

## Supporting Information

### **La-doped NiWO<sub>4</sub> coupled with reduced graphene oxide for effective electrochemical determination of diphenylamine**

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### Calculation of EASA

The EASA of the electrode was calculated by the Randles-Sevick equation:

$$I_{pa} = (2.69 \times 10^5) n^{3/2} ACD^{1/2} \nu^{1/2}$$

where "A" is the active surface area of the electrode, "I<sub>pa</sub>" is the peak current value, "D" is the diffusion coefficient of the electrolyte, "C" is the concentration of ferricyanide solution, "n" is the number of electrons involved in the redox reaction, and "ν" represents the scan rate (V s<sup>-1</sup>).

The current value measured of CV curves was normalized by EASA according to the equation: IEASA = I/EASA, in which I is the current value measured in CV curves.

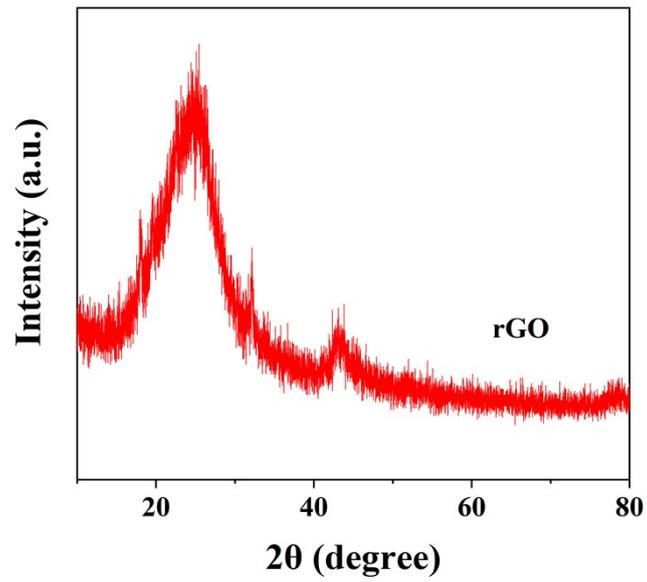
### Calculation of LOD and sensitivity

$$LOD = 3 S/q$$

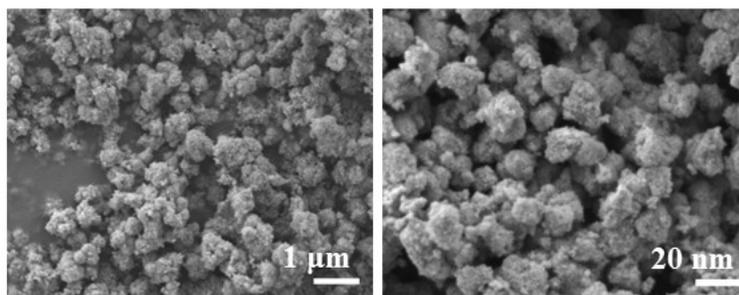
where 'q' is the slope value (0.0477 μA μM<sup>-1</sup>) from the DPV calibration plot, and 'S' is the standard deviation obtained from the ten measurements of the blank signal (0.0000927 μA)

$$\text{sensitivity} = EASA/q$$

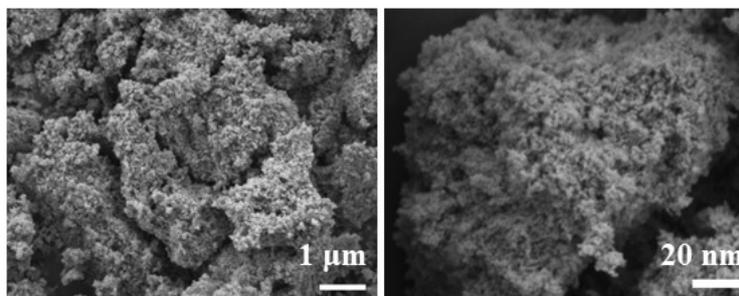
where 'q' is the slope value (0.0477 μA μM<sup>-1</sup>) from the DPV calibration plot, and 'EASA' is the active surface area of the electrode.



