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

Interlayer confinement synthesis of Ir nanodots/dual carbon as an electrocatalyst for overall water splitting†

Yaru Li, Yu-Quan Zhu, Weili Xin, Song Hong, Xiaoying Zhao, Hong Yan* and Sailong Xu*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

*Corresponding authors. E-mails: xusl@mail.buct.edu.cn (S.X.); yanhong@mail.buct.edu.cn (H.Y.)

Figure S1

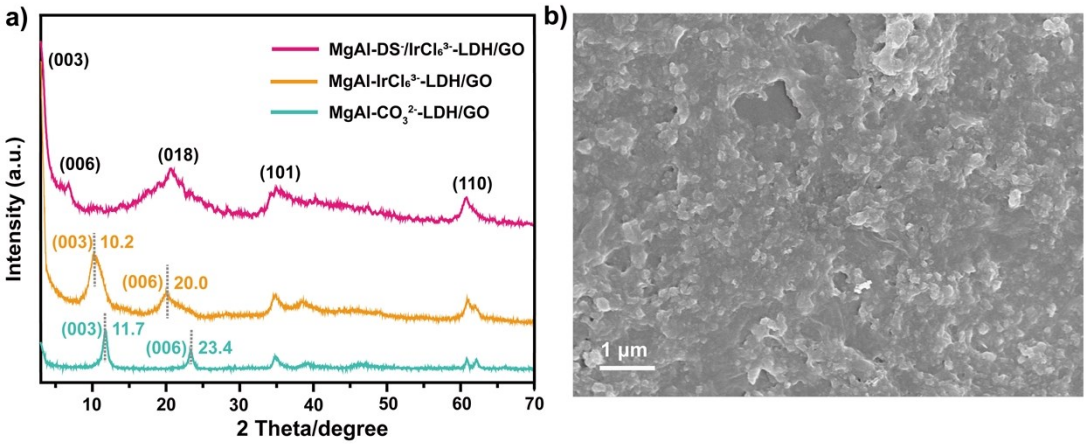

Fig. S1 (a) Comparison of XRD patterns between the MgAl-DS^-/$IrCl_6^{3-}$-LDH/GO precursor, MgAl-$IrCl_6^{3-}$-LDH/GO, and MgAl-CO_3^{2-}-LDH/GO; (b) SEM images of the MgAl-DS^-/$IrCl_6^{3-}$-LDH/GO precursor.

Figure S2

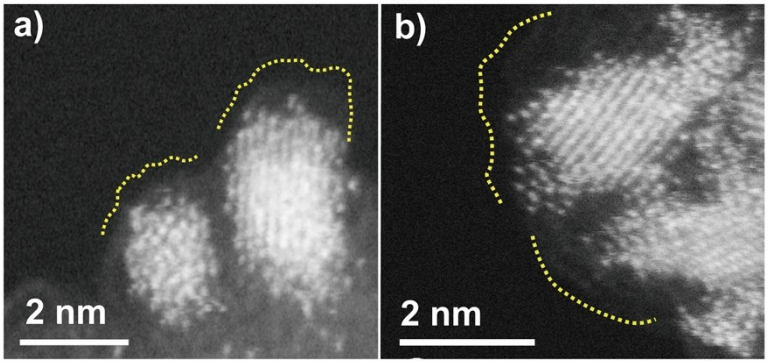

Fig. S2 High-resolution HADDF STEM of Ir@S-C/rGO before test.

Figure S3

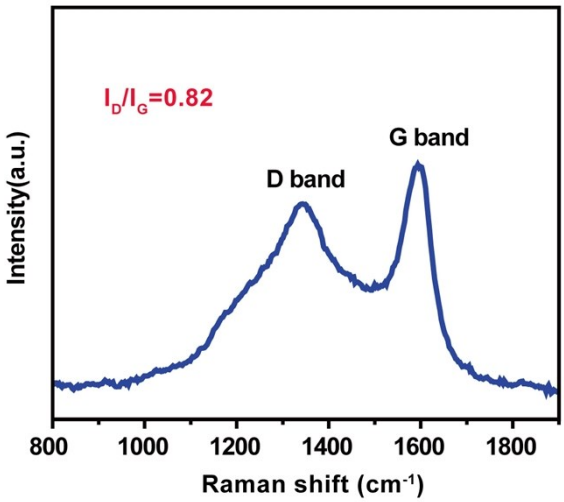

Fig. S3 Raman spectrum of the Ir@S-C/rGO composite before test.

