Supporting information

A simple strategy for carboxylated MWNTs as metal-free electrosensor to anchoring C=N group on RhB

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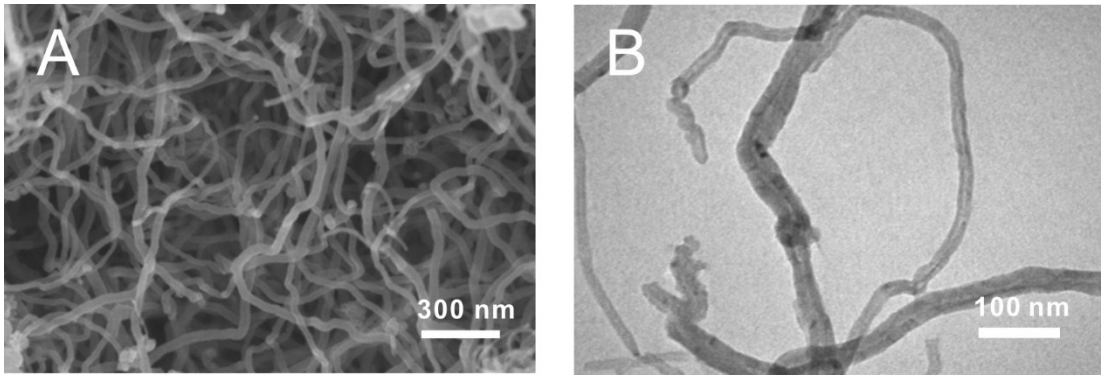

Fig. S1 The SEM (A) and TEM (B) images of MWNTs-COOH.

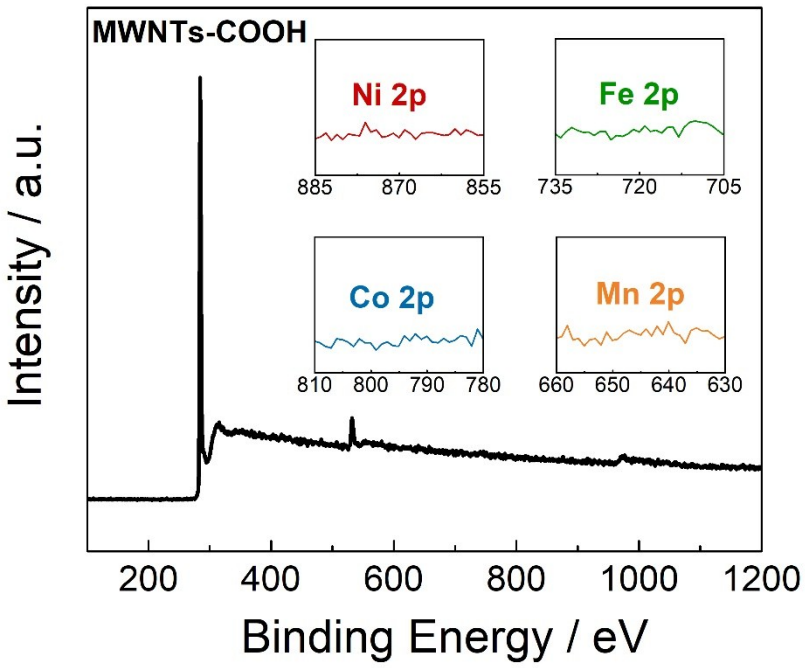

Fig.S2. The high resolution XPS survey spectrum of the MWNTs-COOH.

