

Supplementary Information

Oxygen Reduction Reaction on Core@Shell Nanostructured Au-*d*@Ni_mPt_m: Effect of Core Size and Shell Thickness

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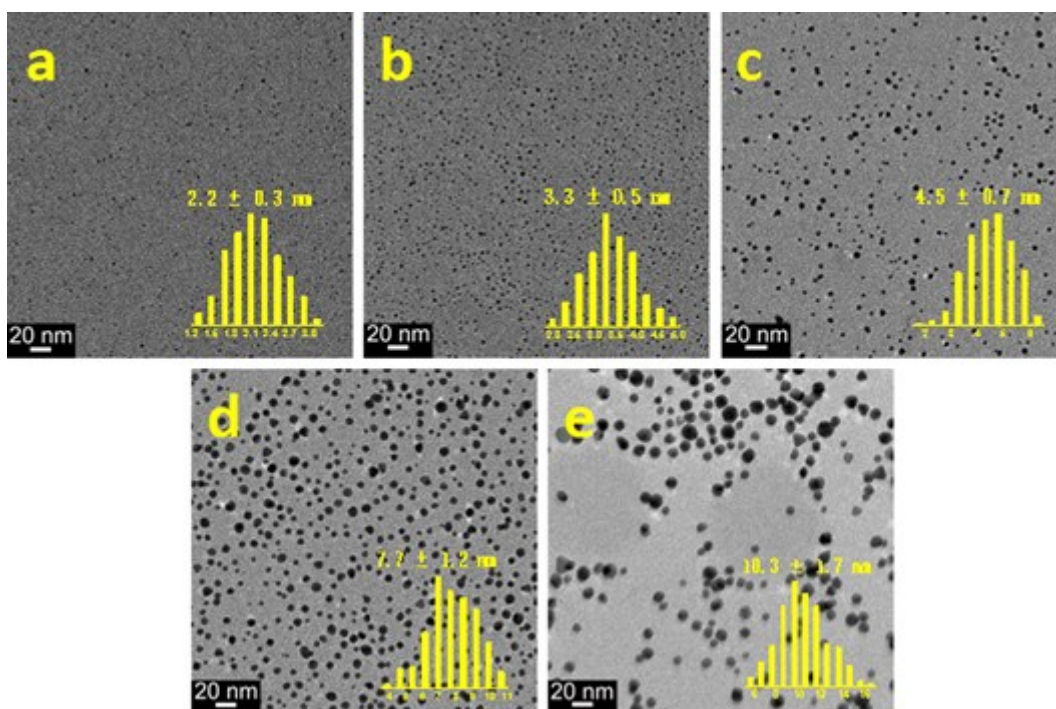


Figure S1. TEM images of (a) $(\text{Pt}_{0.15}^{\text{Au-2.2}})@\text{Ni}_2\text{Pt}_2/\text{C}$, and (b) $(\text{Pt}_{0.25}^{\text{Au-2.2}})@\text{Ni}_2\text{Pt}_2/\text{C}$.