Figure S4

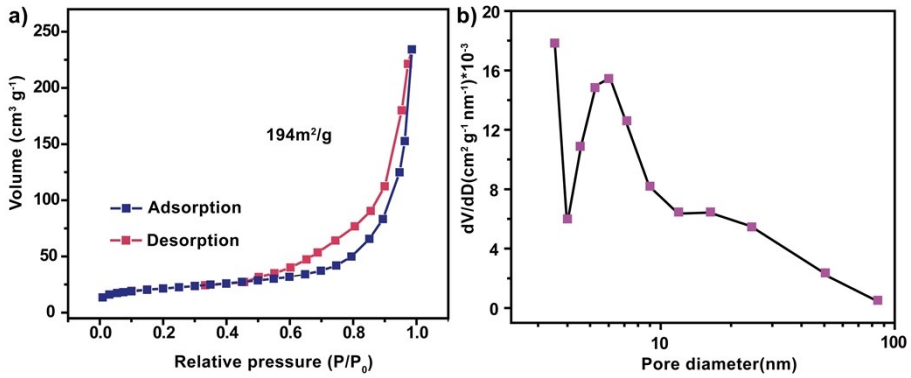

Fig. S4 (a) N_2 adsorption/desorption isotherms and (b) the pore size distribution of the Ir@S-C/rGO composite before test.

Figure S5

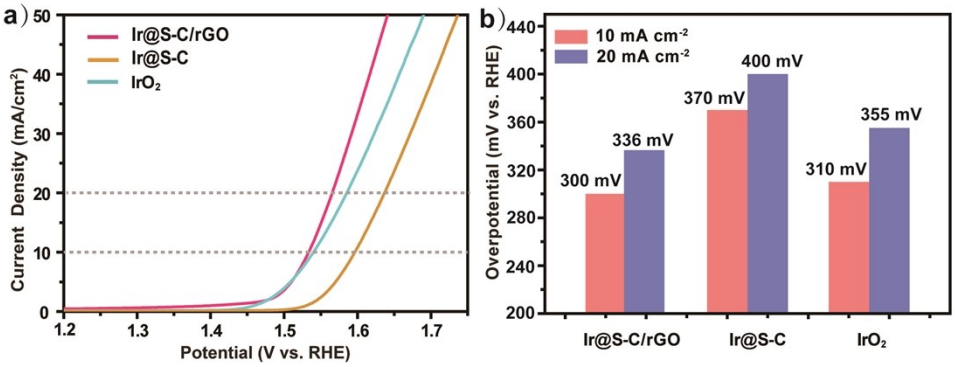

Fig. S5 Electrocatalytic performance for the OER. (a) LSV curves without iR correction, (b) the overpotentials at 10 mA cm^{-2} and 20 mA cm^{-2} that were obtained without iR correction.

In the case of no iR correction for the OER, Fig. S5 shows that the Ir@S-C/rGO electrocatalyst requires an overpotential of 300 mV at a current density of 10 mA cm^{-2}. The overpotential is much lower than those of the commercial IrO_2 (310 mV) and Ir@S-C (370 mV). At a current density of 20 mA cm^{-2}, the Ir@S-C/rGO catalyst requires 336 mV, which is lower than those of commercial IrO_2 (355 mV) and Ir@S-C (400 mV) at the same current density.

Figure S6

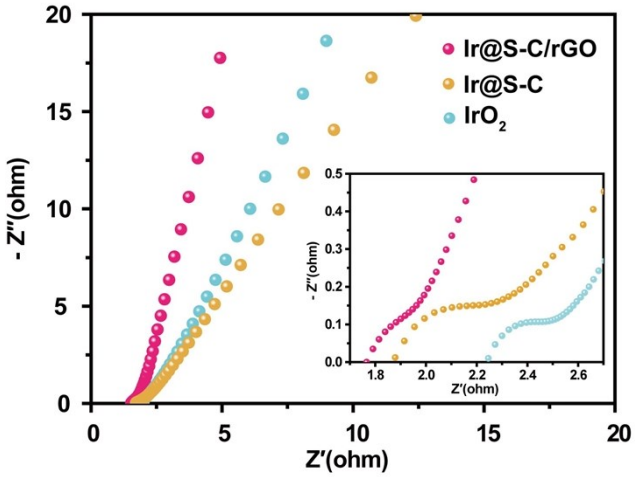

Fig. S6 Electrochemical impedance spectra of Ir@S-C/rGO, Ir@S-C, and IrO_2 for the OER.

