A novel electrochemical sensor for the detection of enrofloxacin based on a 3D flower-like metal tungstate incorporated reduced graphene oxide nanocomposite.

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Instrumentation

Several techniques such as field emission scanning electron microscopy (FESEM, Hitachi S-3000 H), scanning electron microscopy (SEM, JSM-6510), and high-resolution transmission electron microscopy (HRTEM, H-7600, Hitachi, Japan) were used to capture the structural morphology of the as-synthesized composite. An energy-dispersive X-ray (EDX, HORIBA EMAX X-ACT, Sensor +24 V = 16 W, resolution at 5.9 k eV) connected to the HRTEM was used to investigate the chemical composition and elemental percentages. Powder x-ray diffraction (XRD, XPERT-PRO, PAN analytical B.V., The Netherlands) and the diffractometer with Cu Kα radiation (k = 1.54 Å) were used to investigate the crystallographic structure of all synthesized materials. The data of Raman spectrum was collected from the Micro-Raman spectrometer (Raman Dong Woo 500 I, Korea). FT-IR spectroscopy (Perkin-Elmer IR spectrometer), was used to inspected the synthesized nanocomposite functional groups. X-ray photoelectron spectroscopy was used to analyze the chemical and valence state of the composite (XPS, Thermo ESCALAB 250). Electrochemical impedance spectroscopy (EIS) was used to identify the materials, and electrochemical measurements were performed in the electrochemical workstation, such as cyclic voltammetry (CV CHI 1205a) and Amperometry (i-t) measurements were obtained with an analytical rotator with a working area of 0.21 cm^2 of rotating ring disk electrode (RRDE), platinum wire as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. All the experiments were performed triplicate.

Synthesis of graphene oxide (GO)

Firstly,150 mL of H_2SO_4, was added with 2 g of graphite powder in a 500 ml beaker, after an hour of stirring, 4 g of $NaNO_3$ were added. Then 8 g of $KMnO_4$ were added, and the solution was stirred at room temperature for 4 hours. The solution was then gradually diluted with 200 mL of water and stirred for 1 hour. After 20 mL of 30% of H_2O_2 was added to the solution so that the color of the mixture was changed from light brown to yellowish-green. The resulting mixture was centrifuged. The filtrate was then washed with DI water until it was pH neutral. At 80 °C, the mixture was dried for 24 hours. Finally, the powdered graphite oxide was obtained. Next 100 mg of obtained graphite oxide was ground to a smooth consistency. Then 100 mL of DI water was added, and the mixture was stirred for 30 minutes to make it homogeneous, after the homogeneous solution was sonicated for 30 minutes, the GO solution was obtained.

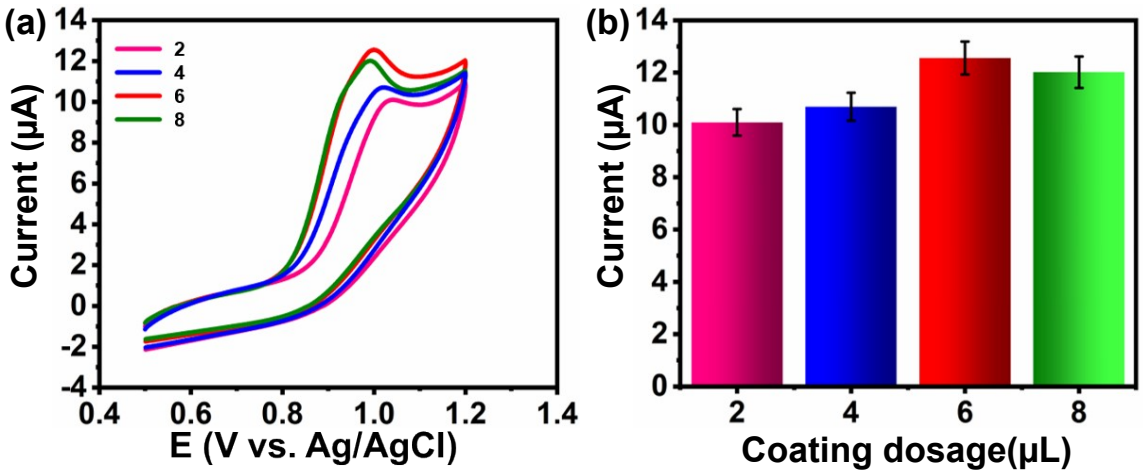

Fig. S1. (a) The CV current response of 50 μM of ENF at CW/RGO/GCE electrode with different amounts of catalyst (CW/RGO) coating on GCE (2, 4, 6, and 8 μL), and (b) the corresponding bar diagram for peak current versus the amount of catalyst CW/RGO loading on GCE (μL).

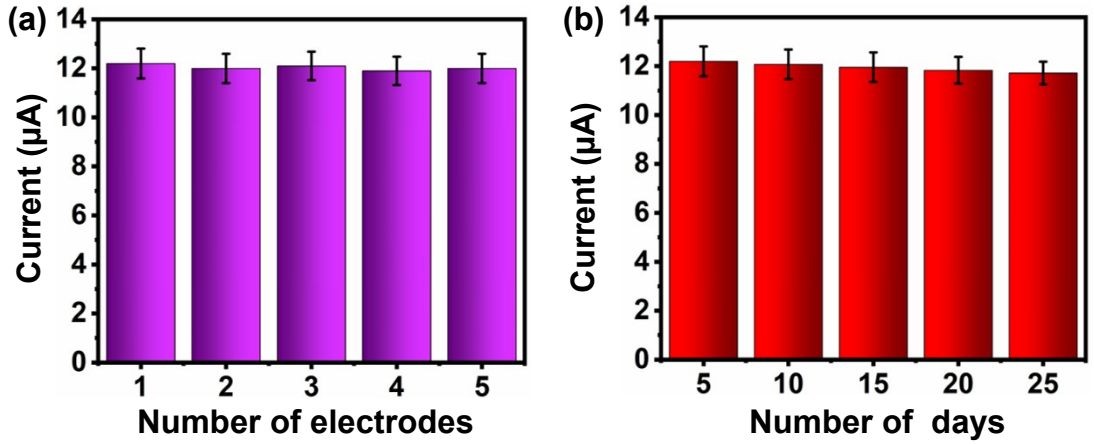

Fig. S2. (a) The bar diagram for the current response of 5 independent CW/RGO/GCE at 50 μM of ENF in 0.1 M PB (pH 7.0) at a scan rate of 50 mV s^{-1}, and (b) The bar diagram for the stability of the CW/RGO/GCE over 25 days.

Table. S1. Determination of ENF in milk sample and river water at CW/RGO/RRDE.

Real samples	Added (µM)	Found (µM)	Recovery (%)	RSD*
Milk	0	-	-	-
	5.0	4.98	99.6	3.6
	10.0	9.95	99.5	3.2
	15.0	14.90	99.3	3.5
River water	0	-	-	-
	5.0	4.97	99.4	3.2
	10.0	9.96	99.6	3.4
	15.0	14.87	99.1	3.1

*Measurement of three experiments (n= 3).