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Supporting information

Fast Charge Transfer between Iodide Ions and Delocalized Electron System on the Graphite Surface for Boosting Hydrogen Production

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Figure S1. (a) All calculated most stable geometric structures of graphite. (b) The charge analysis between graphite and $I_2 + I^- + 2e^-$ and then (c) formation of $I_3^- + 2e^-$.



Figure S2. (a) LSV curves and (b) corresponding Tafel slopes for different carbonaceous materials.



Figure S3. (a) LSV curves of CFP for IOR in the electrolytes of $0.1M \text{ HClO}_4$, $0.25M \text{ LiClO}_4$ and 1M KOH. (b) LSV curves of CFP for IOR at different molar concentrations of NaI dissolved in 0.1 M HClO_4 .

Several controlled reactions have been carried out to optimize the reaction conditions. First, to study the IOR activity of CFP in different electrolytes, the electrochemical reaction was operated in 0.5 M HClO₄, 1.0 M KOH, and 0.25 M LiClO₄ electrolyte with dissolving 1.0 M NaI in each electrolyte. In **Figure S3 (a)**, it is found that CFP displays better IOR activity in acidic condition compared to neutral and basic conditions and the order of activity in terms of pH can be given as 0.5 M HClO₄ > 0.25 M LiClO₄ > 1.0 M KOH. Furthermore, the effect of concentration of iodide anion in 0.5 M HClO₄ was also investigated as shown in **Figure S3 (b)**. Among three different concentrations of NaI (0.1, 0.5 and 1.0 M), the optimum activity of CFP for IOR was found in the concentration of 1.0 M NaI in comparison with other concentrations.



Figure S4. (a) LSV curves of CFP with different surface area for IOR. (b) Chronopotentiometry curves of CFP with different surface area at a current density of 10 mA/cm².



Figure S5. (a) XRD patterns and (b) Raman spectra of CFP before and after reaction (18h). (c) SEM image of CFP after reaction (18h).

To further confirm state and structural stability of CFP after the reactions, post-reaction characterizations including XRD, Raman and SEM were carried out as shown in the **Figure S4**. The characteristic peak of carbon at 26° (2θ) in XRD (**Figure S4 (a)**) and characteristic peaks at 1350 and 1580 cm⁻¹ in Raman spectrum (**Figure S4 (b)**) remains unchanged after the reaction signifying the excellent stability of the CFP towards IOR electrocatalysis. SEM images of CFP after the reaction (**Figure S4 (c)**) also show that unaltered structures of carbon fibers further substantiating the stability of the CFP.



Figure S6. LSV curves of CFP as electrocatalysts for IOR and OER in three-electrode system.



Figure S7. LSV curves of the Pt wire as electrocatalysts for HER in acid electrolyte measured by three-electrode system.



Figure S8. A representative image of a new cell with a distance of 4 cm between the Pt wire and the CFP electrode.



Figure S9. The LSV curves of the electrolyzer when two electrodes are separated apart with a distance of 25 μ m, 0.5 cm, 4cm and 17 cm.



Figure S10. Amount of iodine calculated and experimentally detected by titration. Analysis of the liquid product from the anodic compartment by iodometric titration also shows a good Faradic efficiency of \sim 97% for iodine production.

Anode Catalyst	Solution	Membrane	Current density	Tafel	Ref.
		separated		slope	
CFP (this work)	Anode: 0.1M HClO ₄	Y	0.59V /10mAcm ⁻²	47.78	
	+1 M NaI			mV dec-1	
	Cathode: 0.5M				
	H_2SO_4				
RuTiO-550	Anode: 0.1 M	Y	1.01V /10mAcm ⁻²	-	Applied Catalysis B:
	HClO ₄ +0.1 M NaI				Environmental, 2022: p.
	Cathode: 0.5M				121608.
	H_2SO_4				
RuSn SAO	Anode: 0.1 M	Y	1.07V /10mAcm ⁻²	40	ACS Sustainable Chem. Eng.

Table S1. The comparison of electrochemical performance in various catalysts-electrolysis systems, including IOR, UOR (urea oxidation reaction) and CER (chlorine evolution reaction).

	HClO ₄ +0.1 M NaI			mV dec-1	2021 9 (26), 8803-8812
	Cathode: 0.5M				
	H_2SO_4				
CuCl/rGO	Anode: 1M	Y	0.83V /10mAcm ⁻²	-	Chem. Commun., 2018 , 54,
	KOH+0.5M Urea				2603
	Cathode: 0.5M				
	H_2SO_4				
NiCoP NW/NF	Anode: 1M KOH,	Y	0.95V /10mAcm ⁻²	-	ACS Sustainable Chem. Eng.
	Cathode: 0.5M				2021 9 (48), 16163-16171
	H_2SO_4				
Ru-RuO ₂ -CNT	Anode: 1.0M KOH	Y	0.73V	-	Nano Energy 2019, 61, 576.
	Cathode:		/10mAcm ⁻²		
	$0.5 \mathrm{MH}_2 \mathrm{SO}_4$				
NiF ₃ /Ni ₂ P @CC	1M KOH+ 0.33M	Ν	1.36V /10mAcm ⁻²	33	Chem. Eng. J. 2022, 427,
	Urea			mV dec ⁻¹	130865.
NiCoNx@C/Ni/	1M KOH+ 0.5M	Ν	0.67V /10mAcm ⁻²	76	Mater. Today Energy 2022,
NF	glucose			mV dec ⁻¹	100948.
Pt ₁ /CNT(Cl)-	0.1 M HClO ₄ +1 M	Ν	1.39 /10mAcm ⁻²	37	ACS Catalysis 2021, 11 (19),
800	NaCl			mV dec ⁻¹	12232.
Ni@C-250	1M KOH+0.5M	Ν	1.5V /100 mAcm ⁻²	43	Catal. Sci. Technol., 2021,
	Urea			mV dec ⁻¹	11, 2480
Au@AuIr ₂	$0.5M H_2 SO_4$	Ν	1.53V /300 mAcm ⁻²	58.3	J. Am. Chem. Soc. 2021, 143,
				mV dec ⁻¹	12, 4639–4645
Pt1/CNT	0.1 M HClO ₄ +1 M	Ν	1.4V /10mAcm ⁻²	38	Nature Commun. 2020, 11
	NaCl			mV dec ⁻¹	(1), 412
Ni–Co(OH) ₂	1M KOH+ 0.33 M	N	1.36V /10mAcm ⁻²	47	Nanoscale Adv., 2021 , 3 (2),
	KI			mV dec ⁻¹	604.