

Supporting information (SI) for

Ascorbic-acid-assisted Growth of High Quality M@ZnO: Growth Mechanism and Kinetics Study

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The preparations of 15 nm Ag or 16 nm Pd NPs

Ag NPs was prepared using a modified method reported by Kimizuka's group.¹ Typically, 10 mg AgNO₃ was dissolved in 50 mL water containing 100 mg CTAB. Then 0.5 mL ice-cold NaBH₄ (the molar ratio of NaBH₄/Ag⁺¹ is 0.2) was dropwise added to reduce part of Ag ions under vigorous stirring. Quickly, the solution became yellow due to the formation of Ag NPs. After 2 h, 1 mL AA (the molar ratio of AA/Ag⁺¹=1) was added to reduce the rest of Ag ions to Ag atoms at 70 °C which selectively deposited on preformed NPs to give 15 nm Ag NPs.

The preparation of 50 nm Au NPs

50 nm Au NPs were prepared with modified method reported by Liz-Marzán's and other groups.² Briefly, 10 mg HAuCl₄ was added to 20 mL water containing 100 mg CTAB. Under vigorous stirring, 1 mL ice-cold NaBH₄ was added to reduce Au(III). Quickly, the solution became brown due to the formation of Au NPs. After 3 h, the reaction was finished and the resulting Au colloid acted as seed solution for further growth. For the preparation of growth solution, 20 mg HAuCl₄ was added to 20 mL water containing 100 mg CTAB and then 0.5 mL seed solution was introduced. 1 mL

AA aqueous solution (the molar ratio of AA/ HAuCl₄ is 1.5) was added to induce seeded growth and the formation of 50 nm Au NPs.

The preparation of Au@Ag NPs

Au@Ag NPs were prepared through using 10 nm Au NPs as seeds.² 10 nm Au NPs were prepared with a similar method to 50 nm Au except that a different growth solution was used (2 mg HAuCl₄, 50 mg CTAB). For synthesizing 30 nm Au@Ag NPs, 50 mL AgNO₃ aqueous solution (Ag/Au=10) was added to above 10 nm Au colloid and then AA solution was introduced (AA/ AgNO₃=1). The resulting solution was sealed and heated at 80 °C oven for 24 h.

The preparation of dendrite Pt NPs

Pt nanodendrites were prepared through a one-step method. 100 mg CTAB and 10 mg H₂PtCl₆ were dissolved in 20 mL water. 1 mL AA aqueous solution (AA/H₂PtCl₆=2) was then introduced. The resulting solution was sealed and heated for 12 h at 80 °C oven. A brown colloid containing Pt nanodendrites formed.

The preparation of Pd nanocubes

Pd NPs was synthesized with method reported by Wang's and Xu's groups.³ Briefly, H₂PdCl₄ solution (0.01 M, 0.5 mL) was mixed with CTAB aqueous solution (0.0125 M, 10 mL) homogeneously. The resulting mixture was heated to 96 °C and then an AA aqueous solution (AA/H₂PdCl₄=1.5) was introduced to induce the growth of Pd NPs at the same temperature. The growth needed about 30 min to accomplish.

The preparation of dendrite Pd@Pt or Au@Pt NPs

Pd@Pt or Au@Pt NPs were prepared through heteroepitaxially growing Pt on above Pd nanocubes or 50 nm Au NPs.^{2a} Typically, a calculated amount of H₂PtCl₆ (Pt/Au=1; Pt/Pd=0.5) and AA (AA/Pt³⁺=2; AA/Pd²⁺=1.5) were added to 20 mL seed solution and then the growth proceeded at 80 °C for 8 h.

The preparation of Au nanorods

The classical method developed by Murphy's and Sayed's groups was used to prepare

Au nanorods.⁴ Typically, HAuCl₄ (5 mL, 0.00050M) was mixed with CTAB solution (5 mL, 0.20 M). An ice-cold NaBH₄ (0.6 mL, 0.010 M) was added under vigorous stirring. The growth of Au NPs was finished very quickly. However, before the Au seeds are used to grow Au nanorods, it needs 4 h to decompose NaBH₄ completely. For the growth of Au nanorods, aqueous CTAB (5 mL, 0.20 M), AgNO₃ solution (0.15 mL, 0.0040 M) and 0.0010 M HAuCl₄ (1 mL, 2 mL or 5.0 mL for preparing nanorods with different lengths) were mixed and then AA (70 uL, 0.0788 M) was added. The introduction of AA changes the mixture from yellow to colorless, indicating the reduction of Au³⁺ to Au¹⁺. Finally, 12 uL seed was added to above solution and the growth proceeded at 25-27 °C for 12 h.

The preparation of Au@Ag nanorods

Above Au nanorods acted as seeds for preparing Au@Ag nanorods.² Typically, 1 mL AgNO₃ solution was added to 10 mL as-prepared Au nanorod colloid (Ag/Au=0.2) and then a calculated amount of AA (AA/Ag=1) was introduced. The resulting solution was heated at 60 °C to promote forming Ag atoms which selectively grow on Au NRs surface.

Note: All the NPs prepared using CTAB needs no any purification and the CTAB molecules act as protecting agent for synthesizing M@ZnO NPs.

