Electronic Supplementary Material (ESI) for Nanoscale.

Hollow Alloy Nanostructures Templated by Au Nanorods: Synthesis, Mechanistic Insights, and Electrocatalytic Activity

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Experimental Section

Seeds for Au nanorods (AuNRs) were prepared according to the protocol developed by Nikoobakht and El-Sayed.[1]

Synthesis of AuNRs with an average AR of 5.5. In brief, 2.5 mL of 4.0 mM $AgNO_3$ solution was added to 50 mL of 0.20 M CTAB solution at 28.5 ºC. Afterwards, 50 mL of 1.0 mM $HAuCl_4$ was mildly mixed with the above solution, and then to this mixture, 0.7 mL of 78.8 mM ascorbic acid was added. Finally, 0.12 mL of the seed solution was introduced into the above growth solution and the resulting reaction mixture was aged at 28.5 ºC for 16 h.

Synthesis of AuNRs with an average aspect ratio (AR) of 3. In a similar pathway, 50 mL of 0.20 M CTAB, 2.0 mL of 4.0 mM $AgNO_3$, 50 mL of 1.0 mM $HAuCl_4$, 0.7 mL of 78.8 mM ascorbic acid, and 0.12 mL of the seed solution were used.

1. Nikoobakht, B.; El-Sayed, M. A. Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth Method. *Chem. Mater*. **2003**, *15*, 1957–1962.

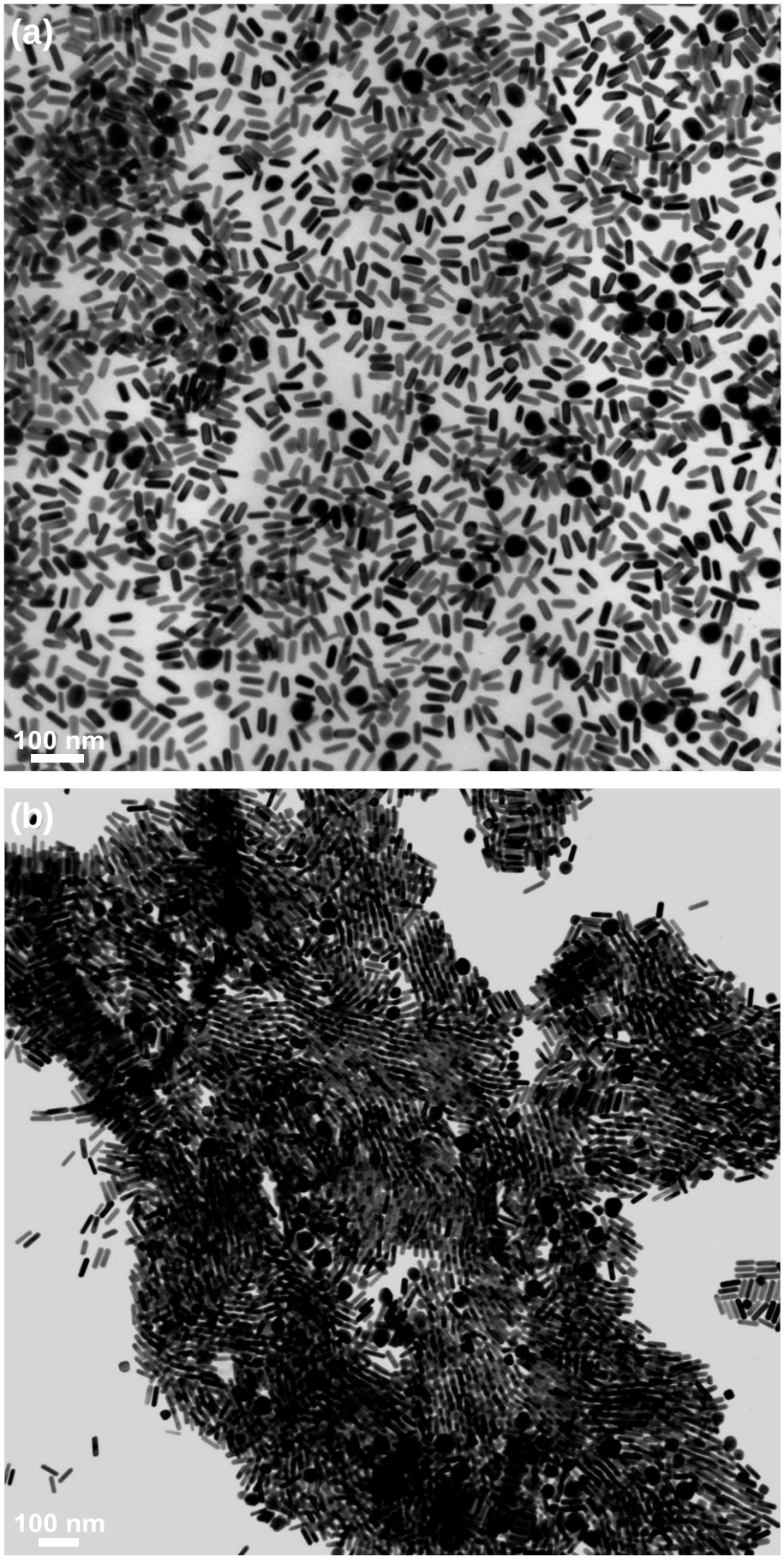


Figure S1. TEM images of the AuNR templates with an average AR of (a) 3 and (b) 5.5.