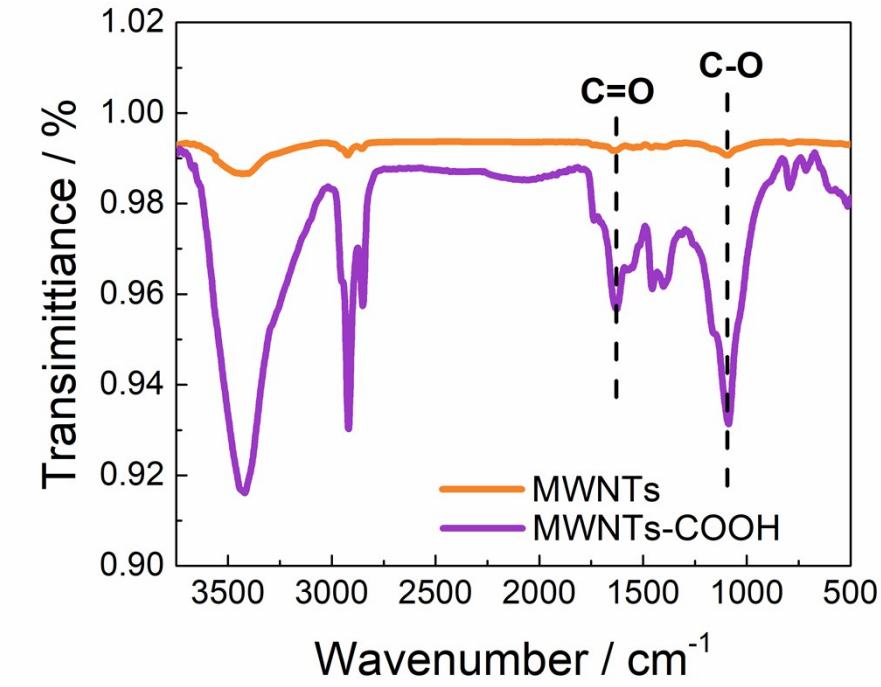

Fig. S3. FT-IR spectrums of MWNTs and MWNTs-COOH, and the image shows the characteristic absorption of C=O and C-O.

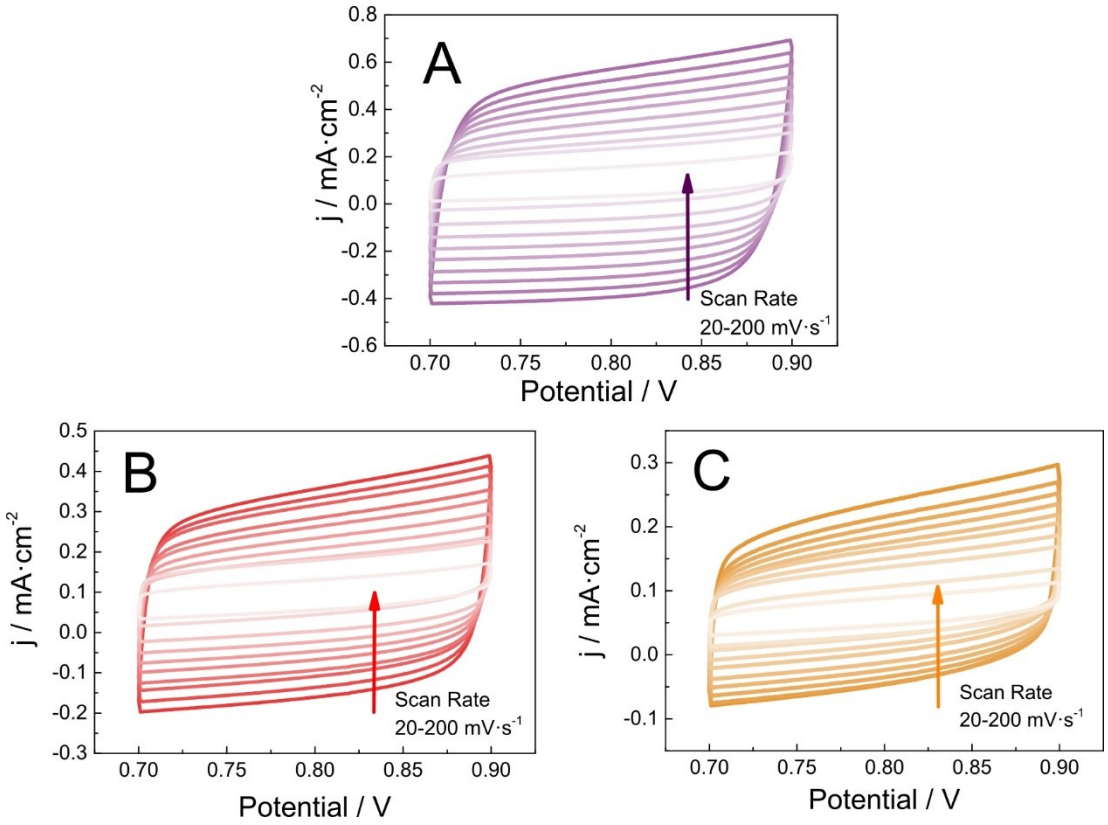

Fig. S4. Electrochemical surface area (ECSA) tests of MWNTs-COOH, o-MWNTs and raw MWNTs in 0.1 M PBS (pH= 5). Cyclic voltammetry curves of MWNTs-COOH (A), o-MWNTs (B) and raw MWNTs (C) with different scanning rates from 20 to 200 mV s^{-1}.

