Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Microwave-assisted Synthesis of Multiply-twinned Au–Ag Nanocrystals on Reduced Graphene Oxide for High Catalytic Performance Towards Hydrogen Evolution Reaction

Yuchen Qin,[a] Xiaoping Dai,[a] Xin Zhang,*[a] Xingliang Huang, [a] Hui Sun,[a] Daowei Gao,[a] Yanbing Yu, [a] Pengfang Zhang [a], Yan Jiang [a], Hongying Zhuo [a] , Axiang Jin [a] and Hai Wang [b]

[a]State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, 102249, P. R. China. E-mail: zhangxin@cup.edu.cn

[b]National Institute of Metrology, Beijing 100013, P. R. China

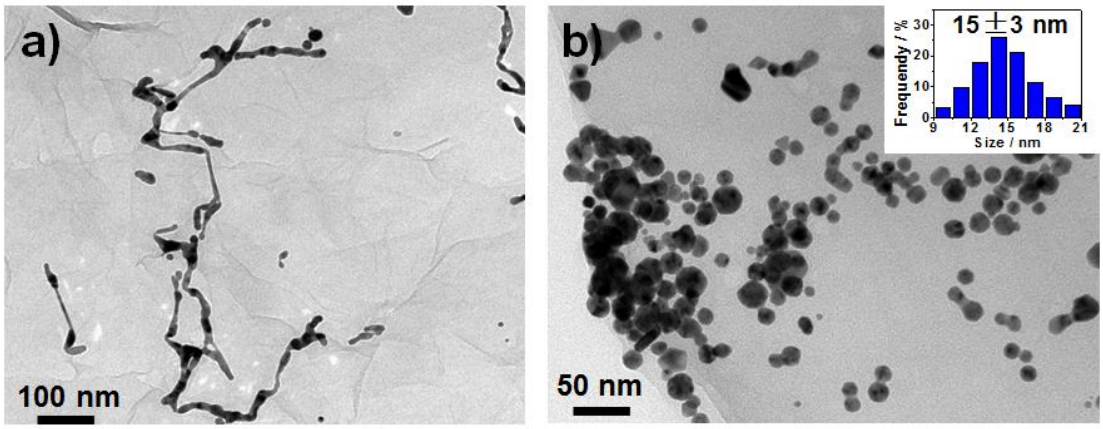

Fig. S1 TEM images of Au-Ag NCs /rGO which prepared in the same reaction system by hydrothermal method at 100 ^{O}C for 3 h. (a) DMF solvent and (b) H_2O solvent.