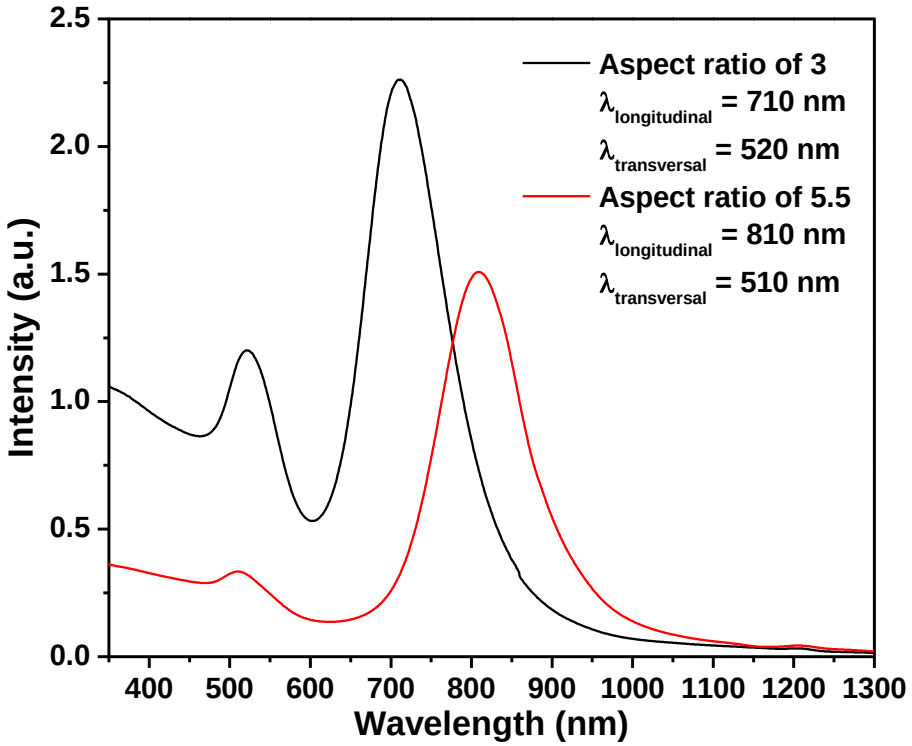


Figure S2. UV–vis–NIR absorption spectra of the AuNR templates with an average AR of 3 and 5.5.

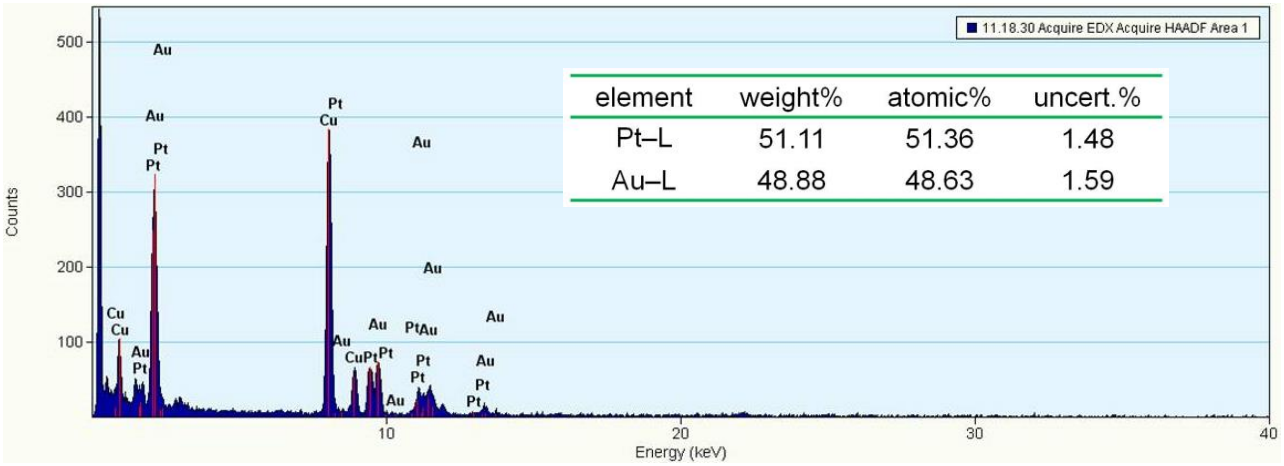


Figure S3. Energy-dispersive X-ray spectrum (EDS) and the composition of the ellipsoidal Pt–Au nanocages prepared by using the AuNR templates an average AR of 3. The AuNR templates were incubated with 0.50 mM $CuCl_2$ for 2.0 h at 60 ºC prior to the alloying reaction between the AuNRs and the reduced Pt atoms.