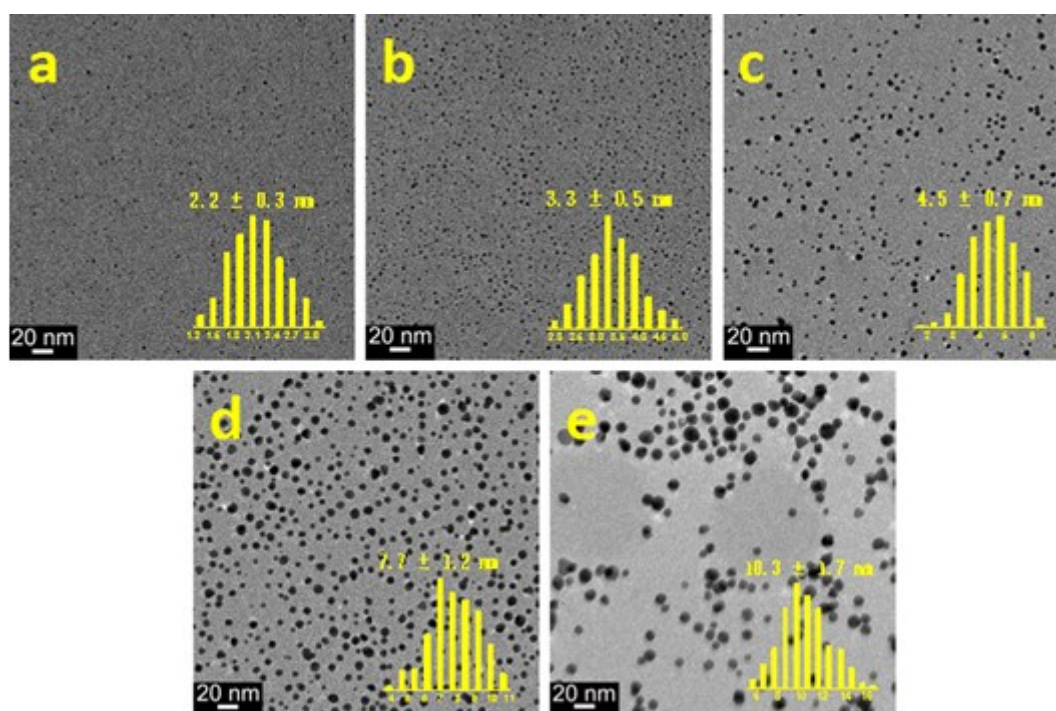


Figure S2. TEM images and their measured size histograms in diameter of Au-*d* NPs: (a) $d = 2.2$, (b) $d = 3.3$, (c) $d = 4.5$, (d) $d = 7.7$, (e) $d = 10.3$.

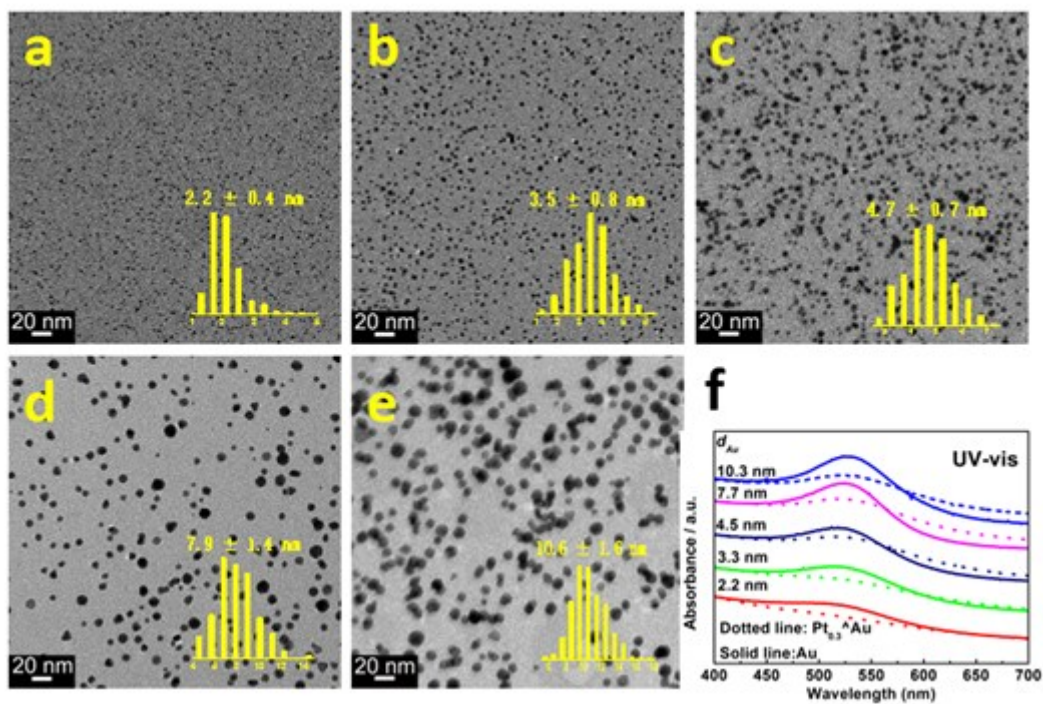


Figure S3. (a) $\text{Pt}_{0.3}\text{Au}-2.2$, (b) $\text{Pt}_{0.3}\text{Au}-3.3$, (c) $\text{Pt}_{0.3}\text{Au}-4.5$, (d) $\text{Pt}_{0.3}\text{Au}-7.7$, (e) $\text{Pt}_{0.3}\text{Au}-10.3$. (f) UV-vis spectra of Au-*d* NPs and $\text{Pt}_{0.3}\text{Au}-d$ NPs.