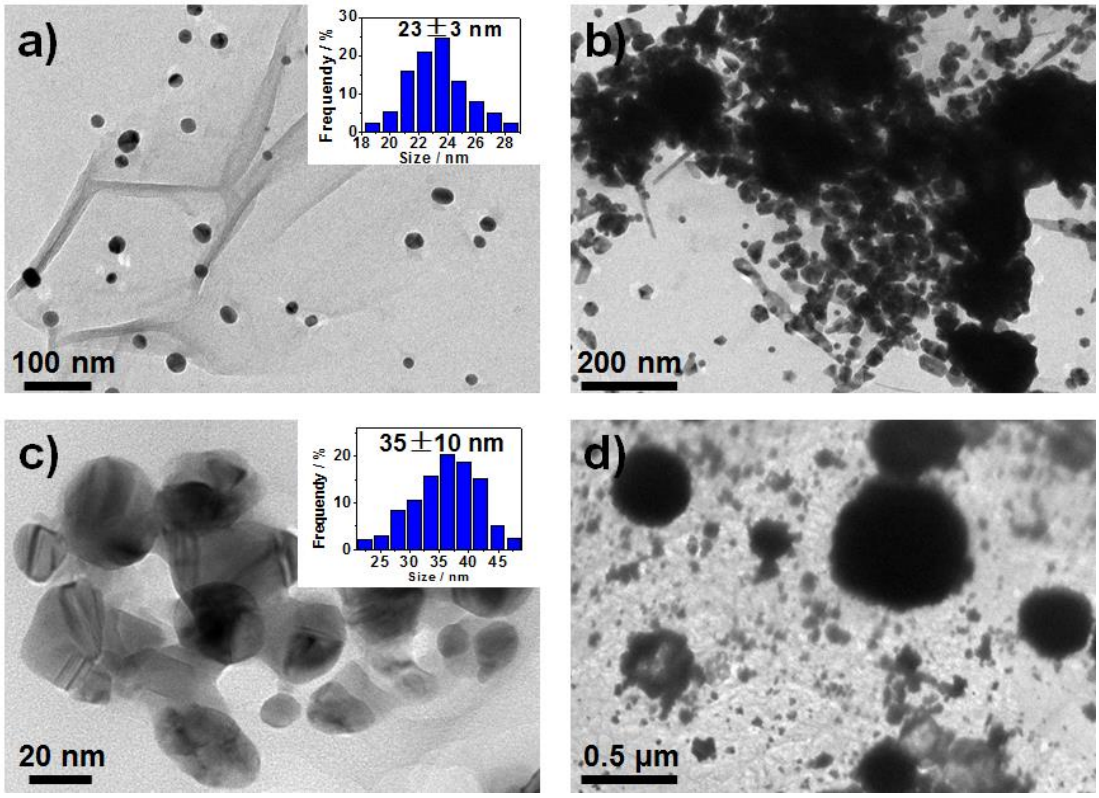

Fig. S2 TEM images(and size-distribution histogram) of Au-Ag NCs /rGO (DMF solvent) prepared in the absence of (a) AA and (b) P123. TEM images of Au-Ag NCs /rGO (H_2O solvent) prepared using the standard procedure in the absence of (c) AA and (d) P123.

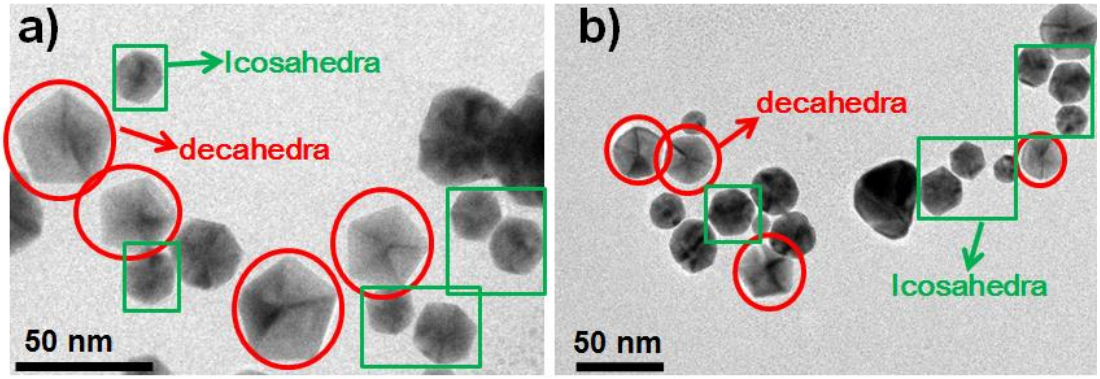

Fig. S3 TEM images of Au-Ag /rGO prepared using the standard procedure for (a) Au-Ag icosahedra /rGO with adding HCl solution (2 mL, 2 mol/L) and (b) Au-Ag decahedra /rGO with adding NaOH solution (2 mL, 0.5 mol/L)