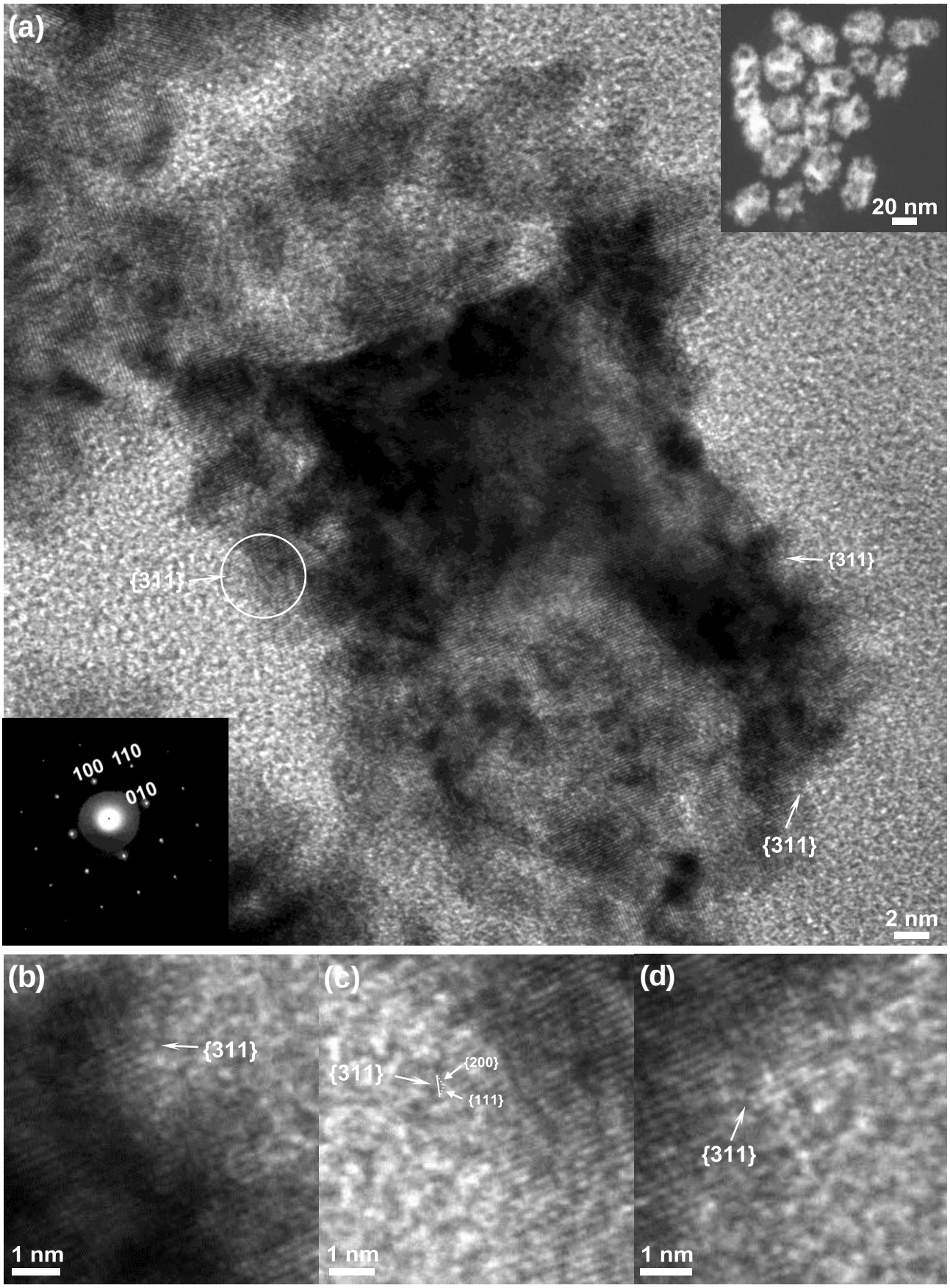


Figure S4. (a) Large-area HRTEM image of the ellipsoidal Pt–Au nanocages. The top and bottom insets show the HAADF-STEM image of the ellipsoidal Pt–Au nanocages and the SAED pattern of the single Pt–Au nanocage, respectively. SAED pattern taken along the [001] zone axis of the nanocage shows a nearly square