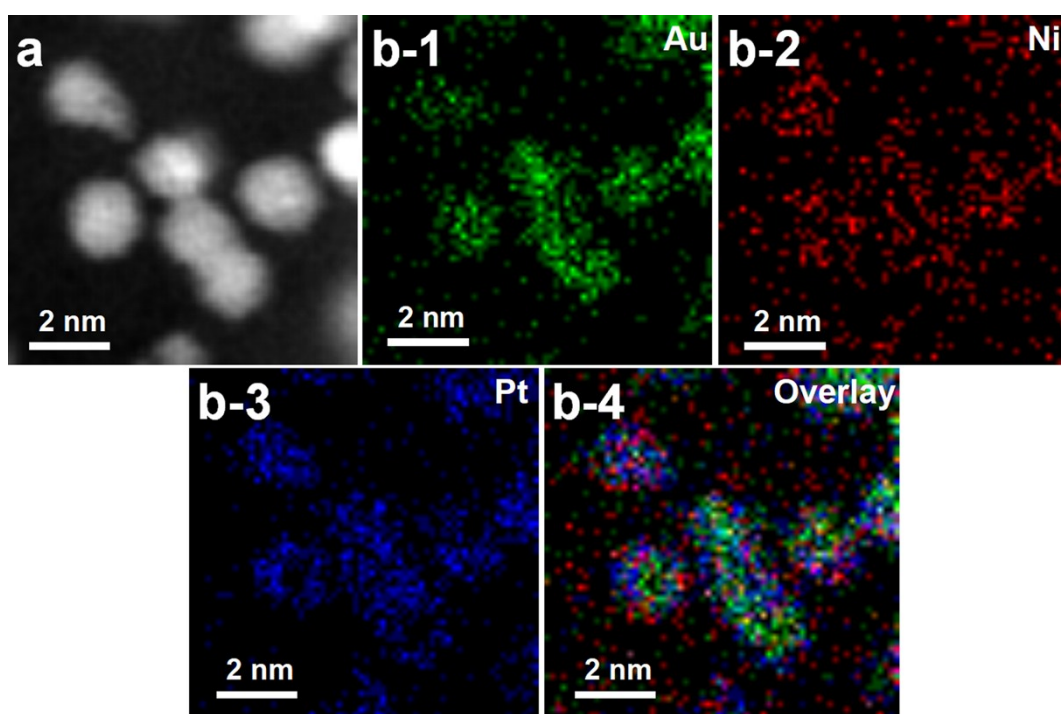


Figure S4. Structure and elemental analysis of as-prepared Au-2.2@Ni_{0.5}Pt_{0.5} NPs. (a) HAADF-STEM images and (b) elemental distribution analysis, elemental mapping of Au (green), Ni (red), Pt (blue) and their overlay.