2.3 The preparation of hydrophobic NPs

The preparation of 6 nm Au NPs

6 nm Au NPs were prepared with our previous methods.⁵ Typically, 3 mL 0.042 M HAuCl₄ aqueous solution was dried completely at 60 °C, and then 45 mL toluene containing 4 g tri-n-octylamine was added. The resulting solution was stirred vigorously to dissolve HAuCl₄ fully. 0.5 mL NaBH₄ water solution (NaBH₄/Au=30) was quickly introduced and solution color changed from yellow to red, indicating the formation of 2 nm Au NPs. After 3h, 2 mL dodecanethiol was added to form stronger protective layer on Au NPs. After another 2 h stirring, the reaction was ended. Most of toluene was removed through vacuum distillation and then 20 mL ethanol was

added to precipitate Au NPs. After the precipitations was washed several times using ethanol, the NPs were dispersed in 5 mL toluene again for further growth. To prepare 6 nm Au NPs, 1 mL 2 nm Au NPs colloid and 2 mL toluene solution (0.4 mL decyl amine and HAuCl₄; Au³⁺/Au⁰=2) were mixed. The solution was heated to 120 °C slowly under magnetic stirring. After 2 h reaction, dodecanethiol (0.5 mL) was added to stabilize gold NPs. After another 30 min, the colloid was cooled to room temperature and then 15 mL ethanol was added to precipitate gold NPs. Precipitation was collected through centrifuge (8000 rpm).

The preparation of 16 nm Au NPs

16 nm Au NPs were prepared with method reported by Li's group.⁶ Typically, 1 mL oleylamine containing 10 mg HAuCl₄ was mixed with 10 mL cyclohexane homogeneously. The yellow solution was sealed in a teflon autoclave and heated at 140 °C for 10 h, producing a red Au colloids. After the solution was cooled to room temperature, a similar process to the purification of 6 nm Au NPs was used to remove excess surfactant and byproduct.

The preparation of 15 nm Ag NPs

15 nm Ag NPs were prepared with method reported by Sun's group.⁷ In a typical synthesis, 170 mg AgNO₃ was dissolved in 20 mL of oleylamine under ultrasonic. The AgNO₃ oleylamine solution was slowly heated to 200 °C in nitrogen environment. After 1 h reaction, the heating resource was removed and the solution was cooled down to room temperature. A similar process to the purification of 6 nm Au NPs was used to remove excess surfactant and byproduct.

The preparation of 15 nm Pd NPs

17 nm Pd NPs were prepared with a modified method reported by Klabunde's group.⁸ Briefly, 0.029 g of Na₂PdCl₄, 10 mL of 4-tert-butyltoluene, 277 mg TOP, and 0.50 mL of oleylamine were mixed through ultrasonic for 20 min. Under nitrogen flow, the mixture was heated in 210 °C oil-bath for 10 h. After the solution was cooled down to room temperature, a similar process to the purification of 6 nm Au NPs was used to

remove excess surfactant and byproduct.

The preparation of cubic Pt-based NPs

Cubic Pt-based NPs were prepared with method reported by Fang's group.⁹ In a typical synthesis of Pt nanocubes, 0.020 g Pt(acac)₂, 8.0 mL of oleylamine, and 2.0 mL of oleic acid were mixed homogeneously. The mixture was heated to 130 °C with vigorous stirring and then 0.05 g of tungsten hexacarbonyl was introduced. The reaction temperature was further raised to 240 °C and NPs growth proceeded at this temperature for 30-60 min. After the solution was cooled down to room temperature, a similar process to the purification of 6 nm Au NPs was used to remove excess surfactant and byproduct. For synthesis of other alloy Pt-Ni and Pt-Fe nanocubes, 0.0125g NiCl₂ and 0.01g FeCl₃ added respectively (other conditions were unchanged). 0.005 g NiCl₂ and 0.005 g FeCl₃ were added to synthesize Pt-Fe-Ni nanocubes.

The preparation of Fe₃O₄ NPs

Fe₃O₄ NPs were prepared with method reported by Sun's group.¹⁰ 0.706 g Fe(acac)₃, 2.58 g 1,2-hexadecanediol, 0.8 mL oleic acid, 0.8 mL oleylamine were mixed in 20 mL phenyl ether, then the solution was heated to 260 °C and kept at this temperature for 30 min. After the solution was cooled down to room temperature, a similar process to the purification of 6 nm Au NPs was used to remove excess surfactant and byproduct.

The preparation of CdS NPs

CdS NPs were prepared with method reported by Hyeon's group.¹¹ Typically, 24 mg sulfur in 5 mL of oleylamine was quickly introduced into 15 mL oleylamine solution containing 274 mg CdCl₂ at 160 °C. The resulting mixture was heated at 160 °C for 6 h. After the solution was cooled down to room temperature, a similar process to the purification of 6 nm Au NPs was used to remove excess surfactant and byproduct.