spot array, reflecting the highly crystalline nature of the product. The area marked with a white circle illustrates the domain of the lattice distortion. Some high-index {311} facets are indicated by the white arrows in panel a and the enlarged HRTEM images (c–d).

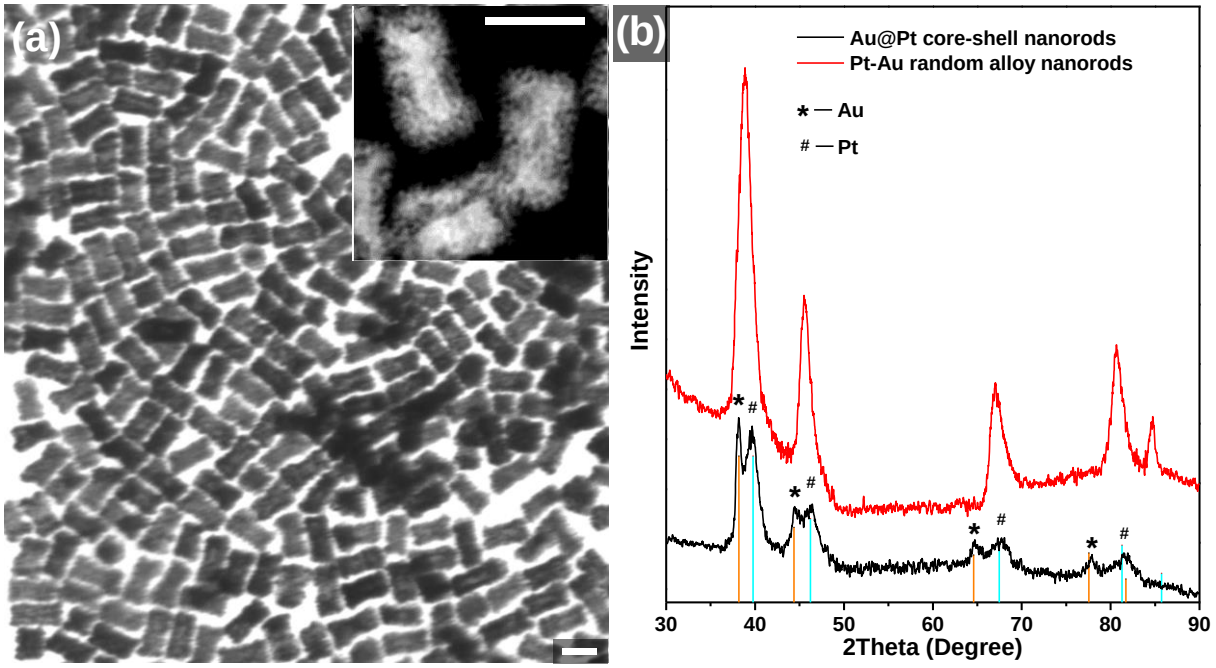
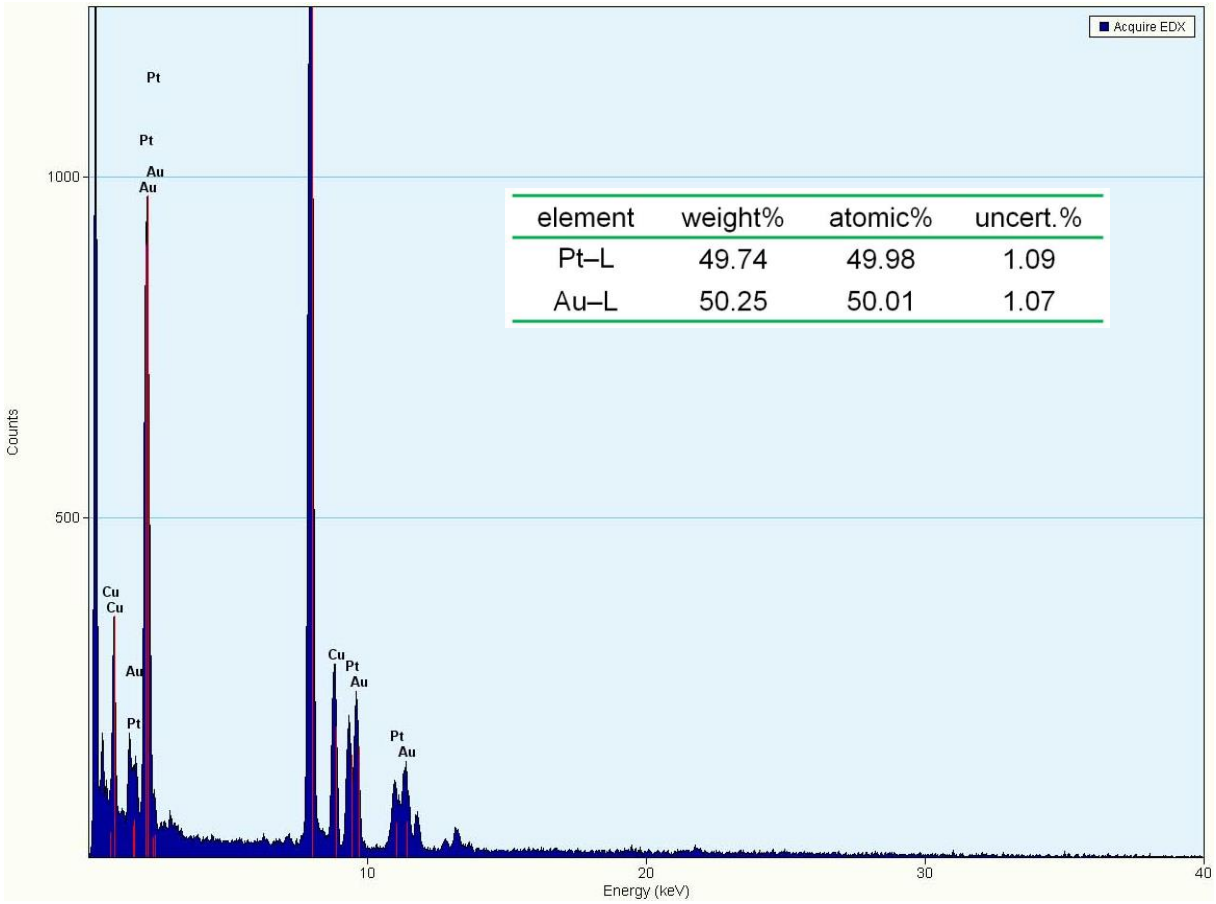