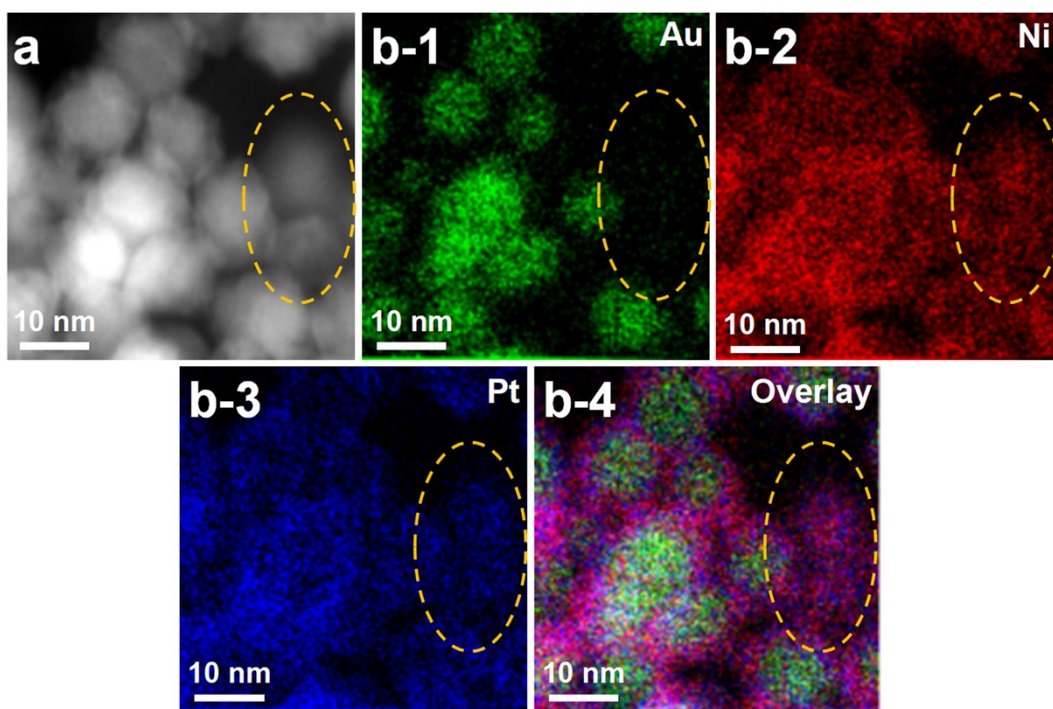


Figure S5. Structure and elemental analysis of as-prepared Au-10.3@Ni₂Pt₂ NPs. (a) HAADF-STEM images and (b) elemental distribution analysis, elemental mapping of Au (green), Ni (red), Pt (blue) and their overlay. The NPs without Au core were marked in the yellow ellipses.

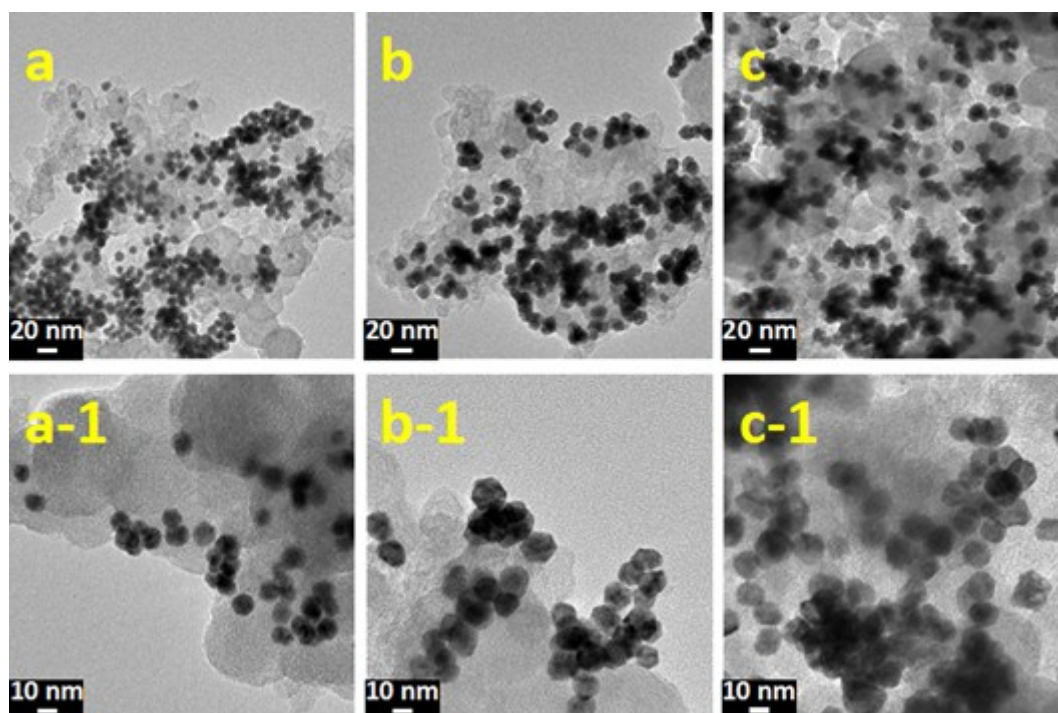


Figure S6. TEM images of Au-7.7@Ni_{*m*}Pt_{*m*}/C samples: (a) *m*=1, (b) *m*=4, (c) *m*=6.