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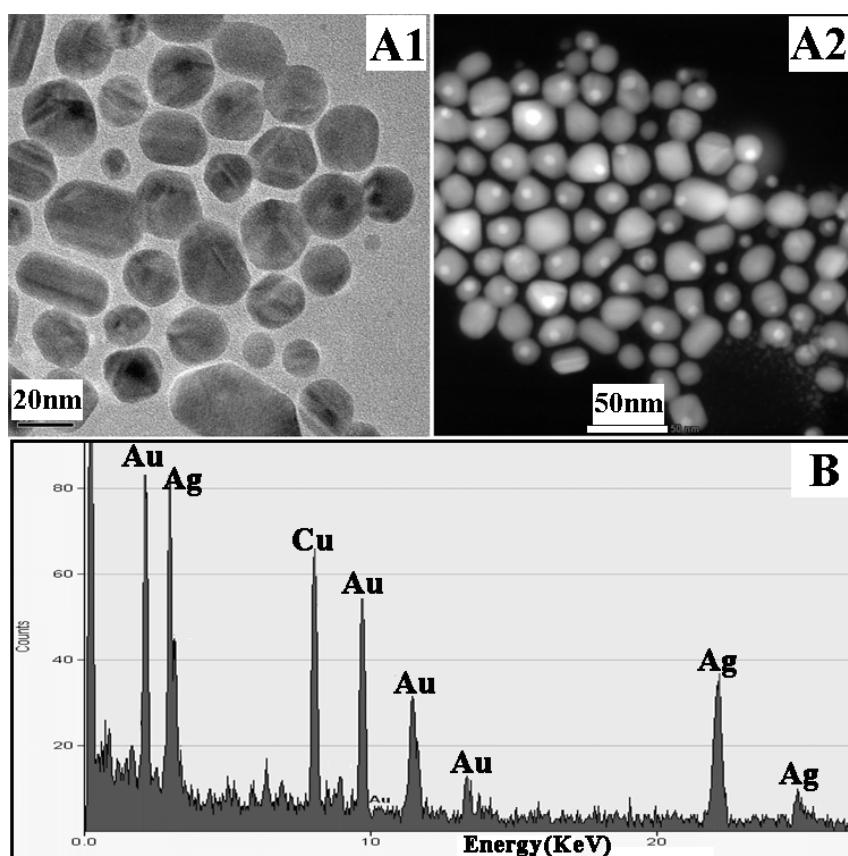


Fig. S1 The typical TEM image, HAADF image and EDS pattern of Au@Ag NPs.

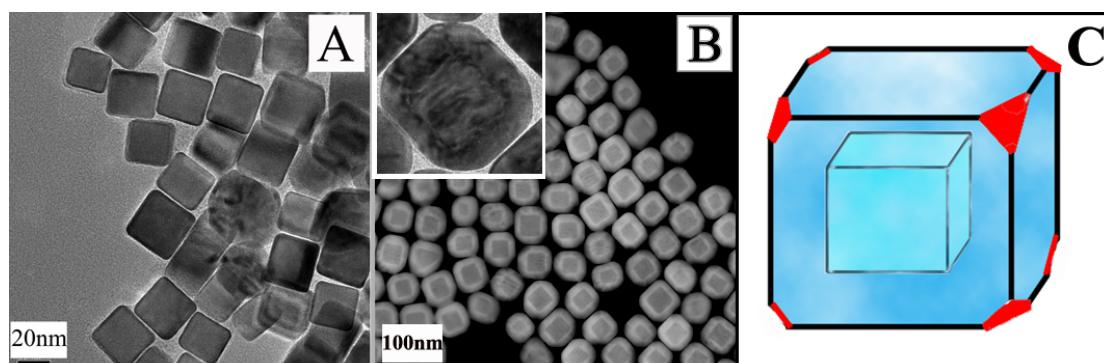


Fig. S2 (A) The typical TEM image of Pd nanocubes; (B-C) the typical HAADF image of Pd@Au NPs and corresponding sketch (inset is the HRTEM).