Figure S7

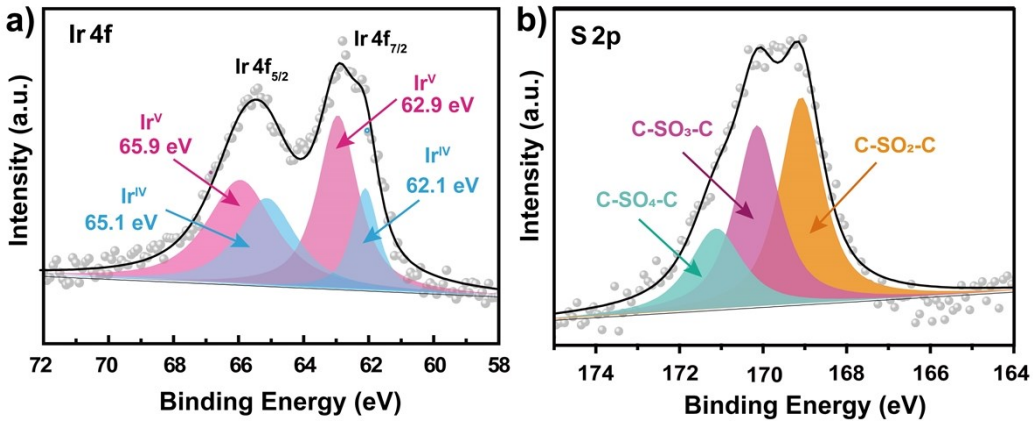

Fig. S7 XPS spectra of the Ir@S-C/rGO composite after the OER testing: (a) Ir 4f and (b) S 2p.

Figure S8

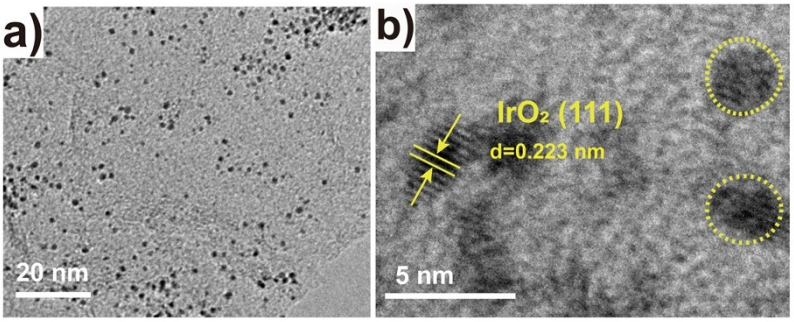

Fig. S8 (a) TEM and (b) HRTEM images of the Ir@S-C/rGO composite after the OER testing.

Figure S9

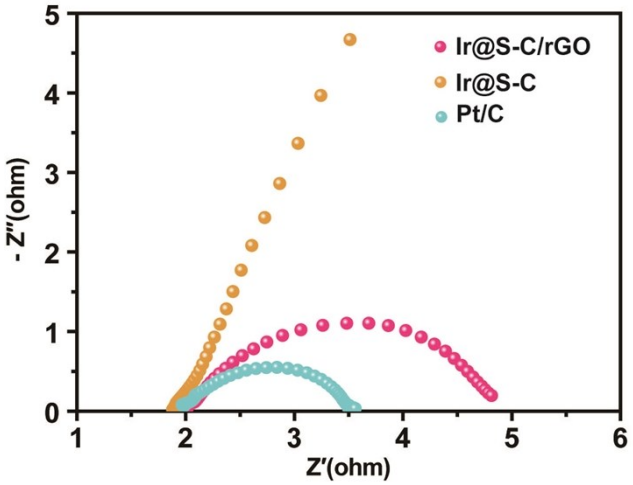

Fig. S9 Electrochemical impedance spectra of Ir@S-C/rGO, Ir@S-C, and Pt/C for the HER.