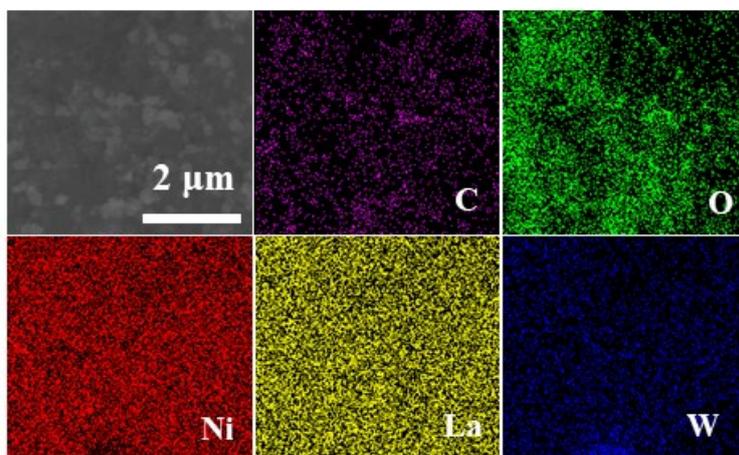
**Fig. S1.** The XRD pattern of GO after ultrasound.



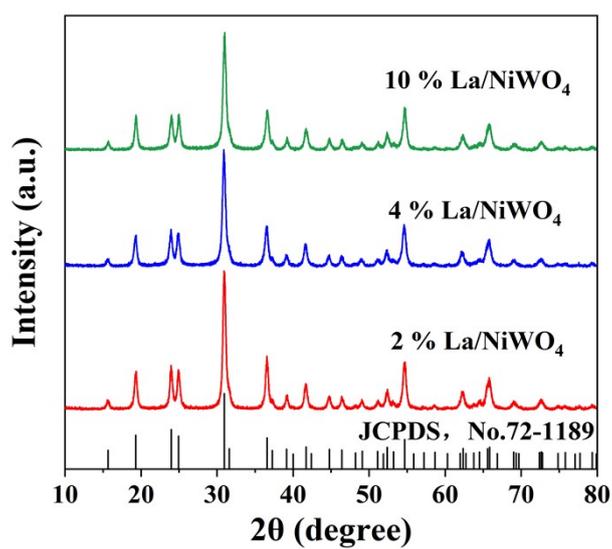
**Fig. S2.** SEM images of La/NiWO<sub>4</sub>.



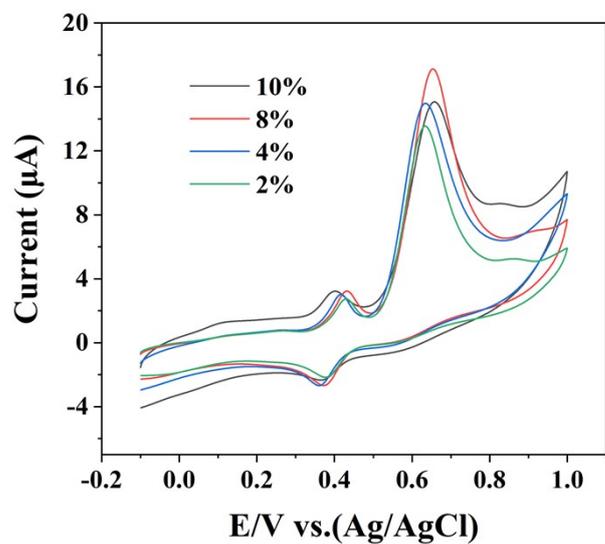
**Fig. S3.** SEM images of NiWO<sub>4</sub>.



