

Supporting Information

Monodisperse CuPt alloy: Synthesis and their superior catalytic performance in hydrogen evolution reaction over the full pH range

Xinmei Liu,^{a*,b} Chen Liang,^b Wenlong Yang,^b Chunyang Yang,^b Jiaqi Lin,² Xue Li^b

a.Foshan (Southern China) Institute for New Materials, Foshan 528200, Guang- dong, People's Republic of China

b.School of Science, Harbin University of Science and Technology, 150080, People's Republic of China

Correspondence: liuxinmei.1990@163.com

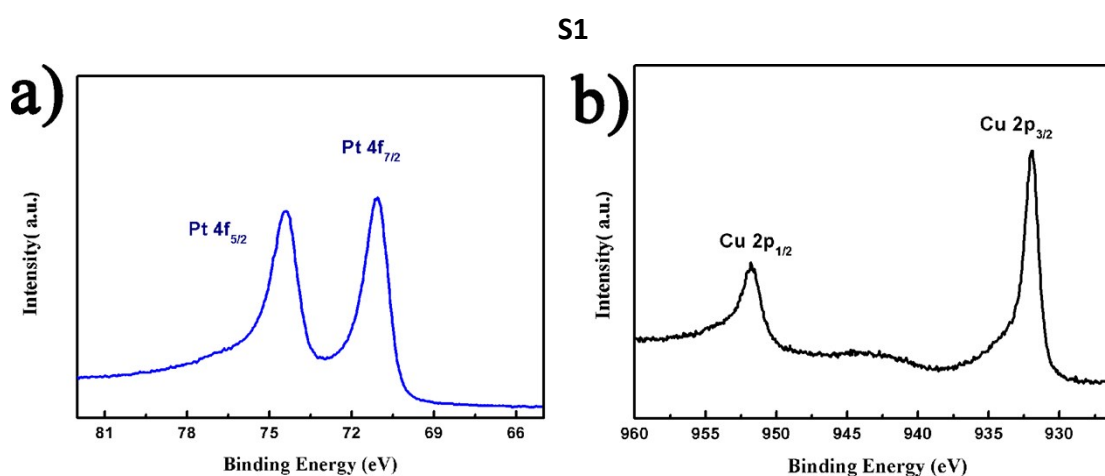


Figure S1 The high-resolution for the Pt 4f and Cu 2p XPS spectra.

As shown the spectra Figure S1a, the peaks at 71.2 and 74.6 eV are corresponded to Pt 4f_{7/2} and Pt 4f_{5/2}, which demonstrate the upward shifts relative to pure Pt (71.0 and 74.4 eV).

Most importantly, the downshift of Pt induced by the lattice compression would reduce the binding energy to the reactive intermediates, thereby improving the HER performance.^[1-2] As the Cu 2p XPS region in Figure S1b, the distinct peaks at 951.8 and 932.0 eV reveal that there is no oxide layer on the CuPt alloy surface. Owing to the strong interactions between Cu and Pt 2p_{3/2} peak (932.0 eV) demonstrate a downshift alternative to pure Cu (932.8 eV). This result is agreed well with the HRTEM images in Figure 1d.

S2

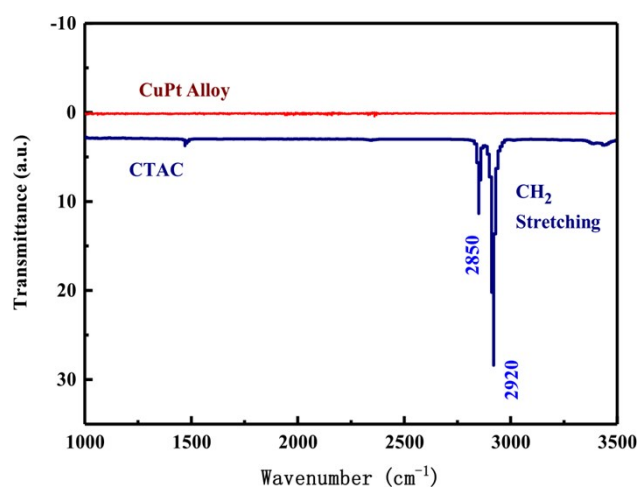


Figure S2. Fourier-transform infrared spectroscopy transmittance spectra for the CTAC and as-prepared CuPt alloy