1. XRD characterizations

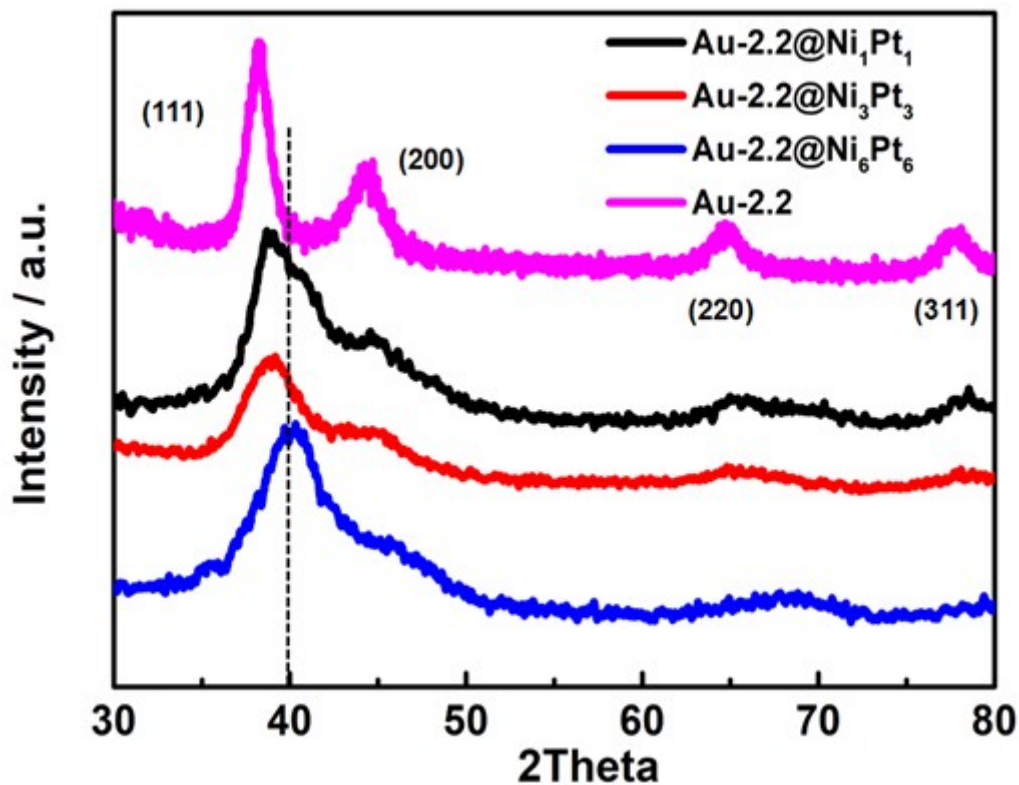


Figure S7. XRD patterns for Au-2.2@Ni₁Pt₁/C, Au-2.2@Ni₃Pt₃/C, Au-2.2@Ni₆Pt₆/C, Au-2.2/C and PtNi/C.

2. Activity of Au-7.7@Ni_mPt_m/C samples

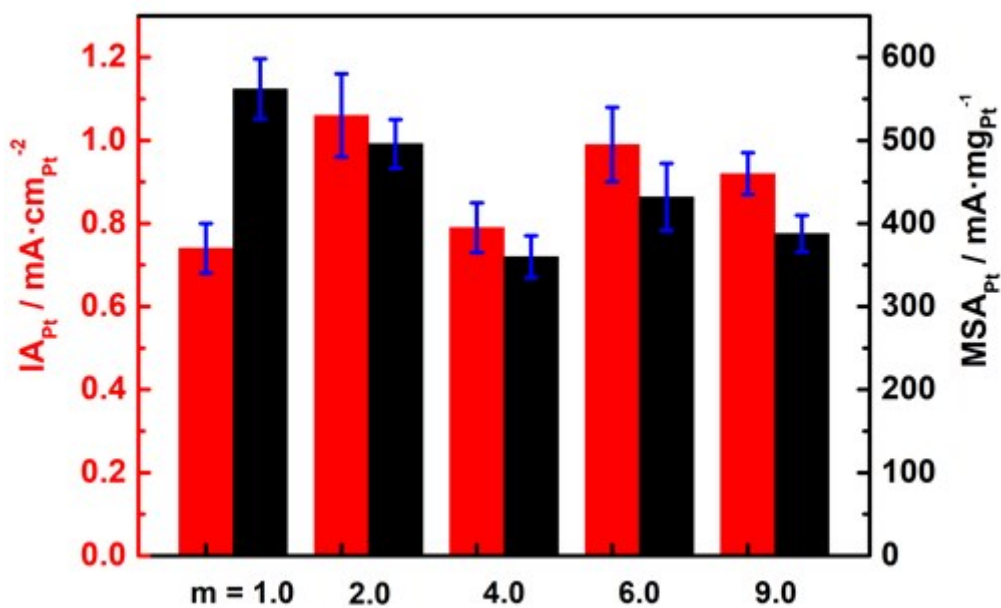


Figure S8. (a) MSA_{Pt} and IA_{Pt} data of Au-7.7@Ni_mPt_m/C samples ($m=1, 2, 4, 6, 9$) at 0.9 V.

