Fe_3O_4@TiO_2/Au@SiO_2/Pd$, and (c) $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ microspheres, and (B) BJH measurements of (a) $Fe_3O_4@TiO_2/Au$, (b) $Fe_3O_4@TiO_2/Au@SiO_2/Pd$, and (c) $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ microspheres.



Figure S3. (a)TEM and HRTEM images of Fe_3O_4 @TiO₂/Au@Pd@TiO₂ microsphere calcined at 900 °C for 2 h under Ar atmosphere.



Figure S4. UV-vis spectra of the reduction of 4-NP to 4-AP over (a) Au sol, (b) Pd sol, (c) $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ (700 °C) and (d) $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ (900 °C) catalysts; (e) Plot of $Ln(C_t/C_0)$ against the reaction time of the reduction of 4-NP over $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ (700 °C) and $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ (900 °C) catalysts.



Figure S5. XRD patterns of (a) $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ (700 °C) and (b) $Fe_3O_4@TiO_2/Au@Pd@TiO_2$ (900 °C) microspheres.

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