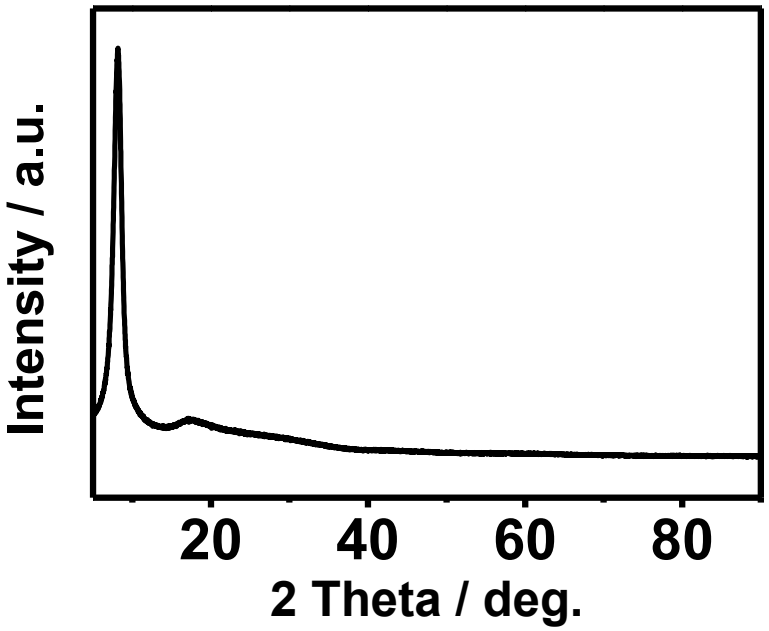

Fig. S4 XRD pattern of GO

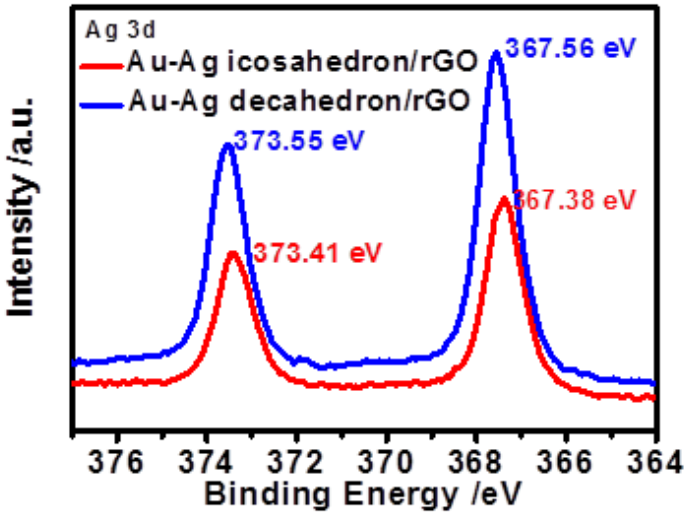

Fig. S5 XPS patterns of the Ag 3d of as-prepared Au–Ag decahedra/rGO and Au–Ag icosahedra/rGO.