Figure S10

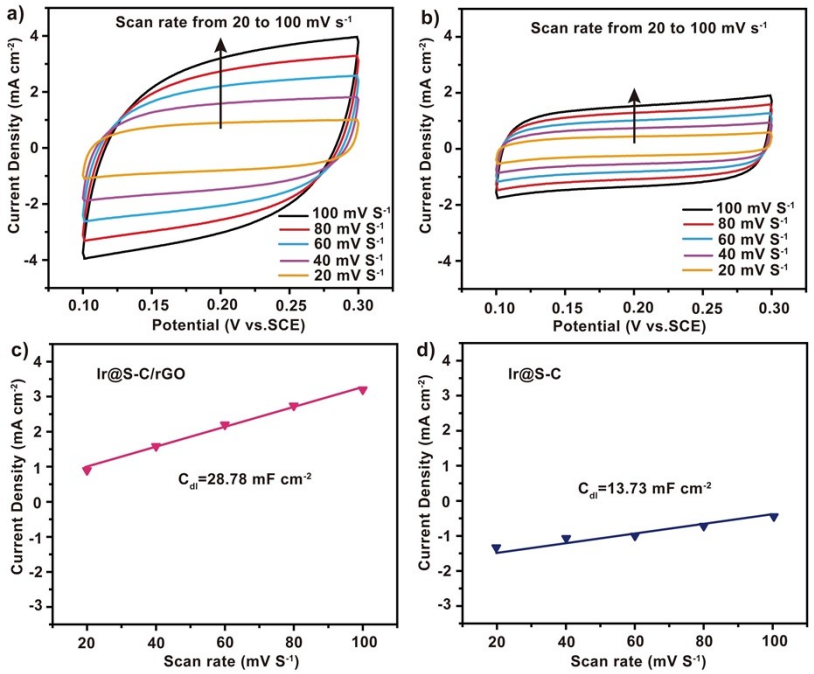

Fig. S10 (a, b) Cyclic voltammograms (CVs) and (c, d) the current densities at 0.2 V vs SCE at the scan rates from 20 to 100 mV/s: (a, c) Ir@S-C/rGO, (b, d) Ir@S-C.

Figure S11

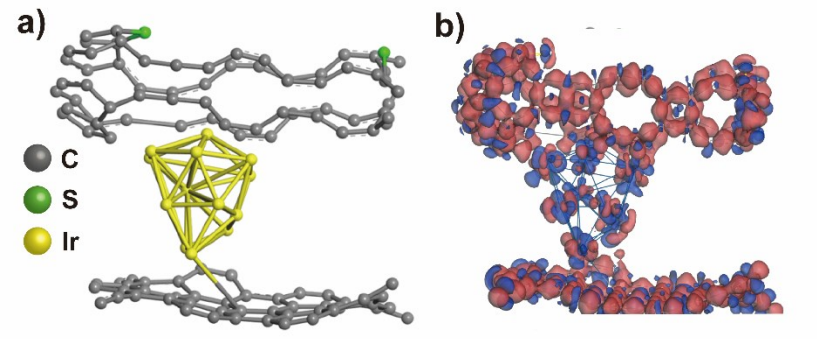

Fig. S11 (a) The optimized structure of Ir@S-C/rGO from the side views of *xz* plane; (b) The electronic density difference of Ir@S-C/rGO from the side views of *xz* plane. The red region presented the electrons accumulation, and the blue region indicated the positive charges (isovalue = 0.1 e $Å^{-3}$)

The simulation model of Ir@S-C/rGO was consisted of reduced graphene oxide (rGO), Ir_{13} cluster and sulfur-doped amorphous carbon (S-C) (as shown in Fig. S11a). The structural parameters were derived from the experimental data.[1,2] The model of the graphene without hydroxyl groups or functional groups containing oxygen atoms were built as the substrate. And the model of S-C was constructed by replacing two carbon atoms with two sulfur atoms. The optimized structures were presented (as shown in Fig. S11a). In addition, the electronic density difference was calculated to illustrate the charge redistribution after bonding (Fig. S11b).

References:

1. M. Guo, Y. Liu, S. Dong, X. Jiao, T. Wang and D. Chen, *ChemSusChem*, 2018, **11**, 4150-4155.
2. X. Zhu, X. Zhang, B. Huang, J. Li and E. Wang, *J. Mater. Chem. A*, 2019, **7**, 18304-18310.

Table S1

Comparison of OER performance at 10 mA cm^{-2} between the Ir@S-C/rGO composite and the Ir based electrocatalysts reported previously (in 1.0 M KOH solution).