Figure S5. (a) TEM image of the Au@Pt core–shell nanorods. (b) XRD diffractograms of the Au@Pt core–shell nanorods and the porous Pt–Au solid solution nanorods. The inset shows the corresponding HAADF-STEM image, illustrating an enhanced elemental contrast at the center of each Au@Pt core–shell nanorod due to an AuNR residing therein. For synthesizing the Au@Pt core–shell nanorods and the porous Pt–Au solid solution nanorods, the AuNR templates (AR = 5.5) are incubated with 0.50 mM $CuCl_2$ for 0.5 and 1.5 h at 60 ºC, respectively. Scale bars: 50 nm.



element	weight%	atomic%	uncert.%
Pt–L	49.74	49.98	1.09
Au–L	50.25	50.01	1.07

Figure S6. EDS and the composition of the cylindrical Pt–Au nanocages.

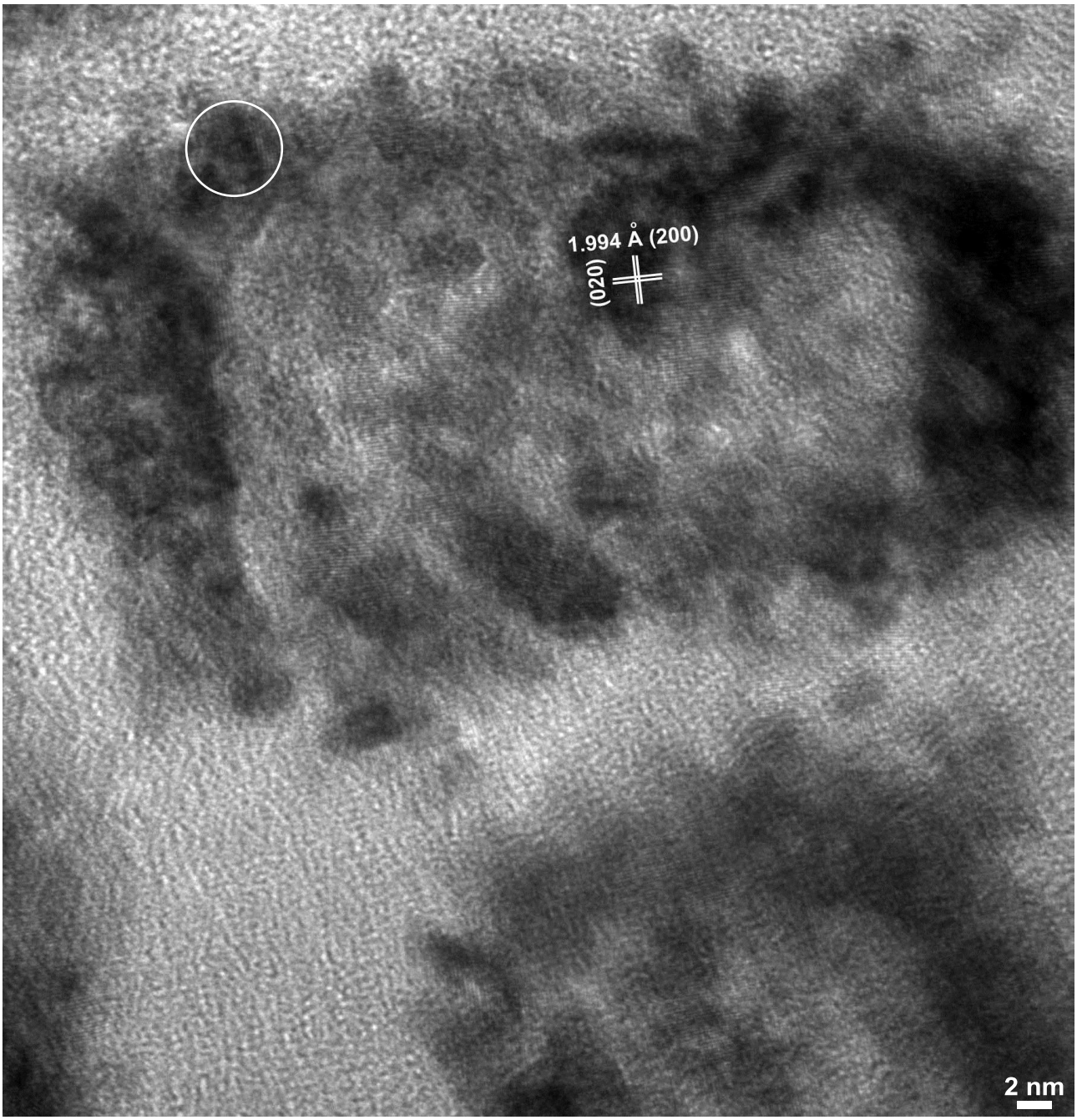
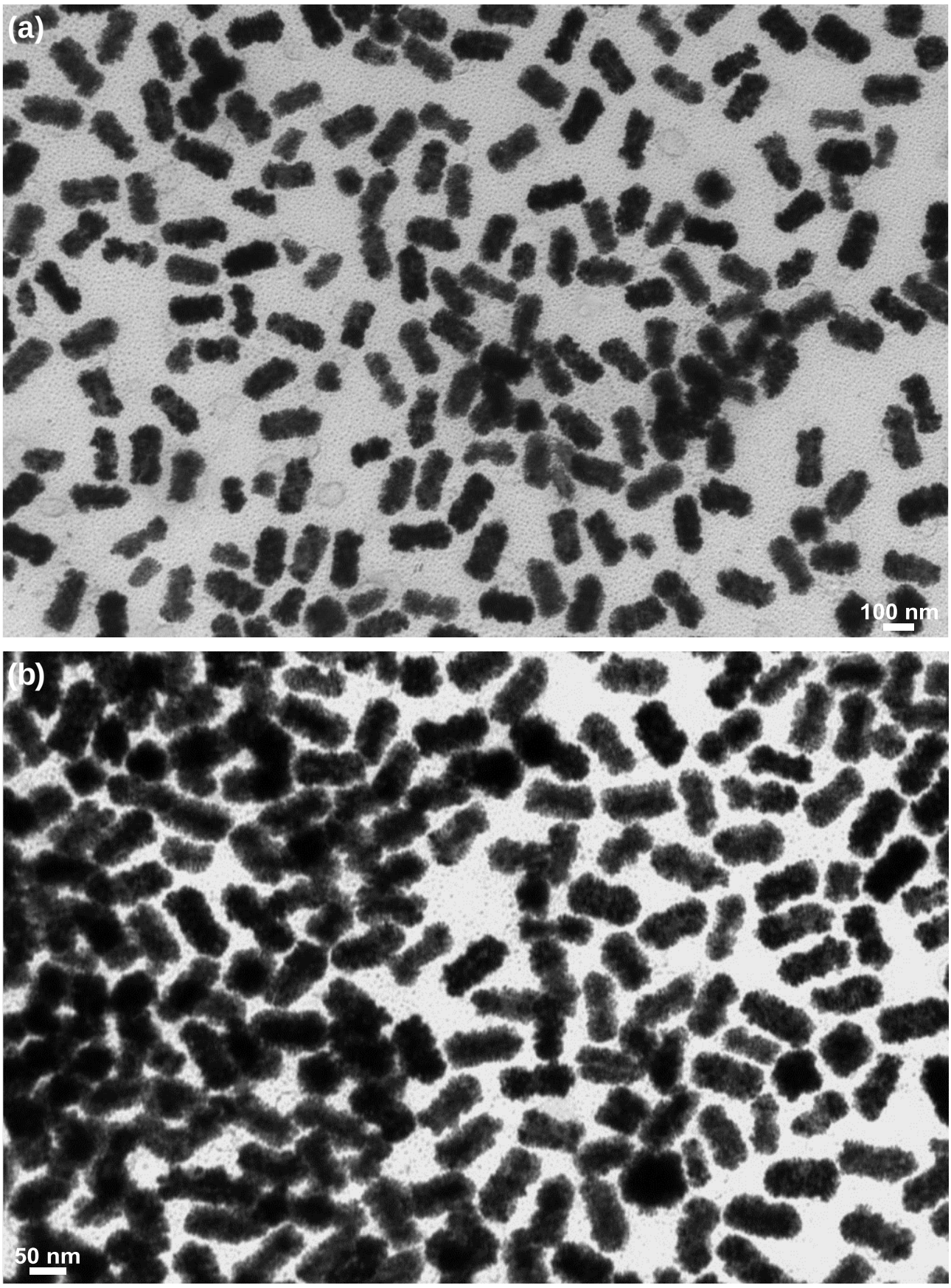


Figure S7. Large-area HRTEM image of the cylindrical Pt–Au nanocages. The marked area with a white circle shows the domain of the lattice distortion.