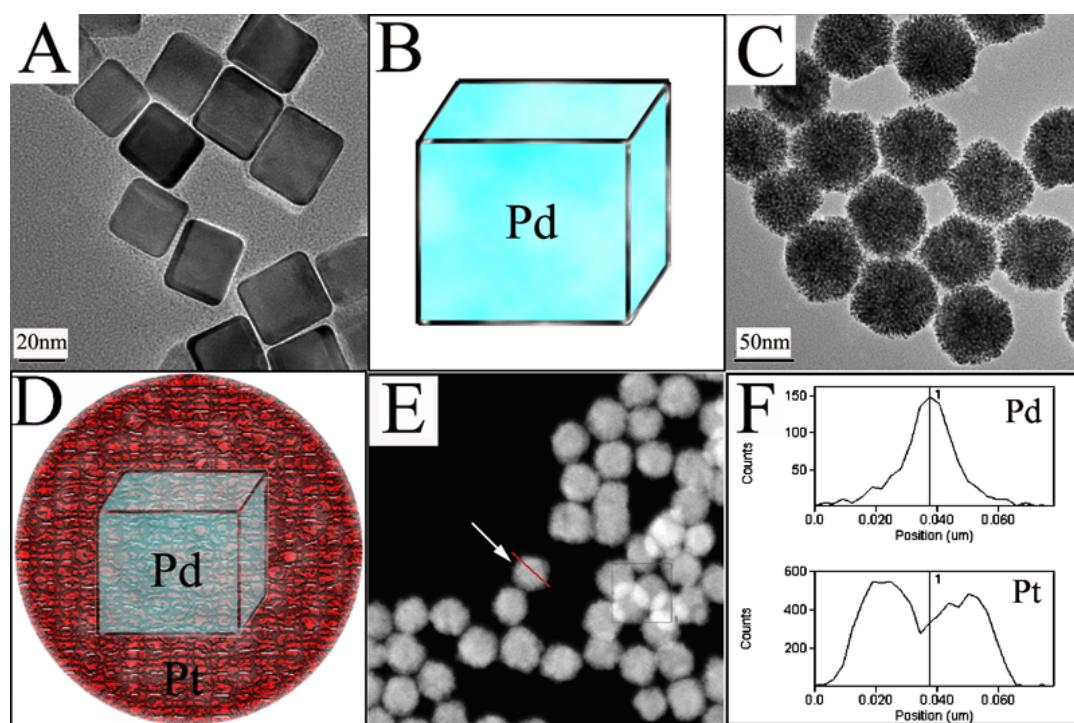


Fig. S3 (A-B) The typical TEM image of Pd NPs and corresponding sketch; (C-F) The typical TEM, HAADF, scheme images of Pd@Pt NPs and elemental line scanning patterns.

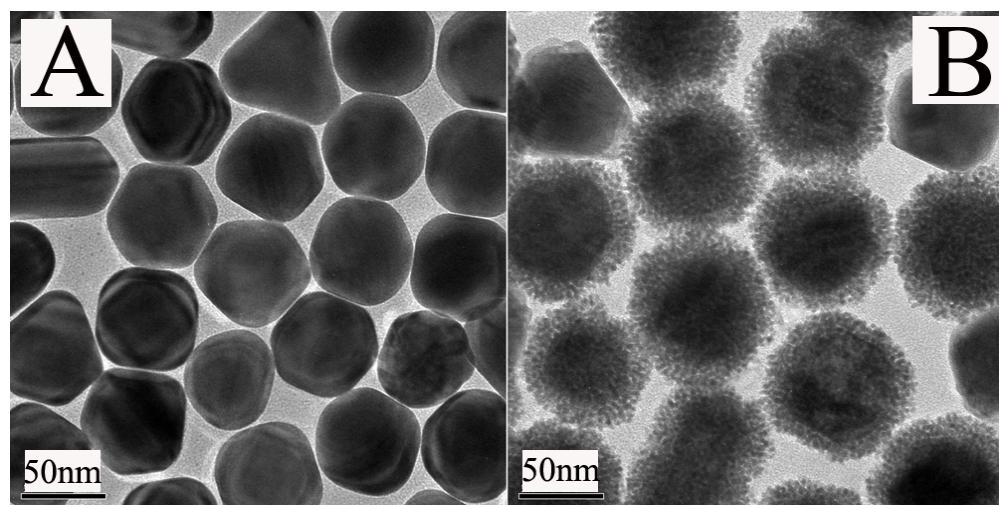


Fig. S4 The typical TEM images of (A) 50 nm Au NPs and (B) corresponding Au@Pt NPs.