S3

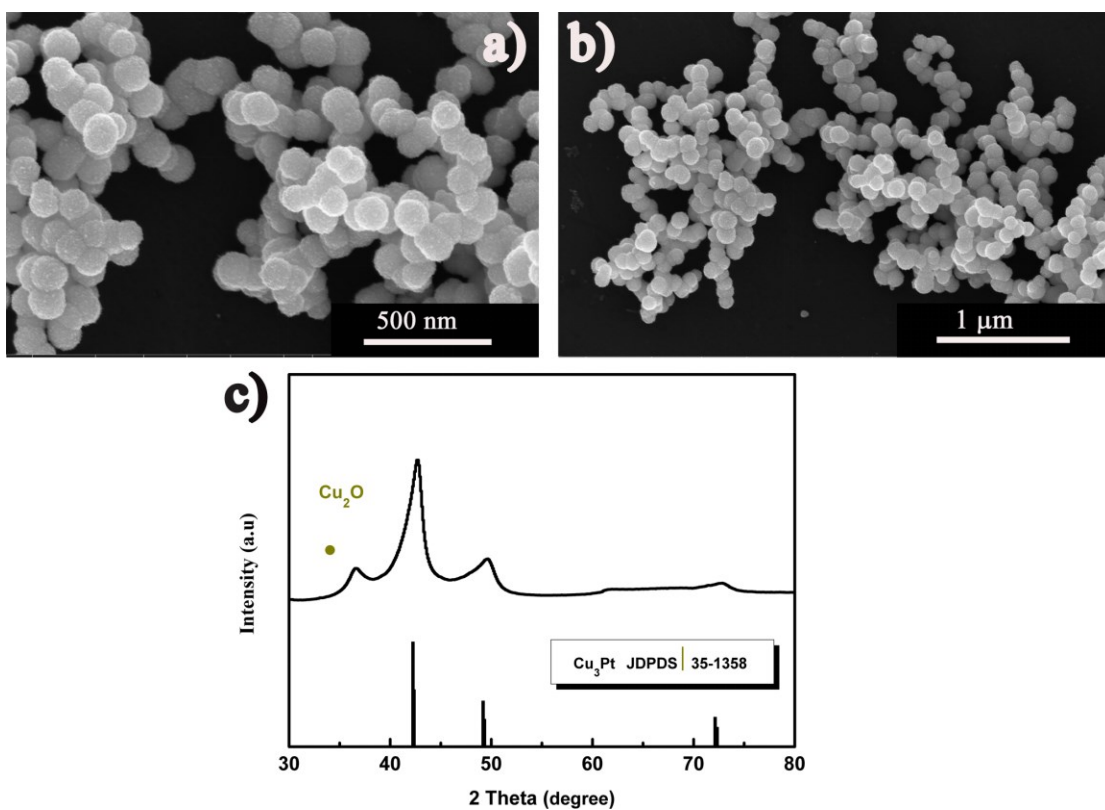


Figure S3. a-b)FESEM image;c) and XRD patterns for the sample as-prepared when no CTAC was employed.

Synthesis of monodisperse Pt NPs

Following a typical procedure, 1 mL of 10 mM HPtCl_4 was dissolved in 15 mL H_2O . After the CuCl_2 was dissolved, 1.0 g CTAC was added to this solution. The solution was magnetically stirred for 5 min. Subsequently, 5 mL of 1 M AA was added. The final solution was magnetically stirred for 20 min and maintained at 99 °C for 30 min. The final product was collected by a centrifugation and general washing technique.