Catalysts	Ir content (wt%)	Overpotential (mV)	Tafel (mv dec^{-1})	References
Ir@Co/NC	2.2	260	163	*Angew. Chem. Int. Ed.* 2019, **58**, 11868
Ir@N-G	3.2	270	60	*Nano Energy* 2019, **62**, 117
Ir@G	5.8	329	90	
NiIr/rGO	4.9	272	56	*J. Energy Chem.* 2020, **49**, 166
IrOOH/Ir	7.2	266	29	*Natl. Sci. Rev.* 2020, in press (DOI: 10.1093/nsr/nwaa058)
Co@Ir/NC	7.5	280	74	*ACS Sustain. Chem .Eng.* 2018, **6**, 5105
IrO_2	56.0	349	79	
Ir/MoS_2	9.8	330	44	*ACS Energy Lett.* 2018, **4**, 368
$Ir_{18wt\%}$/NiO	18.0	215	38	*J. Am. Chem. Soc.* 2020, **16**, 7425–7433
Ir/C	20.0	284	87	*ACS Energy Lett.* 2019, **4**, 1823
NiVIr-LDH	26.4	203	54	
Ir/CN	-	265	35	*ACS Appl. Mater. Interfaces* 2018, **10**, 22340
Ir/vertical GO	-	320	52	*J. Mater. Chem. A.* 2019, **7**, 20590.
Ir@S-C/rGO	6.2	280	54	**This work**

Table S2

Comparison of HER performance at 10 mA cm^{-2} between the Ir@S-C/rGO composite and the Ir based electrocatalysts reported previously (in 1.0 M KOH solution).

Catalysts	Ir content (wt%)	Overpotential (mV)	Tafel (mv dec^{-1})	References
Ir@Co/NC	2.2	55	119	*Angew. Chem. Int. Ed. Eng*. 2019, **58**, 11868
Ir@N-G	3.2	43	35	*Nano Energy*, 2019, **62**, 117
Ir@G	5.8	150	85	
NiIr/rGO	4.9	33	64	*J. Energy Chem.*, 2020, **49**, 166.
IrOOH/Ir	7.2	50	29	*Natl. Sci. Rev.* 2020, in press (DOI: 10.1093/nsr/nwaa058)
Co@Ir/NC	7.5	121	98	*ACS Sustainable Chem. Eng.* 2018, **6**, 5105
Ir/MoS_2	9.8	44	32	*ACS Energy Lett.* 2018, **4**, 368
Ir@3DCON	20.5	13.5	29	*Adv. Mater.* 2018, **30**, e1805606
Ir NP/C	23.0	29	42	*Adv. Energy Mater.* 2018, **8**, 1801698
Ir/C	20.0	28	32	*ACS Energy Lett.* 2019, **4**, 1823
NiVIr-LDH	26.4	41	36	
Ir/CN	-	12	28	*ACS Appl. Mater. Interfaces* 2018, **10**, 22340
Ir/vertical GO	-	17	29	*J. Mater. Chem. A* 2019, **7**, 20590
Ir@S-C/rGO	6.2	20	21	**This work**

Table S3

Comparison of overall-water-splitting performance at 10 mA cm^{-2} between the Ir@S-C/rGO composite and the Ir based electrocatalysts reported previously (in 1.0 M KOH solution).

Catalysts	Ir content (wt%)	Overall voltage (V)	Durability (h)	References
Ir@Co/NC	2.2	1.60	5	*Angew. Chem. Int. Ed.* 2019, **58**, 11868.
NiIr/rGO	4.9	1.55	24	*J. Energy Chem.* 2020, **49**, 166.
Ir/CN	-	1.51	2	*ACS Appl. Mater. Interfaces* 2018, **10**, 22340.
Ir@N-G	3.2	1.51	40	*Nano Energy* 2019, **62**, 117.
Ir@G	5.8	1.59	40	
IrOOH/Ir	7.2	1.58	10	*Natl. Sci. Rev.* 2020, in press (DOI: 10.1093/nsr/nwaa058)
Co@Ir/NC	7.5	1.51	12	*ACS Sustain. Chem. Eng.* 2018, **6**, 5105.
Ir/MoS_2	9.8	1.57	12	*ACS Energy Lett.* 2018, **4**, 368.
NiVIr-LDH	26.4	1.49	15	*ACS Energy Lett.* 2019, **4**, 1823.
Ir/C-Pt/C	20.0	1.60	16	
Ir/vertical GO	-	1.57	24	*J. Mater. Chem. A* 2019, **7**, 20590.
Ir@S-C/rGO	6.2	1.51	24	**This work**