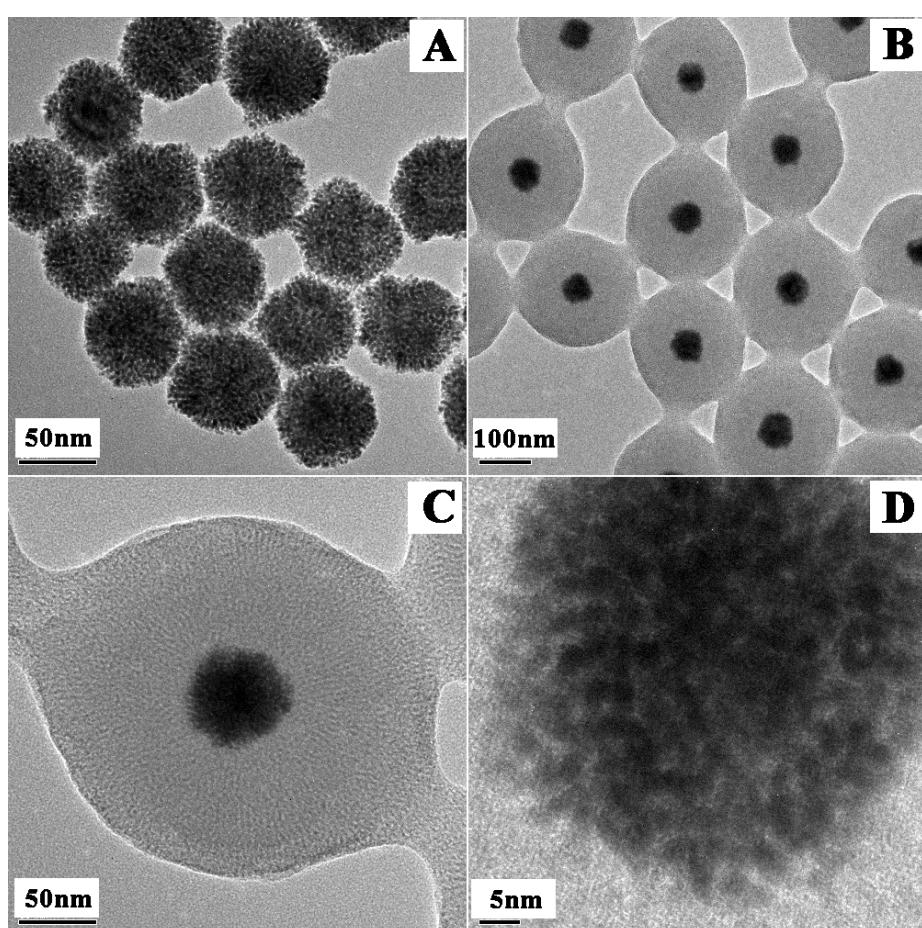


Fig. S5 The typical TEM and HRTEM images of (A) Pd@Pt NPs and (B-D)
Pd@Pt@ZnO NPs

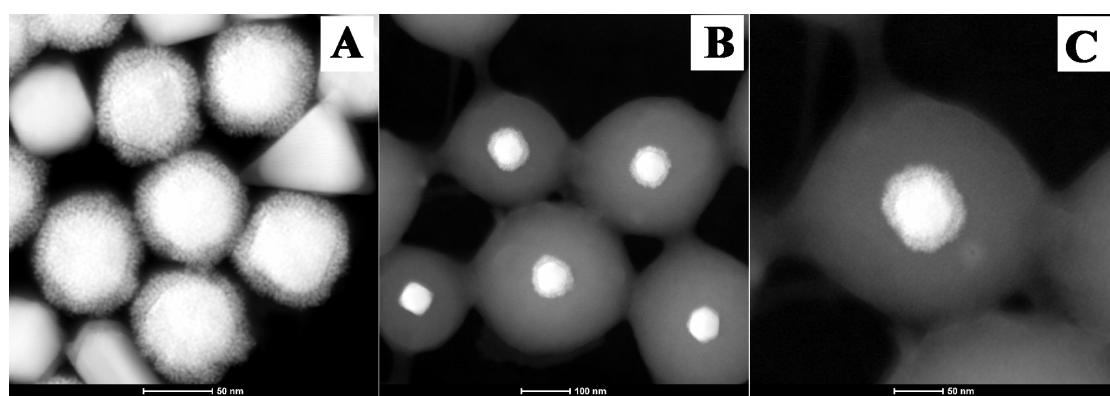


Fig. S6 The typical HAADF images of (A) Au@Pt NPs and (B-C) Au@Pt@ZnO
NPs.

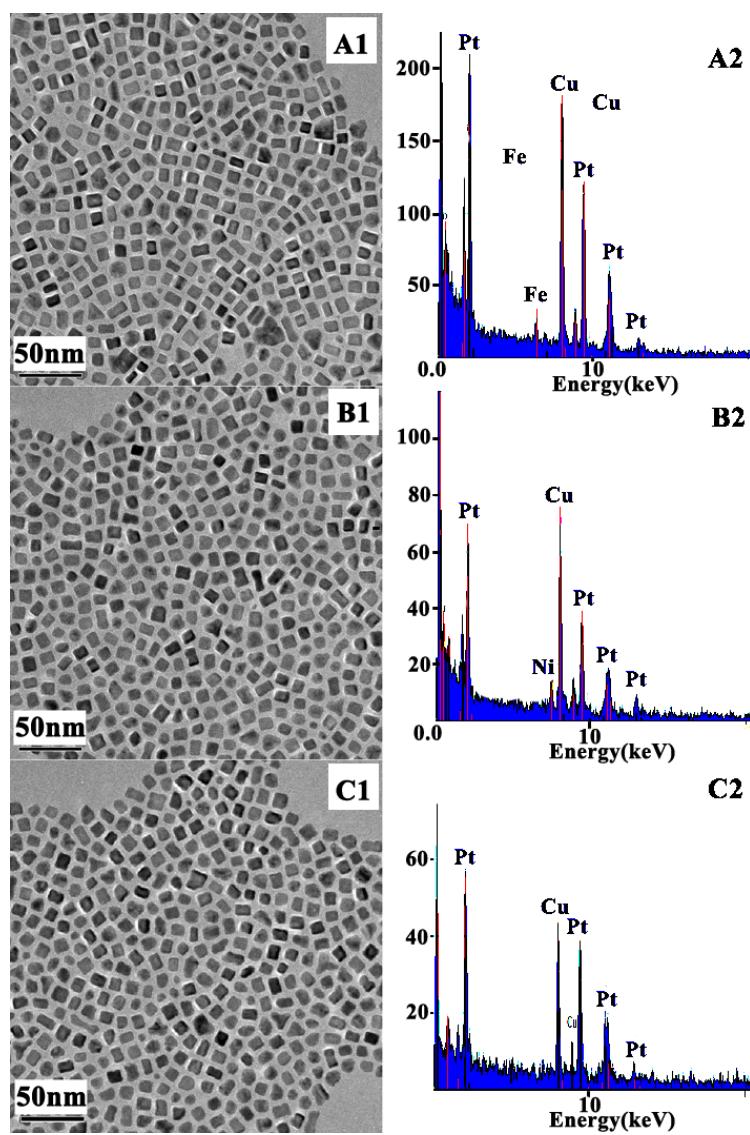


Fig. S7 The typical TEM images and corresponding EDS results of Pt-based nanocubes: (A) Pt-Fe; (B) Pt-Ni; (C) Pt.