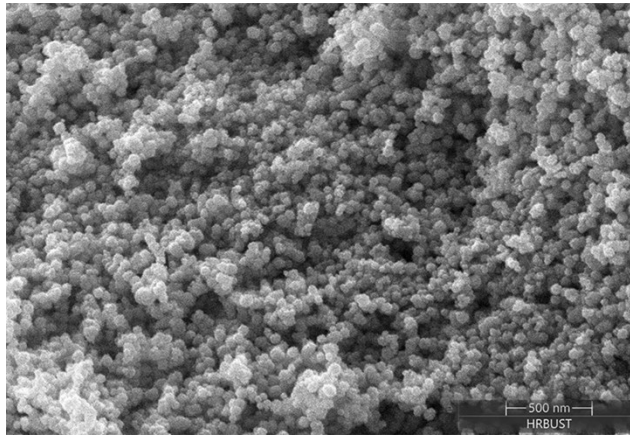


Figure S4 FESEM of the Pt NPs in this work.

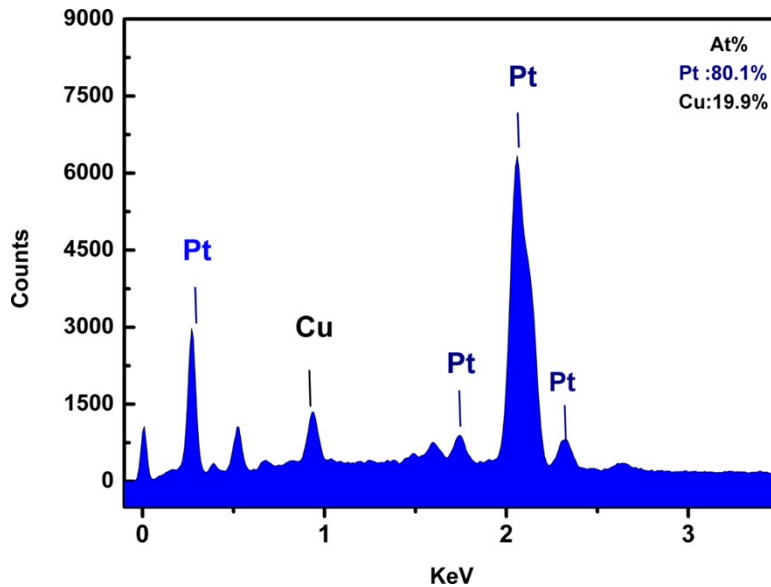


Figure S5. EDX for the CuPt alloy after the chronopotentiometric measurement.

S6

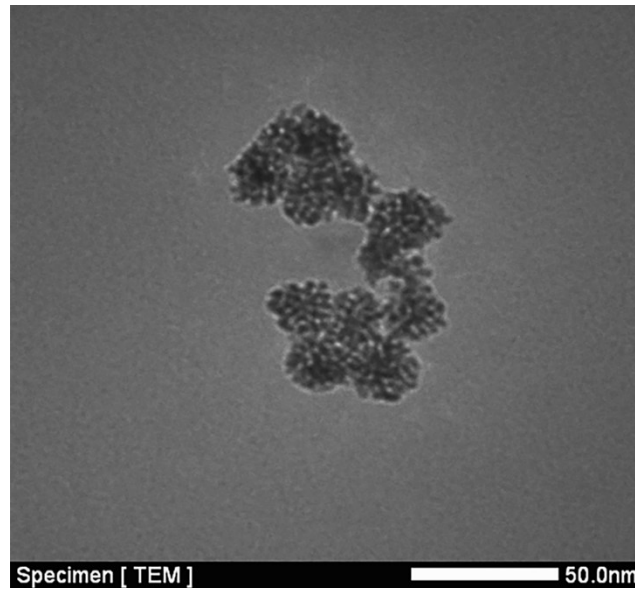


Figure S6. TEM for the CuPt alloy after the chronopotentiometric measurement in the acidic medias.

S7

The TOF value is calculated from the equation^[3-4]:

$$\text{TOF} = (J \times A) / (2 \times F \times n)$$

where J is the current density of at overpotential of 0.30 V , A is the area of the GCE (0.071 cm² in this work), F is the Faraday constant (with a value of 96485 C/ mol) ,and n is the mole number of the active metal sites of the catalyst that is deposited on the electrode. (which is 8.76×10^{-5} in work).The results are shown as Table S1.

Table S1. Catalytic parameters for CuPt alloy and Pt NPs in PBS solution.