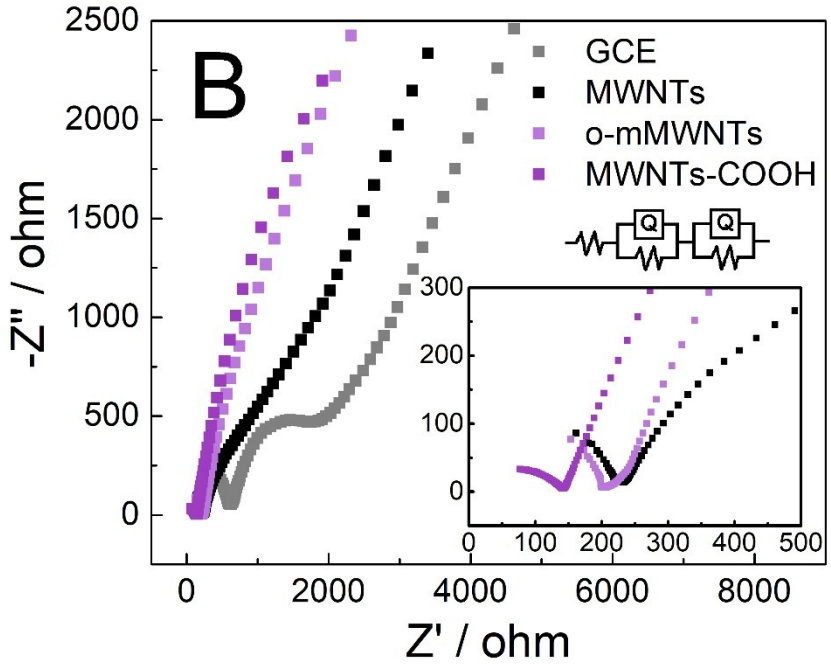

Fig. S5. EIS plots of bare GCE, MWNTs, o-MWNTs and MWNTs-COOH in 0.1 M KCl containing 1.0 mM $[Fe(CN)_6]^{4-/3-}$ with a frequency range from 0.1 to 10^6 Hz. The equivalent circuit was stimulated in the inset.

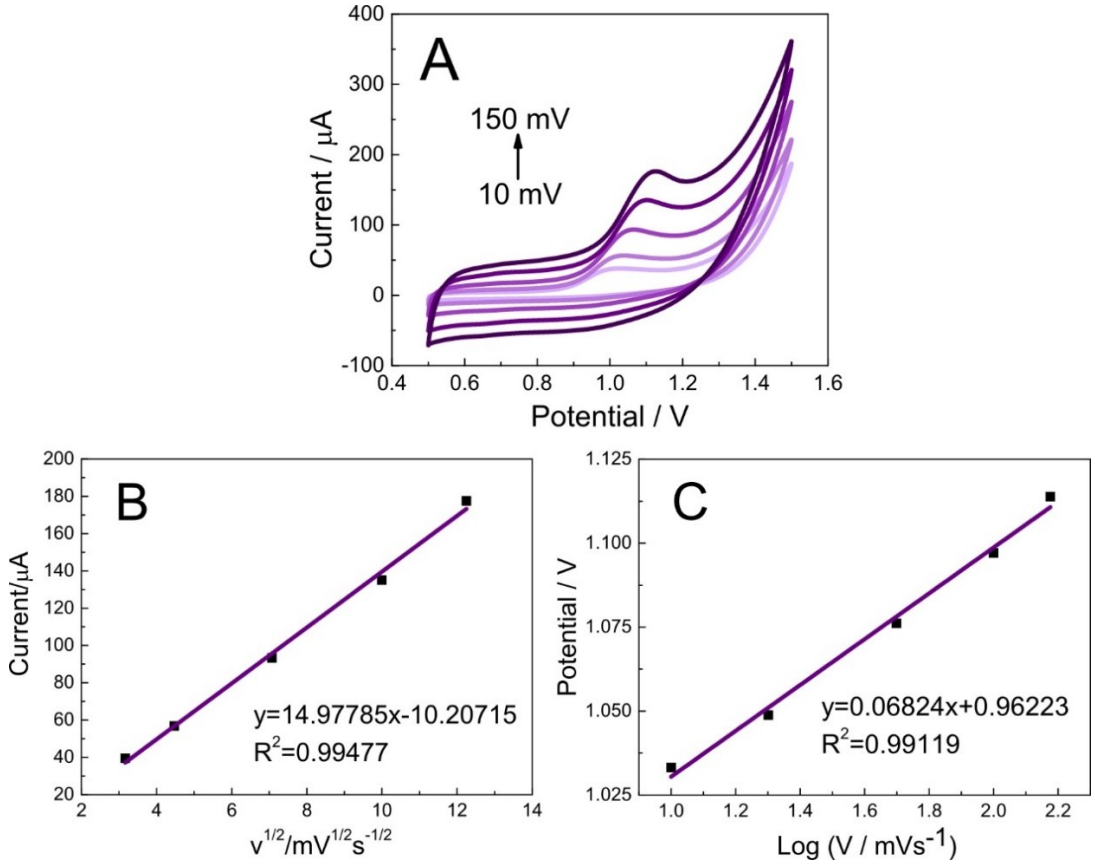

Fig. S6. (A) CVs of the MWNTs-COOH/GCE in 0.1 M PBS (pH=5) including 0.5mM RhB solution at different scan rates of 10, 20, 50, 100 and 150 mV s^{-1}; (B) The plots of peak current versus the square root of scan rate for RhB; (C) Plots of reduction peak potential vs. log ν for RhB.