(a)
100 nm
(b)
50 nm

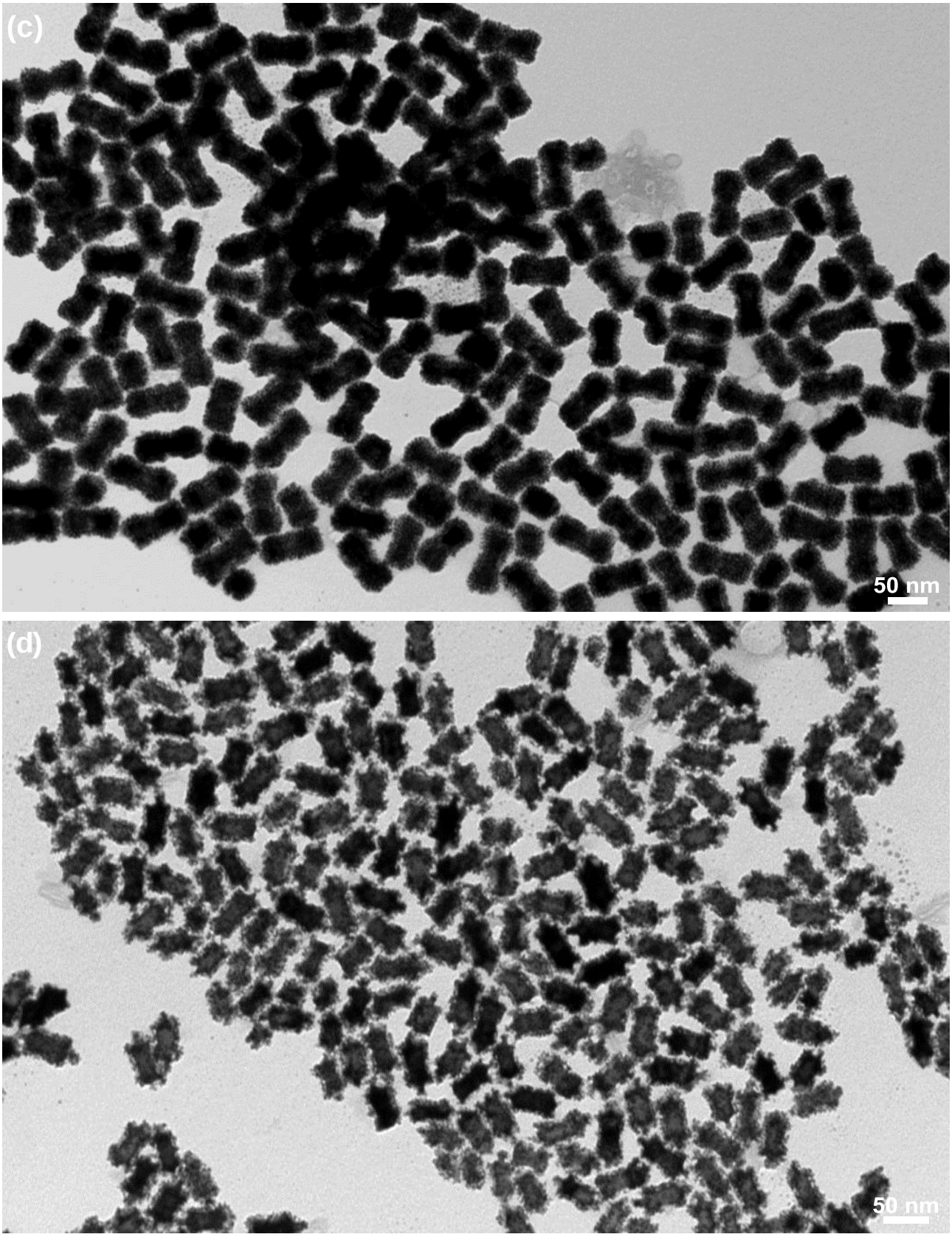


Figure S8. TEM images of the Au@Pt core–shell nanorods prepared by incubating AuNRs with (a) 0.50 mM $ZnCl_2$, (b) 0.50 mM NaCl, (c) without any additives, and (d) 0.50 mM $CuCl_2$ in the presence of (a–c) CTAB or (d) PVP for 2.5 h at 60 ºC prior to reducing $PtCl_6^{2-}$. The other experimental parameters are kept the same as those for the synthesis of the cylindrical Pt–Au nanocages. A distinct variation in contrast between the darker AuNR core and the relatively lighter platinum shell is demonstrated in each image, clearly manifesting the formation of a Pt shell around each AuNR core.