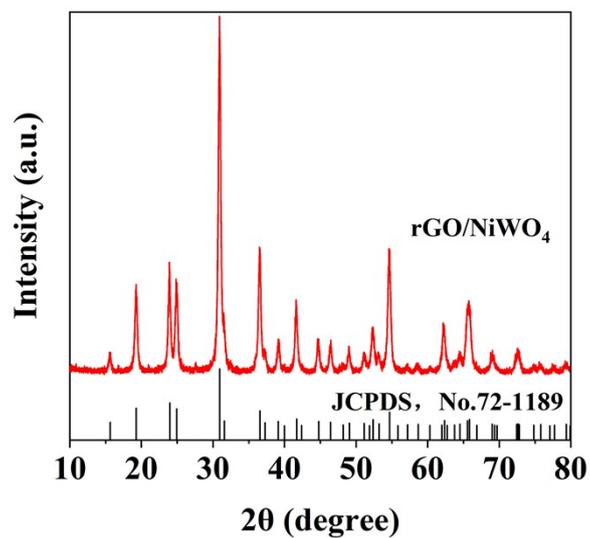
**Fig. S4.** Elemental mapping images of C, O, Ni, La and W elements of rGO/La/NiWO<sub>4</sub> obtained by SEM.



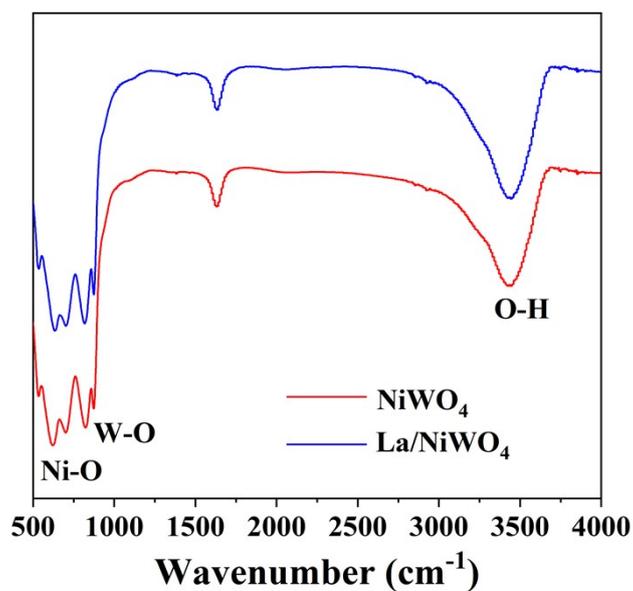
**Fig. S5.** XRD patterns of rGO/La/NiWO<sub>4</sub> with different La doping ratios.



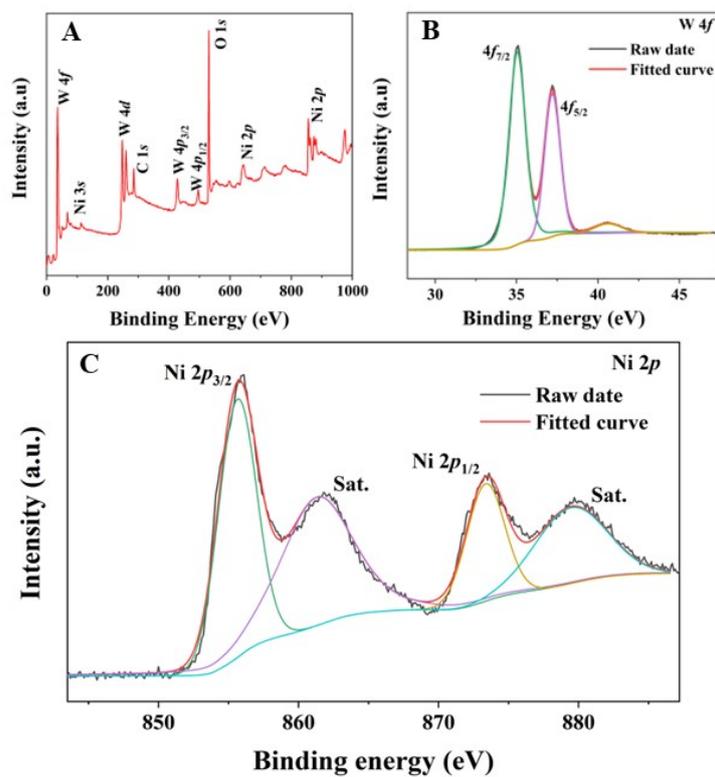
**Fig. S6.** CV curves of different lanthanum doping ratios with presences of DPA (100  $\mu M$ ) in saturated 0.1M PBS (pH 7) at scan rate of 50  $mVs^{-1}$ .