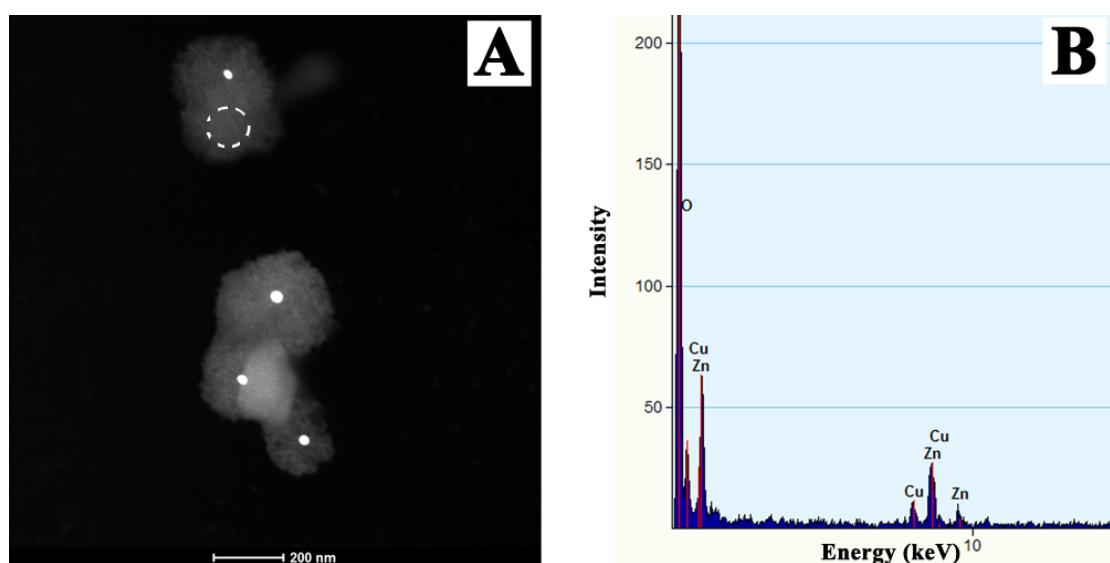


Fig. S8 The HAADF image of product (85 °C, 2h) and (B) corresponding EDS pattern of area marked by the circle in (A).

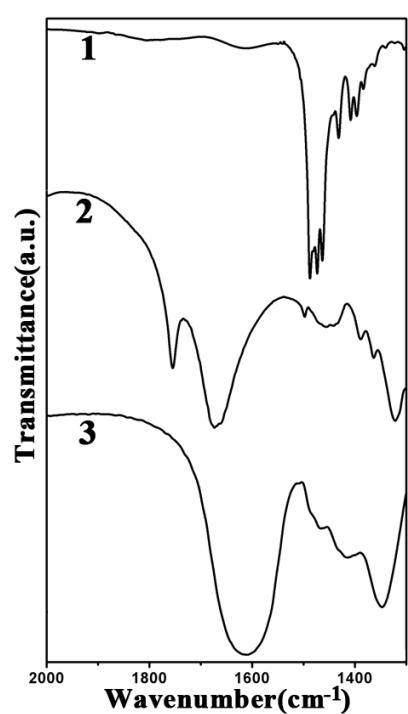


Fig. S9 FTIR spectra of (1) CTAB; (A2) AA; (B1) ZnO prepared in the presence of both AA and CTAB.