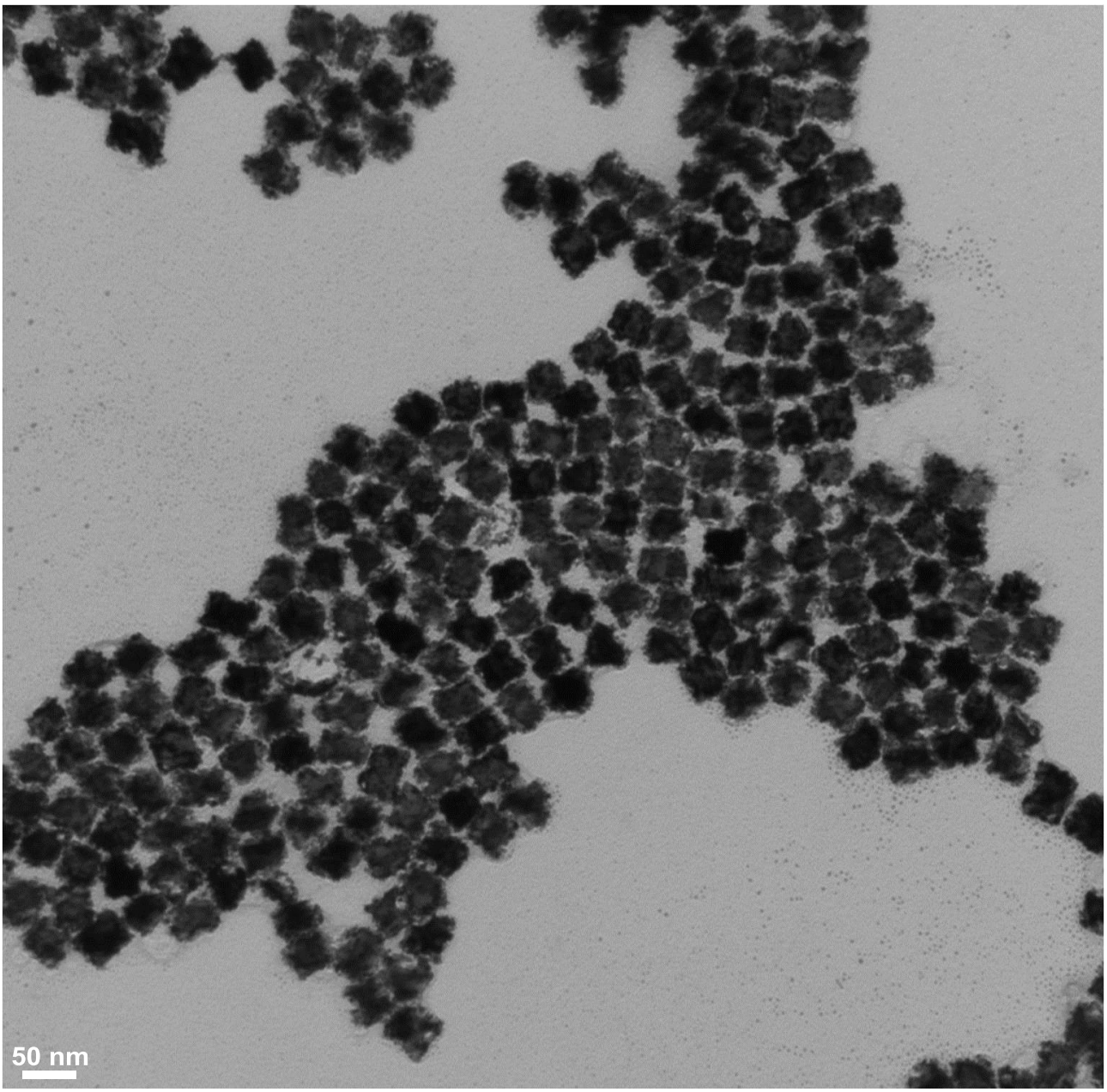


Figure S9. TEM image of the Au@Pt core–shell nanocubes prepared by incubating AuNRs with 1 mM $CuCl_2$ for 2.5 h at 60 ºC before reducing $PtCl_6^{2-}$.

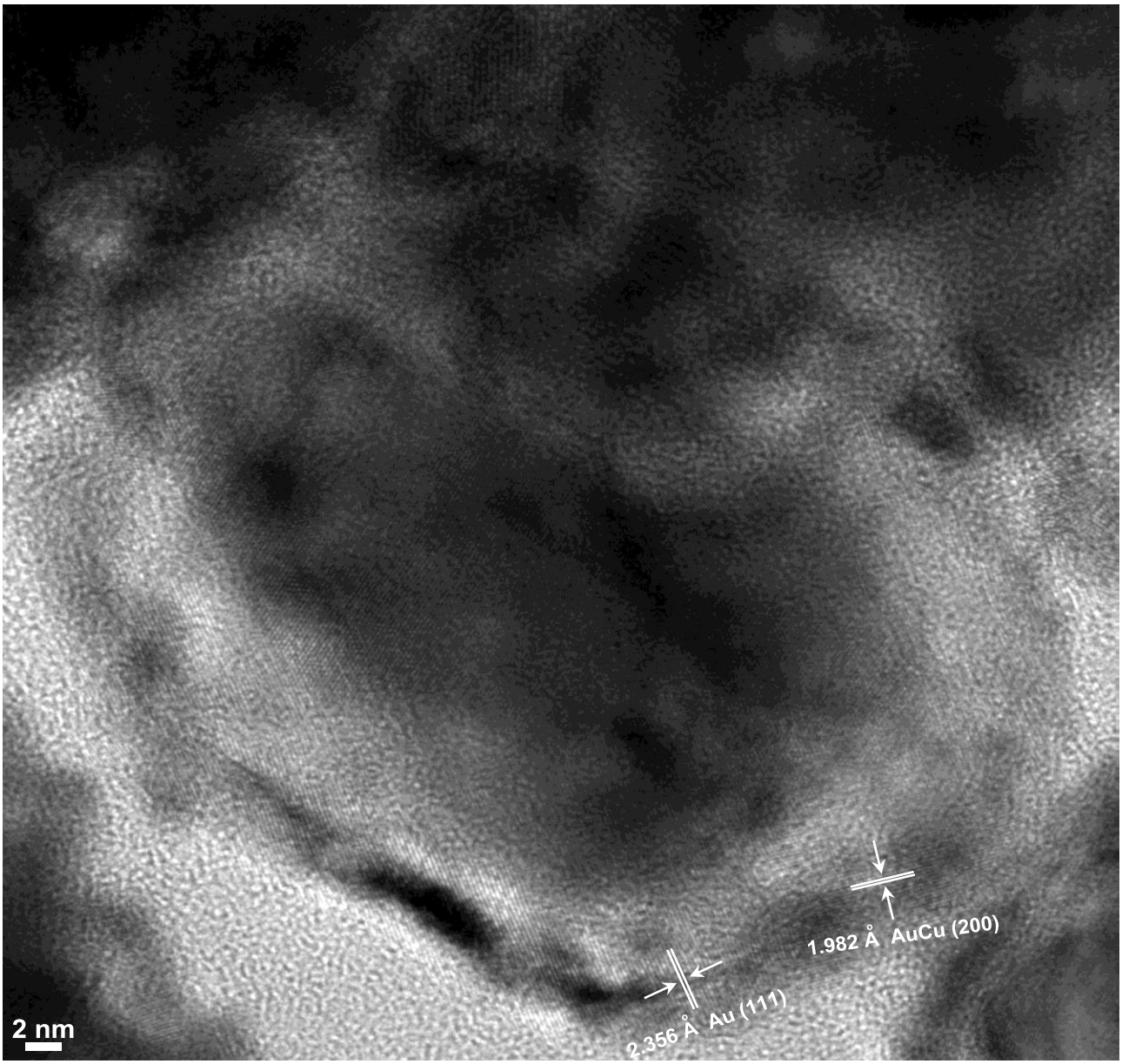


Figure S10. Large-area HRTEM image of the rattle-type Cu–Au hollow nanoheterostructures with Au nanorods encapsulated in the center.