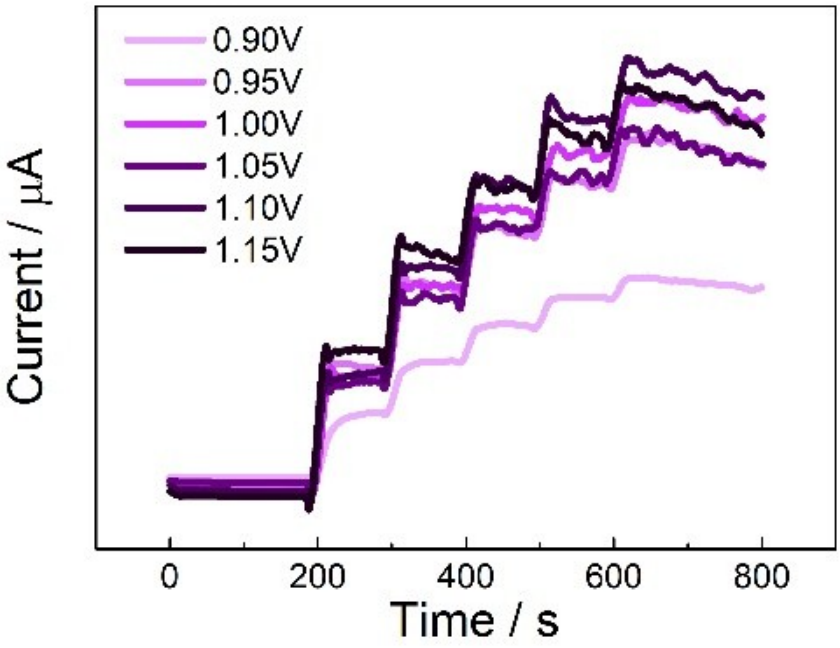

Fig. S7. Amperometric responses of MWNTs-COOH modified GCE for RhB at different potentials (0.90 to 1.15 V).

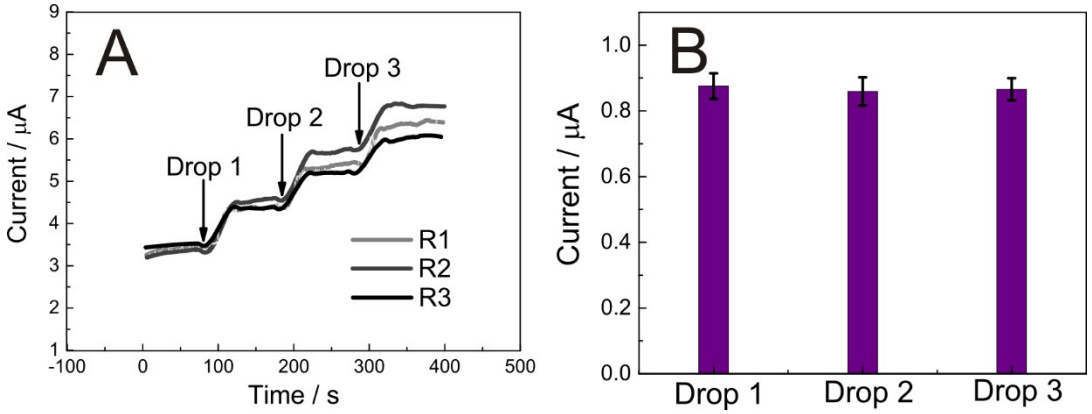

Fig. S8. (A)The reproducibility investigation of 3 amperometric experiments (R1–R3) with 3 successive dropwise addition of 5 μM RhB; (B) The reproducibility investigation of 3 reduplicative experiments (Drop 1- Drop 3) for amperometric determination of RhB at the applied potential of 1.0V.

Table S1. ICP-AES detection of metal impurities in MWNTs.

Materials	Fe/ppm	Co/ppm	Ni/ppm	Mn/ppm
MWNTs	0.868	0.015	0.250	0.044
MWNTs-COOH	0.135	0.008	0.074	0.001