

# **Electrochemical-reduction-assisted assembly of ternary Ag nanoparticles/ polyoxometalate/ graphene nanohybrids and its activity in the electrocatalysis of oxygen reduction**

**Rongji Liu,<sup>a#</sup> Zhaowei Xian,<sup>b#</sup> Shuangshuang Zhang,<sup>ac</sup> Chunhua Chen,<sup>\*b</sup> Zhihua Yang,<sup>b</sup> Hang Li,<sup>d</sup> Wanquan Zheng,<sup>d</sup> Guangjin Zhang<sup>\*a</sup> and Hongbin Cao<sup>\*a</sup>**

*<sup>a</sup>Key laboratory of Green Process and Engineering, Chinese Academy of Sciences, 100190, Beijing, China*

Email: zhanggj@ipe.ac.cn; hbcao@ipe.ac.cn

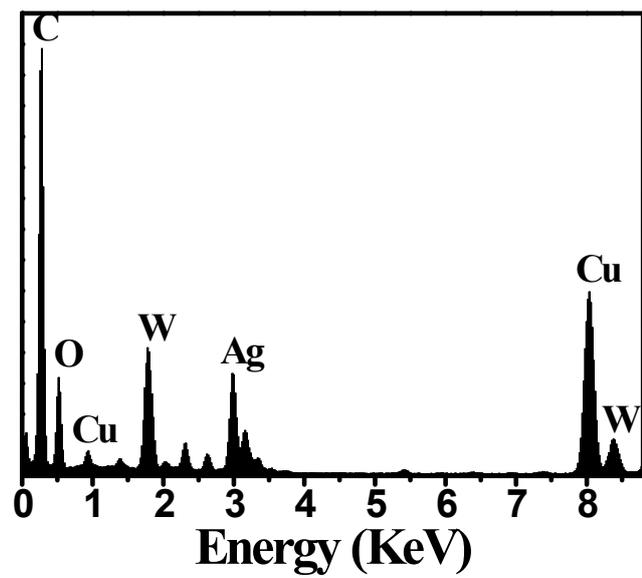
*<sup>b</sup>Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, College of Chemical and Environmental Engineering, Jiangnan University, 430056, Wuhan, China*

Email: cch1003@163.com

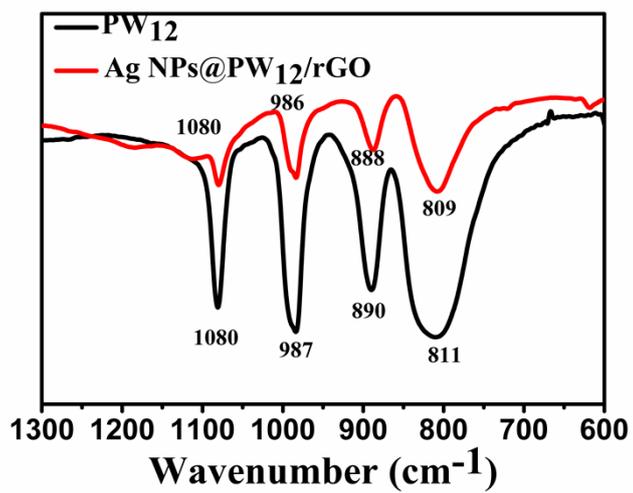
*<sup>c</sup>University of Chinese Academy of Sciences, 100049, Beijing, China*

*<sup>d</sup>Jiangnan University Institute for Interdisciplinary Research, 430056, Wuhan, China*

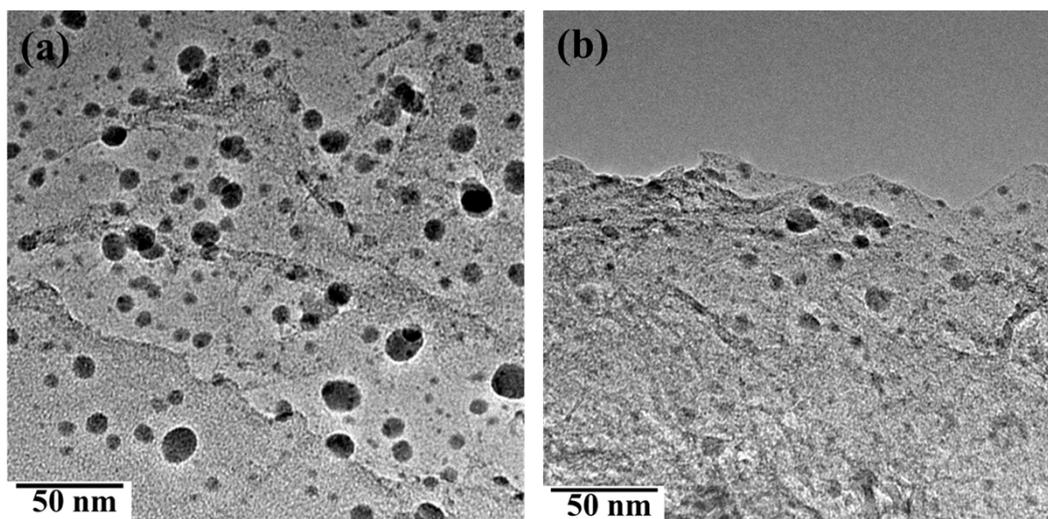
*<sup>#</sup>These authors contributed equally to this work*