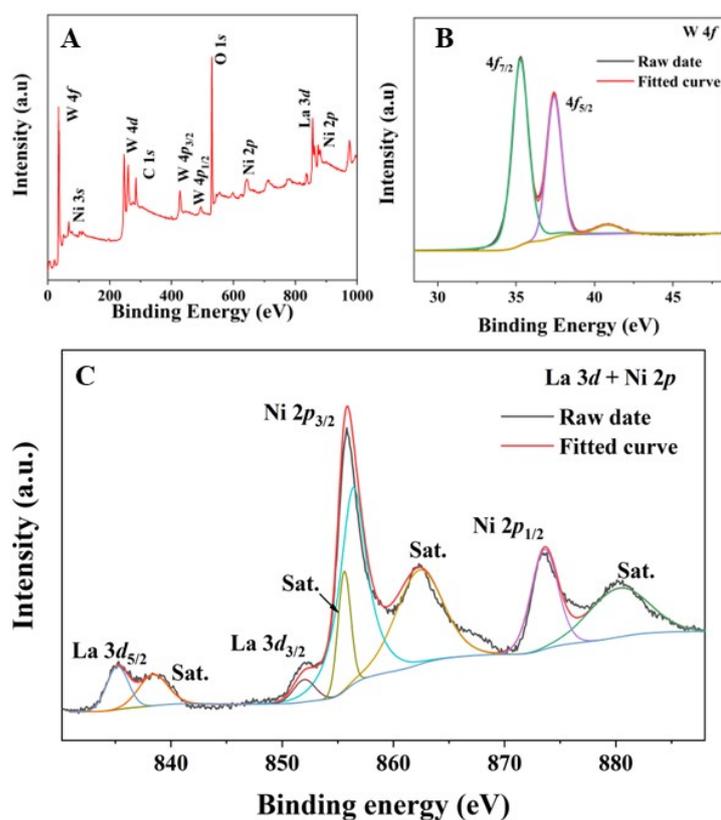
**Fig. S7.** The XRD pattern of rGO/NiWO<sub>4</sub>.



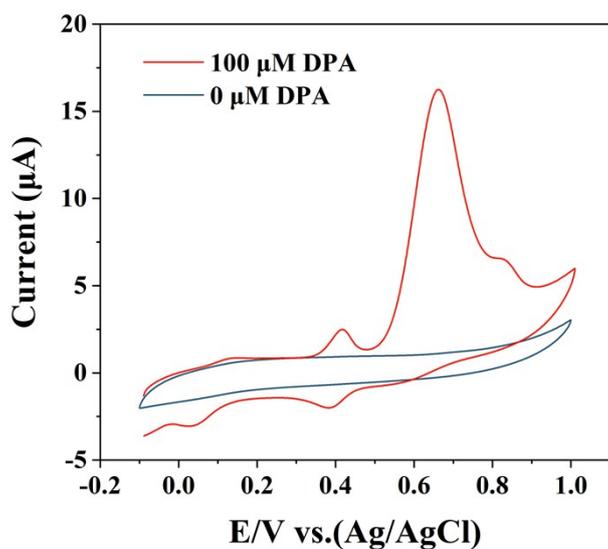
**Fig. S8.** FTIR spectra of NiWO<sub>4</sub> and La/NiWO<sub>4</sub>.



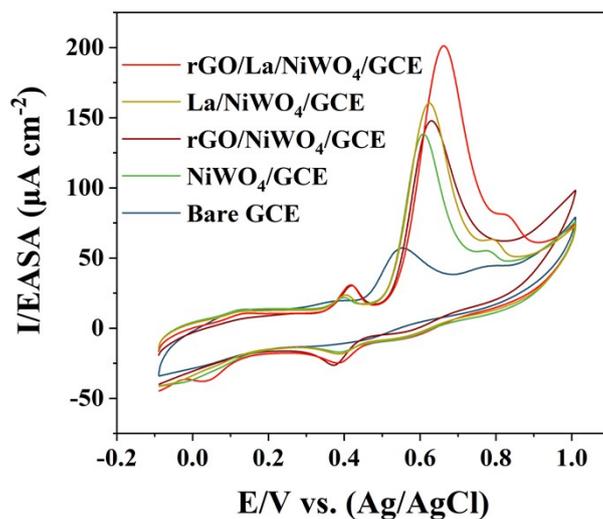
**Fig. S9.** (A) The XPS survey scan, (B) W 4f XPS spectrum and (C) Ni 2p XPS spectrum of pure NiWO<sub>4</sub>.