	Pt NPs	CuPt alloy
TOF(/s)	1.52×10^{-2}	5.30×10^{-2}
Decline rate of overpotential(mV/s)	1.09×10^{-2}	1.17×10^{-4}

All the results indicted that the performance of CuPt alloy was elevated after yielding 1.2×10^5 s hydrogen in the alkaline media, which are agreed well with the chronopotentiometric curves.

S8

Table S2 Summary of TOF of CuPt alloy and Pt NPs under 1 M KOH solution.

	Pt NPs	CuPt alloy
Initial TOF(/s)	1.16×10^{-1}	3.58×10^{-2}
Terminal TOF(/s)	9.20×10^{-2}	8.86×10^{-2}

As show the Table S2, the catalytic parameters for CuPt alloy are much superior to Pt NPs. It revealed that preferable d-band structure would endow the CuPt alloy an enhanced activity.

S9

Table S3.Catalytic parameters for commercial Pt/C and Pt NPs.

Electrolyte	0.05 M H ₂ SO ₄	PBS	1M KOH	Electrocatalyst
Overpotential (mV)	86	299	134 mV	Pt/C
	61	282	128 mV	Pt NPs.
Decline rate of overpotential(mV/s)	7.05×10^{-3}	3.88×10^{-2}	2.90×10^{-2}	Pt/C
	5.33×10^{-5}	1.09×10^{-2}	7.48×10^{-4}	Pt NPs.

As shown in the Table S3, all parameters indicate that the pure Pt NPs show a superior durability and low overpotential. This contrast can be attributed to the high mass ratio of Pt and small diameter for the Pt NPs.

S10

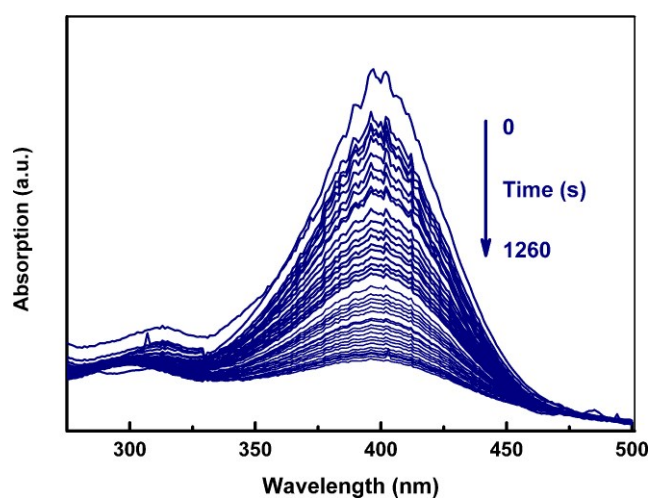


Figure S7. The plot of $\ln(C/C_0)$ versus time for the reduction of 4-NP that catalyzed by the pure Pt NPs.

Notes and references

- [1].Zhang, X.-F., A.-J. Wang, L. Zhang, J. Yuan, Z. Li and J.-J. Feng (2018). "Solvothermal Synthesis of Monodisperse PtCu Dodecahedral Nanoframes with Enhanced Catalytic Activity and Durability for Hydrogen Evolution Reaction." *ACS Applied Energy Materials* 1(9): 5054-5061.
- [2].Cao, L., G. Zhang, W. Lu, X. Qin, Z. Shao and B. Yi (2016). "Preparation of hollow PtCu nanoparticles as high-performance electrocatalysts for oxygen reduction reaction in the absence of a surfactant." *RSC Advances* 6(46): 39993-40001.
- [3] Ni, Y., L. Yao, Y. Wang, B. Liu, M. Cao and C. Hu (2017). "Construction of hierarchically porous graphitized carbon-supported NiFe layered double hydroxides with a core–shell structure as an enhanced electrocatalyst for the oxygen evolution reaction." *Nanoscale* 9(32): 11596-11604.
- [4] Jin, H., H. Zhang, J. Chen, S. Mao, Z. Jiang and Y. Wang (2018). "A general synthetic approach for hexagonal phase tungsten nitride composites and their application in the hydrogen evolution reaction." *Journal of Materials Chemistry A* 6(23): 10967-10975.