3. Detailed information for Au-*d*@Ni_{*m*}Pt_{*m*}/C samples

Table S1. Electrochemical properties of the Au-*d*@Ni_{*m*}Pt_{*m*}/C samples.

| Sample | EAS _{Pt} (m ² ·g _{Pt} ⁻¹) | Half-wave Potentials (V) | IA _{Pt} (mA·cm _{Pt} ⁻²) | MSA _{Pt} (mA·mg _{Pt} ⁻¹) |
|--|---|-----------------------------|--|---|
| Au-2.2@Ni _{0.5} Pt _{0.5} | 102 (58)* | 0.86 | 0.15 (0.1)* | 157 (59)* |
| Au-2.2@Ni ₁ Pt ₁ | 86 | 0.91 | 0.37 | 328 |
| Au-2.2@Ni ₂ Pt ₂ | 83 | 0.92 | 0.51 | 423 |
| Au-2.2@Ni _{2.5} Pt _{2.5} | 81 | 0.92 | 0.42 | 346 |
| Au-2.2@Ni ₃ Pt ₃ | 78 (48)* | 0.91 | 0.43 (0.31)* | 330 (153)* |
| Au-2.2@Ni ₆ Pt ₆ | 57 (40)* | 0.91 | 0.48 (0.45)* | 278 (184)* |
| Au-3.3@Ni ₂ Pt ₂ | 71 | 0.91 | 0.56 | 402 |
| Au-4.5@Ni ₂ Pt ₂ | 61 | 0.91 | 0.60 | 363 |
| Au-7.7@Ni ₂ Pt ₂ | 47 (33)* | 0.93 | 1.06 (0.98)* | 496 (322)* |
| Au-7.7@Ni ₁ Pt ₁ | 76 | 0.93 | 0.74 | 562 |
| Au-7.7@Ni ₄ Pt ₄ | 45 | 0.93 | 0.79 | 360 |
| Au-7.7@Ni ₆ Pt ₆ | 44 | 0.94 | 0.99 | 432 |
| Au-7.7@Ni ₉ Pt ₉ | 42 | 0.93 | 0.92 | 388 |
| Au-10.3@Ni ₂ Pt ₂ | 36 | 0.92 | 1.09 | 392 |
| Pt/C (E-TEK) | 76 (32)* | 0.88 | 0.25 (0.17)* | 189 (66)* |
| PtNi/C | 39 (35)* | 0.92 | 1.01 (0.37)* | 389 (135)* |

* The numbers in the parentheses were obtained in the measurements after ADT.

Table S2. Detailed experimental parameters/conditions for the synthesis of Au NPs of different sizes

| Sample | <i>d</i> _{seeds} (nm) ^a | V _{seeds} (ml) ^b | V _{HAuCl₄} (ml) ^c | V _{AA} (ml) ^d | D (nm) ^e |
|---------|---|--------------------------------------|--|-----------------------------------|---------------------|
| Au-2.2 | - | - | 1.00 | - | 2.2 ± 0.3 |
| Au-3.3 | 2.2 | 10.0 | 0.25 | 3.8 | 3.3 ± 0.5 |
| Au-4.5 | 2.2 | 10.0 | 1.00 | 15.0 | 4.5 ± 0.7 |
| Au-7.7 | 4.7 | 8.2 | 0.50 | 7.5 | 7.7 ± 1.2 |
| Au-10.3 | 4.7 | 5.8 | 1.00 | 15.0 | 10.3 ± 1.9 |

^a Average size by diameter of Au seeds. ^b The concentration of Au was 1.0 × 10⁻³ M. ^c The concentration of HAuCl₄ was 5.0 × 10⁻³ M. ^d The concentration of ascorbic acid was 5.0 × 10⁻³ M. ^e Average size by diameter of Au NPs.