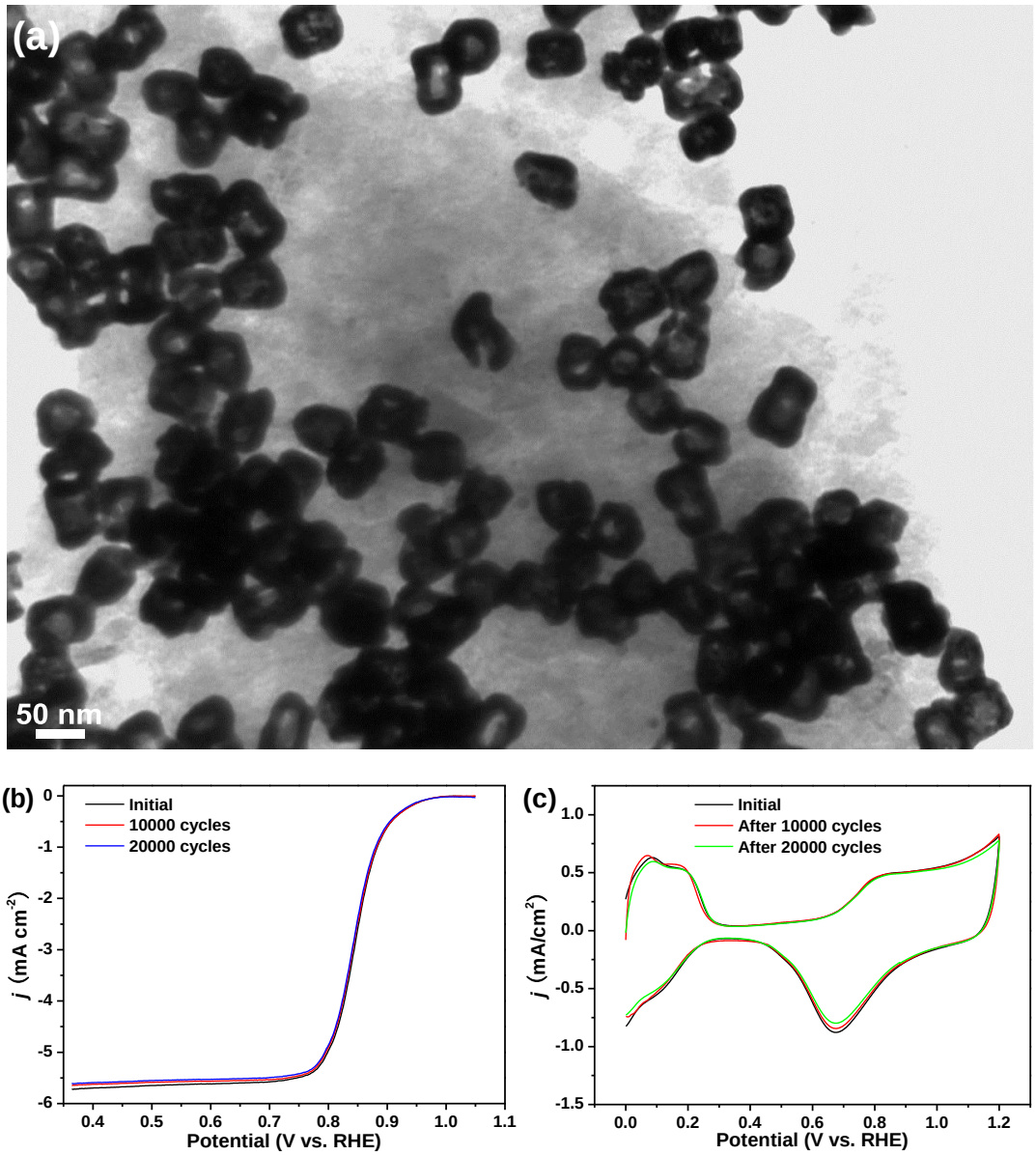


Figure S11. (a) TEM image of the carbon supported cylindrical Pt–Au nanocage catalyst after the 20000-cycle stability test. (b) ORR polarization curves of the cylindrical Pt–Au nanocage catalyst in an O_2-saturated 0.1 M $HClO_4$ solution at ambient temperature after 1, 10000, and 20000 potential cycles between 0.4 and 0.8 V vs Ag/AgCl in an O_2-saturated 0.1 M $HClO_4$ solution. (c) CV curves obtained after 1, 10000, and 20000 potential cycles of the durability test. The potential scan rate = 10 mV/s; Electrode rotation speed = 1600 rpm.

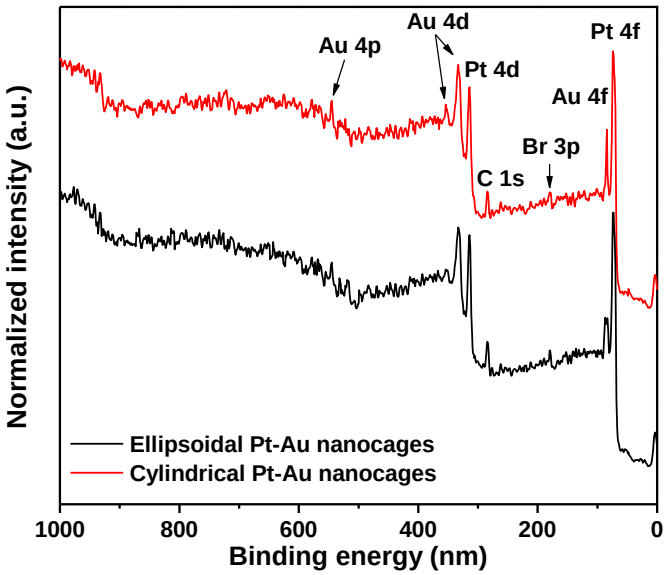


Figure S12. XPS survey spectra recorded from the ellipsoidal and cylindrical Pt-Au nanocages.