**Fig. S1** EDX analysis of 30% Ag NPs@POM/rGO nanohybrids.



**Fig. S2** FT-IR spectra of the prepared 30% Ag NPs@PW<sub>12</sub>/rGO nanohybrid as well as the pure PW<sub>12</sub>.



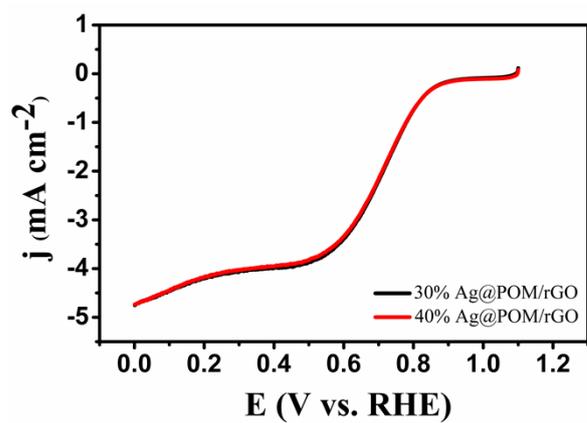
**Fig. S3** Typical TEM images of (a) 20% Ag NPs@POM/rGO and (b) 10% Ag NPs@POM/rGO.

**Table S1** The main characteristics determined from the voltammograms on the five electrodes as shown in Fig. 5 in the text.

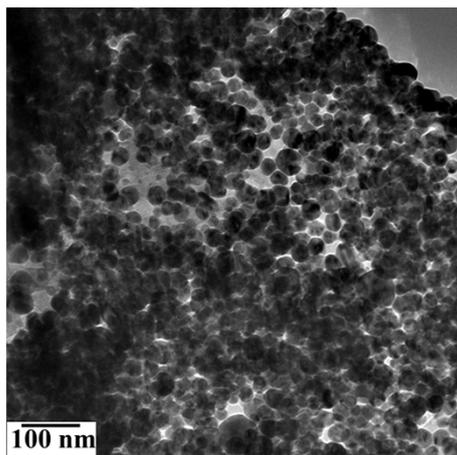
Electrode material	$E_{pc}$ / V vs. RHE	$i_{pc}$ / mA cm <sup>-2</sup>
Ag NPs@POM	0.55	-0.52
POM/rGO	0.53	-0.73
10% Ag NPs@POM/rGO	0.60	-1.17
20% Ag NPs@POM/rGO	0.71	-1.34
30% Ag NPs@POM/rGO	0.74	-1.42

**Table S2** The numbers of electrons transferred for ORR on the five electrodes calculated from the slopes of the Koutecky–Levich plots (shown in Fig. 6, see in the text) at various potentials.

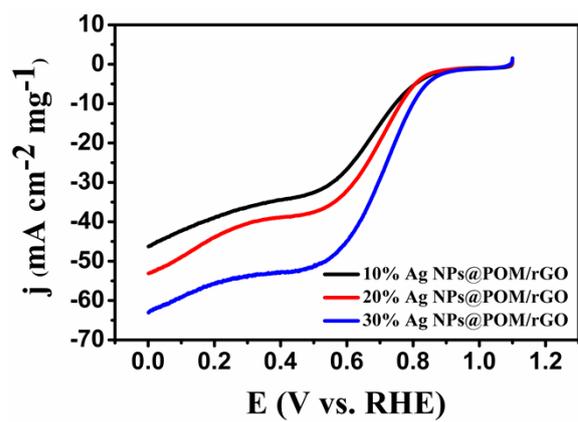
Electron number Potential	Electrode	Ag NPs@POM	POM/rGO	10% Ag NPs@POM/rGO	20% Ag NPs@POM/rGO	30% Ag NPs@POM/rGO
		0.15 V vs. RHE	1.90	2.43	3.82	3.95
0.25 V vs. RHE	1.83	2.26	3.92	3.73	4.06	
0.35 V vs. RHE	1.71	2.05	4.2	3.57	3.97	
0.45 V vs. RHE	1.60	1.88	4.33	3.65	4.01	
0.55 V vs. RHE	1.52	1.72	4.28	3.67	4.04	



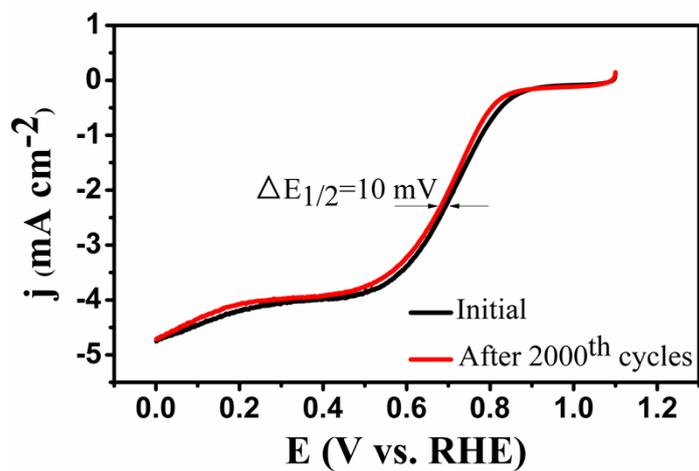
**Fig. S4** Linear sweep voltammetry curves of ORR in  $\text{O}_2$ -saturated 0.1 M KOH solutions at a scan rate of  $10 \text{ mV s}^{-1}$ . The rotation rate is 1600 rpm.



**Fig. S5** Typical TEM image of 40% Ag NPs@POM/rGO.



**Fig. S6** RDE polarization curves of Ag NPs@POM/rGO with different Ag loadings at a scan rate of 10 mV s<sup>-1</sup>. The rotation rate is 1600 rpm.



**Fig. S7** RDE polarization curves of 30% Ag NPs@POM/rGO at a scan rate of  $10 \text{ mV s}^{-1}$  before and after 2000 potential cycles in  $\text{O}_2$ -saturated 0.1 M KOH solution. The rotation rate is 1600 rpm.