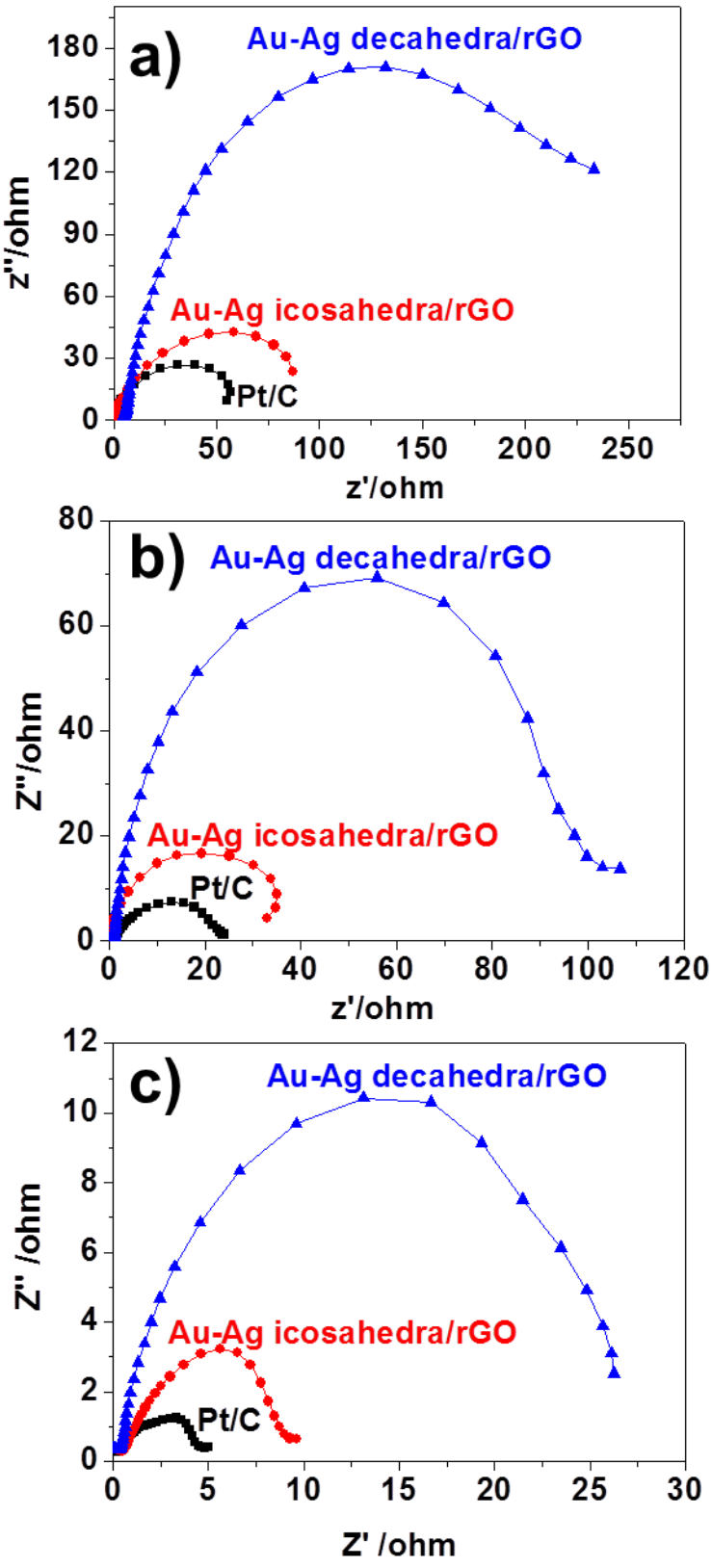

Fig. S6 Nyquist plots of electrochemical impedance spectra (EIS) for various eletrocatalysts at overpotential of (a) 20 mV, (b) 40 mV and (c) 60mV.

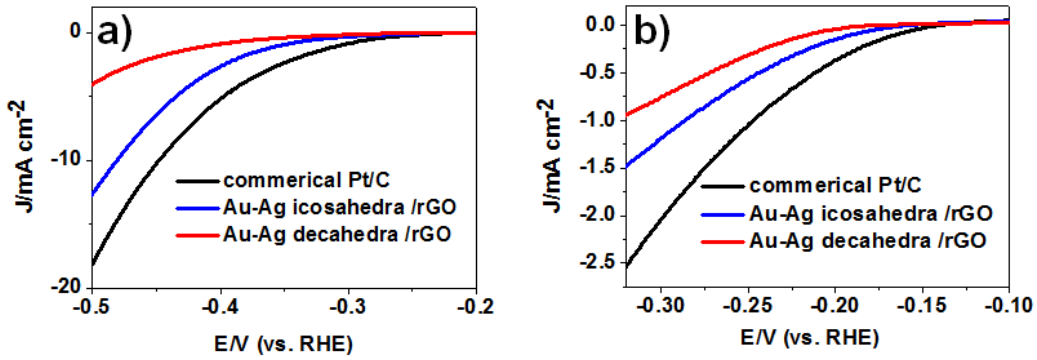

Fig. S7 The HER polarization curves of as-prepared Au–Ag/rGO and commercial Pt/C in (a) phosphate buffer (pH=7) and (b) 0.1 M NaOH (pH=13) solutions.