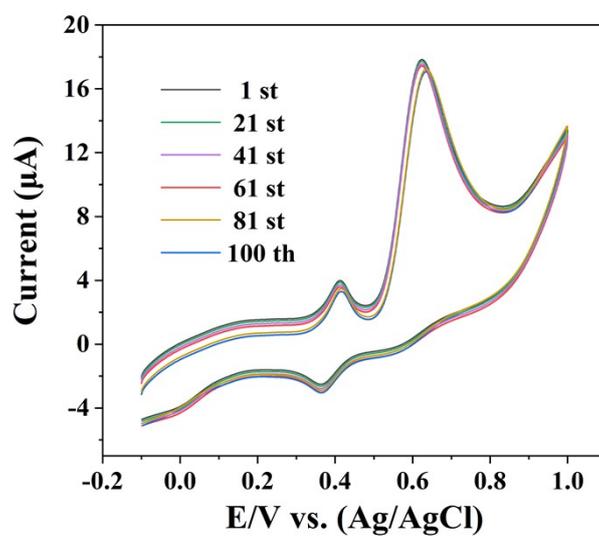
**Fig. S10.** (A) The XPS survey scan, (B) W 4f XPS spectrum and (C) La 3d + Ni 2p XPS spectrum of La/NiWO<sub>4</sub>.



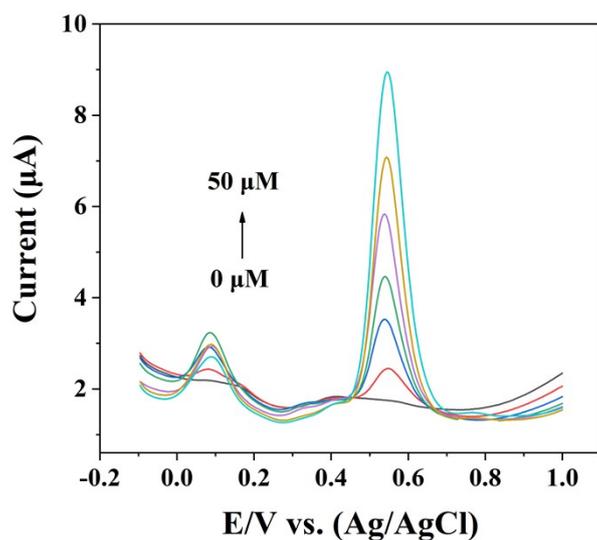
**Fig. S11.** CV curves of rGO/La/NiWO<sub>4</sub>/GCE in 0 and 100 μM DPA in saturated 0.1M PBS at a scan rate of 50 mV s<sup>-1</sup>.



**Fig. S12.** EASA normalized CV curves of bare GCE, NiWO<sub>4</sub>/GCE, rGO/NiWO<sub>4</sub>/GCE, La/NiWO<sub>4</sub>/GCE and rGO/La/NiWO<sub>4</sub>/GCE.



**Fig. S13.** The 1st, 21st, 61st, 81st and 100th CV curves of the cycling performance test of rGO/La/NiWO<sub>4</sub>/GCE in 100 μM DPA.



**Fig. S14.** DPV curves of real sample analysis in spiked apple juice.

**Table S1.** Determination of DPA in the spiked apple juice sample.

Real sample	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)	RSD (%)*
Apple juice	0	Not found	Not found	Not found
	5	4.96	99.20	0.57
	10	10.16	101.60	1.12
	20	19.83	99.15	0.60
	30	29.74	99.13	0.62
	40	39.86	99.65	0.25
	50	50.41	100.82	0.58

\*Measurement of 3 experiment (n=3).