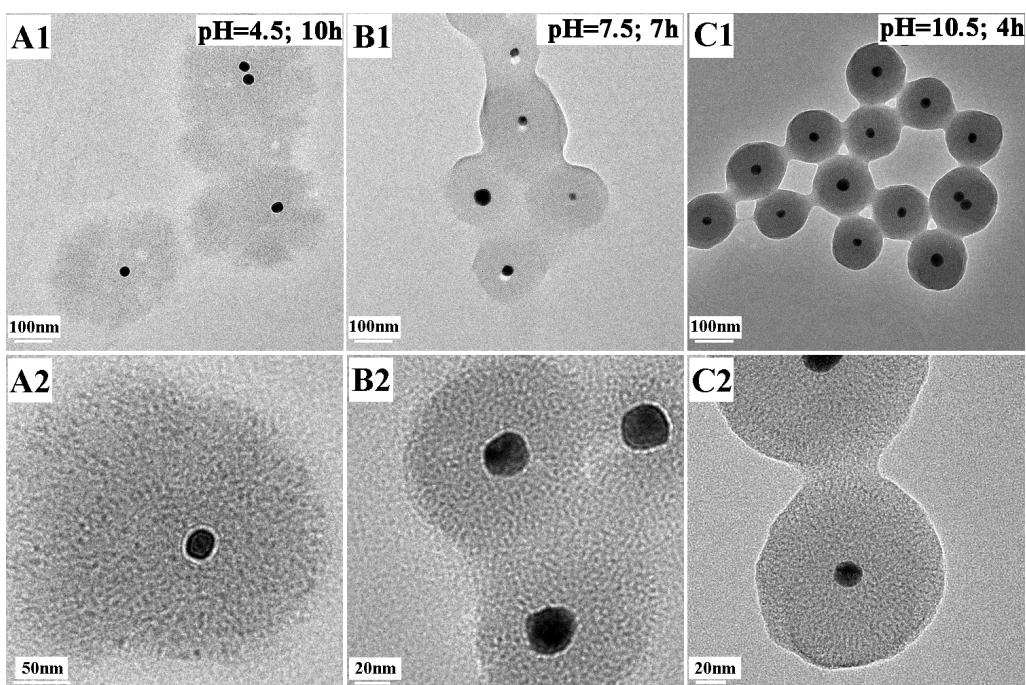


Fig. S10 The typical TEM images of products prepared at different pH and reaction times at 80 °C (Zn/Au=20).

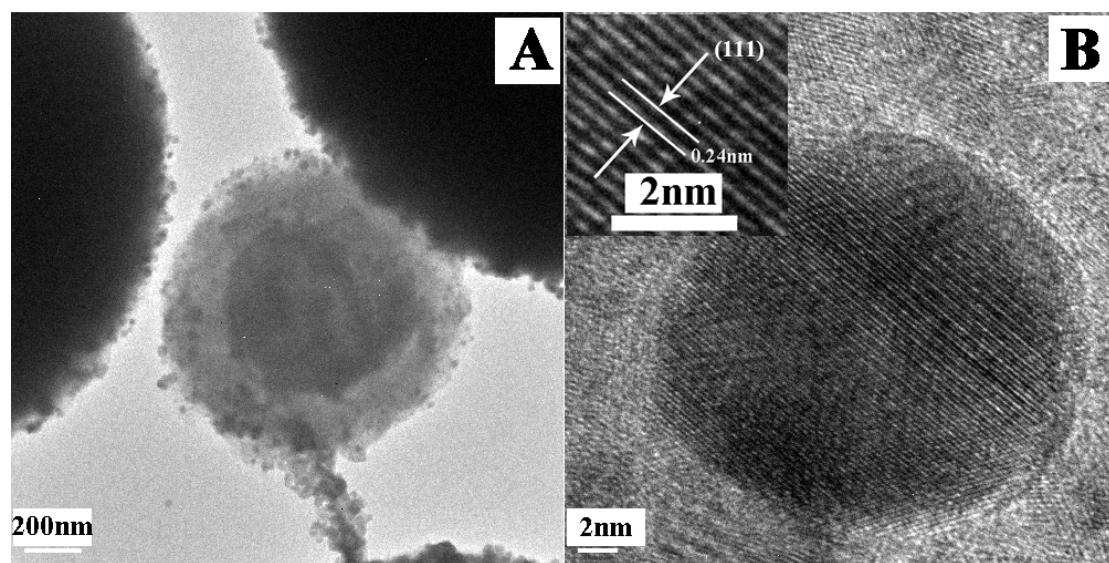


Fig. S11 The TEM and HRTEM images of product prepared at 85 °C (pH=12).

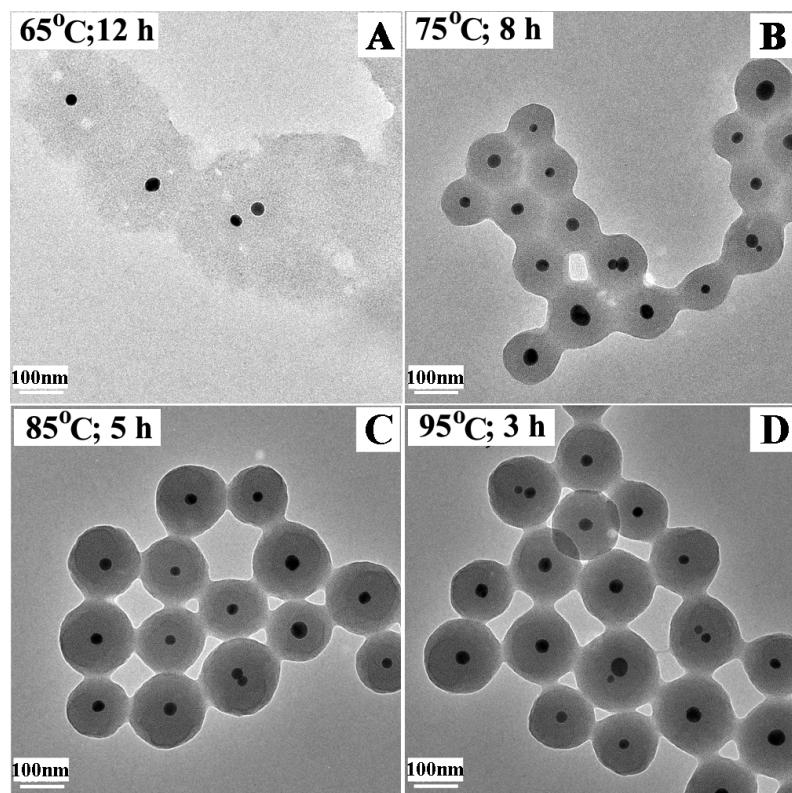


Fig. S12 The typical TEM images of products prepared at different temperatures ($\text{pH}=8.5$) ($\text{Zn}/\text{Au}=20$).