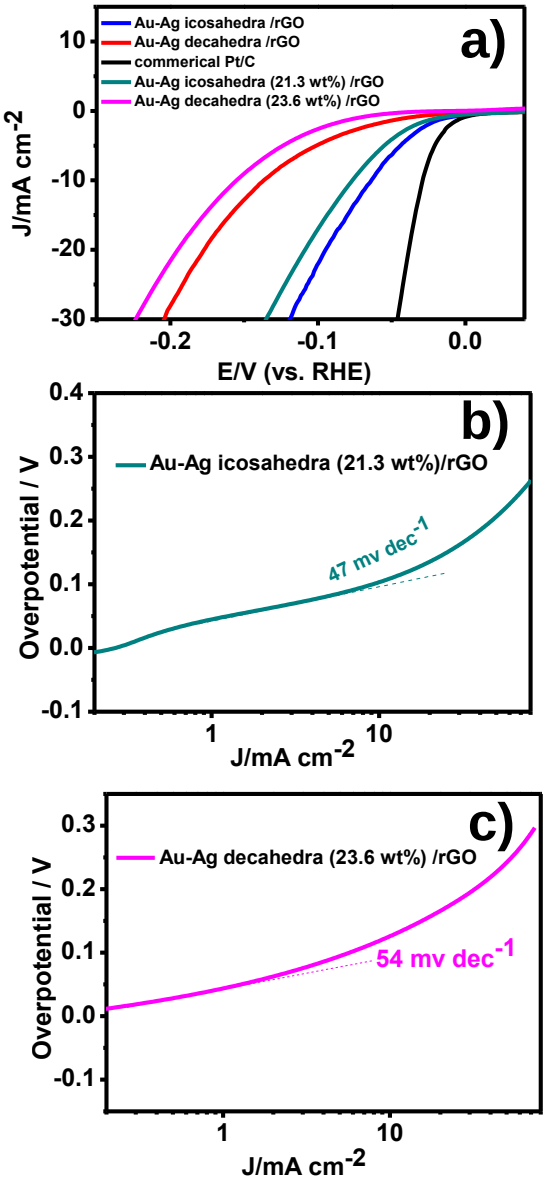

Fig. S8 (a) The HER polarization curves of commercial Pt/C and as-prepared Au–Ag/rGO under different Au-Ag loadings. (b) and (c) Tafel plots recorded on the corresponding catalysts in 0.5 M H2SO4 solution.

For compared with Pt/C (20 wt%) under the similar metal loadings. We decreased the Au-Ag loadings and prepared Au-Ag decahedra/rGO (Au-Ag loading: 23.6 wt%) and Au-Ag icohedra/rGO (Au-Ag loading: 21.3 wt%). As Fig. S8 shown, the electrocatalytic activity of Au-Ag icohedra/rGO (21.3 wt%) was a little lower than that of Au-Ag icohedra/rGO (50.6 wt%) and the Tafel slope of 47 mv dec^{-1} was a little larger than that of Au-Ag icohedra/rGO (39 mv dec^{-1}). When the Au-Ag decahedra loadings decreased to 23.6 wt%, the electrocatalytic performance was also lower than that of Au-Ag decahedra/rGO (52.3 wt%) and the Tafel slope of 54 mv dec^{-1} was closed to that of Au-Ag decahedra/rGO (52.3 wt%). It demonstrated that the Au-Ag loadings of Au-Ag/rGO hybrids has a small effect on the electrocatalytic activity for HER.

Table S1. The specific surface area and pore volume of Au–Ag NCs/rGO

Sample	S_{BET} ($m^2 g^{-1}$)	V_{pore} ($cm^3 g^{-1}$)
rGO	**46.3**	**0.14**
Au-Ag decahedra/rGO	**83.4**	**0.26**
Au–Ag icosahedra/rGO	**89.9**	**0.33**

"Nitrogen physisorption measurements were performed at liquid-nitrogen temperature with a Micromeritics TriStar 3020 apparatus. Prior to the measurements, all samples were vacuum-degassed at 373 K for 12 h. The total surface area was determined by the BET method. The pore size distribution profile and the mesopore volume were obtained by the BJH method with the N_2 desorption isotherm.

From Table S1, we could found that the specific surface area (S_{BET}) of Au-Ag decahedra/rGO and Au–Ag icosahedra/rGO were 83.4 and 89.9 $m^2 g^{-1}$, which were similar to the S_{BET} of rGO (~ 46.3 $m^2 g^{-1}$). The pore volume of rGO and Au-Ag NCs/rGO were all small.

Table S2. Performance of Au-based catalyst for HER and several results from previous published works

Ref.	Catalyst	Scan rate (mV/s)	Solution	Temperature (°C)	Tafel slope (mV dec^{-1})
This work	**Au-Ag icosahedra/rGO**	**10**	**0.5 M H_2SO_4**	**Room temperature**	**39**
1	**Pd–Au/CFP**	**5**	**0.5 M H_2SO_4**	**Room temperature**	**47**
2	**Au NPs/rGO**	**5**	**0.5 M H_2SO_4**	**Room temperature**	**39.2**
3	**NiAu/Au**	**2**	**0.5 M H_2SO_4**	**Room temperature**	**36**

References

1. Z. Zhuang, F. Wang, R. Naidu and Z. Chen, *J. Power Sources*, 2015, **291**, 132-137.
2. G. Darabdhara, M. A. Amin, G. A. M. Mersal, E. M. Ahmed, M. R. Das, M. B. Zakaria, V. Malgras, S. M. Alshehri, Y. Yamauchi, S. Szunerits and R. Boukherroub, *J. Mater. Chem. A*, 2015, **3**, 20254-20266.
3. H. Lv, Z. Xi, Z. Chen, S. Guo, Y. Yu, W. Zhu, Q. Li, X. Zhang, M. Pan, G. Lu, S. Mu and S. Sun, *J. Am. Chem. Soc.*, 2015, **137**, 5859-5862.