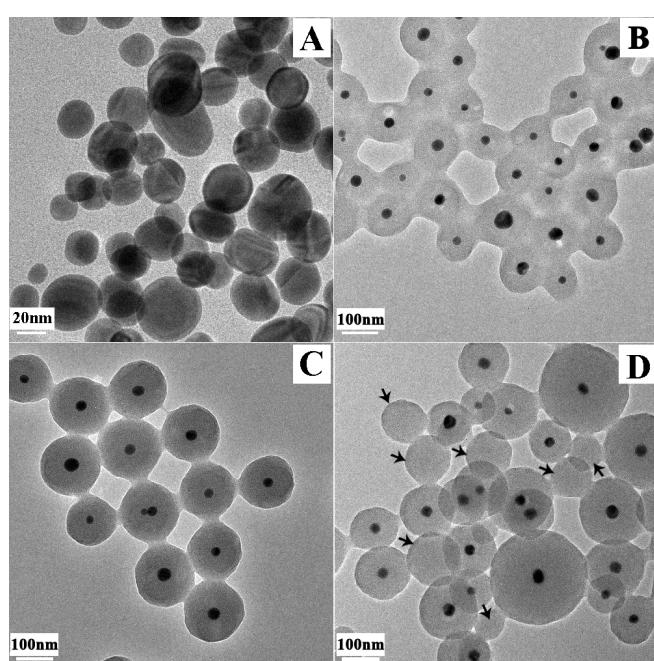


Fig. S13 The typical TEM images of products prepared with different concentration of Zn^{2+} at 85°C for 8 h: (A) 0.2 mg/mL; (B) 1 mg/mL; (C) 2 mg/mL; (D) 6 mg/mL (pure ZnO NPs marked by arrows).

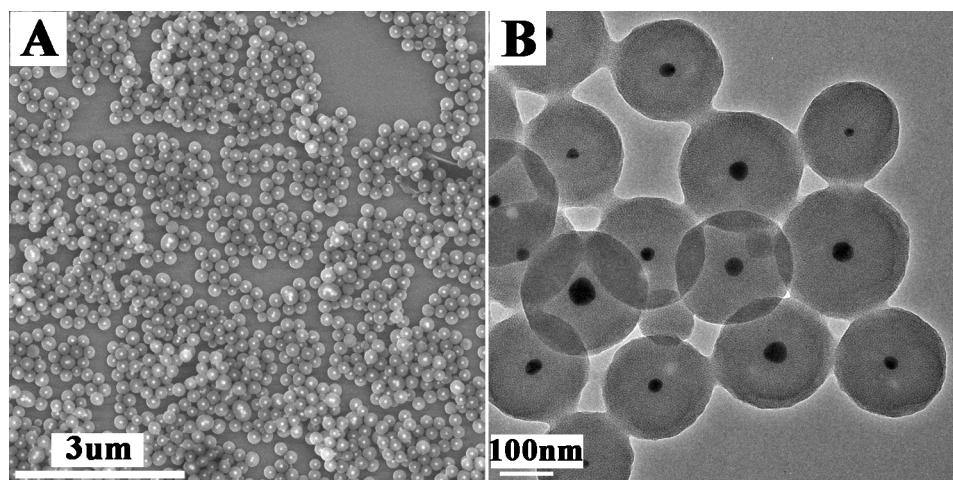


Fig. S14 The typical SEM images of Au@ZnO NPs prepared using programmed heating (75 °C for 5 h and then 85 °C for another 5 h).

Formula derivation of equation ($R = \frac{C_{ZnO}}{S_{Au}} = kdC_{ZnO}$)

Given that each Au NP has the same diameter (d) and the ρ of Au has no size-dependence, the surface area (s), volume (v) and mass (m) of single Au NP can be calculated according to equation 1, 2 and 3 (π is constant).

$$s = \pi d^2 \quad (1)$$

$$v = \frac{\pi d^3}{6} \quad (2)$$

$$m = \rho v = \frac{\rho \pi d^3}{6} \quad (3)$$

Because the total mass of Au (M) in our experiment was unchanged, the total number of Au NPs can be calculated with equation (4),

$$n = \frac{M}{m} = \frac{6M}{\rho \pi d^3} \quad (4)$$

Then total surface of Au NPs seeds (S_{Au}) can be known from equation 5,

$$S_{Au} = ns = \frac{6M}{\rho \pi d^3} \times \pi d^2 = \frac{6M}{\rho d} \quad (5)$$

Now, R is easily calculated through using the following equation (6),

$$R = \frac{C_{ZnO}}{S_{Au}} = \frac{\rho d C_{ZnO}}{6M} \quad (7)$$

If we use a constant ($k = \frac{\rho}{6M}$), then equation 7 can be simplified to equation 8,

$$R = \frac{C_{ZnO}}{S_{Au}} = kdC_{ZnO} \quad (8)$$