# Design strategy of rGO-HNT-AgNPs based hybrid nanocomposite with enhanced performance for electrochemical detection of 4-nitrophenol

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#### S.1.1: Preparation of rGO

The graphene oxide (GO) was prepared by following the improved Hummer's method. Briefly, 230 mL of concentrated H<sub>2</sub>SO<sub>4</sub> (98%) was added to a mixture of graphite powder (15 g), sodium nitrate (15 g) and KMnO<sub>4</sub> (45 g). The reaction was then heated at 0°C in an ice bath and stirred for 3 h. The mixture was then heated to 95°C temperature and added (460 mL) of H<sub>2</sub>O with continuous stirring for 15 min. Later, 75 mL of H<sub>2</sub>O<sub>2</sub> was introduced into the solution and allowed to stirring for more 1 h. After that, the mixture was centrifuged (5000 rpm for 30 min). The remaining solid material was then washed in succession with 450 mL of 37% HCl for 5 times, and 200 mL of double distilled water for 5 times until it reaches the pH at 6.5-7.0. For each wash, the mixture was centrifuged (5000 rpm for 15 min) and the remaining solid product was collected. Finally, the resulting material was kept in a refrigerator for 1 h at -20°C.<sup>1</sup> Finally, it was dried in vacuum dryer for 24 h to obtain graphene oxide. 0.4g of GO was dissolved in 400 ml of ddH<sub>2</sub>O, and ultrasonicated for 2 hr. The pH was adjusted to 10 with 1 M NaOH and stirred for 30 min. 2.8g of ascorbic acid was added and stirred for another 30 min. The flask was transferred to an oil bath and heated up to 95°C and stirred for 4 hrs. The product was precipitated down, the upper liquid layer was removed using a motor and the product was incubated at -20°C.<sup>2</sup>

### S.1.2. Preparation of silver nanoparticles

In the process of preparing silver nanoparticles, 20 mL of silver nitrated merged with ethanol solution is poured on a 50 mL jar attached with a magnetic stir bar. Continuing, the jar is maintained in 30°C water bath which is supervised by thermometer, to which 20 mL of PVP mixed ethanol solution is added with a rate of 0.667 mL/mins. Later, for another 90 mins the reaction mixture is heated continuously at 30°C. In this typical synthesis the mixture is changed in to pale yellow to light brown stable color. Then, silver nanoparticles are extracted from ethanol by dissolving it in a huge amount of acetone, which is later sonicated for 30 mins and centrifuged at 8000 rpm for 45 mins at 30°C. Finally, the mixture is extracted and re-dispersed in ethanol for further use.<sup>3</sup>



Fig.S.1. Structure of HNT.<sup>4</sup>



Fig.S2. (A-B) TEM & FESEM of reduced graphene oxide



**Fig.S3.** FESEM of (A) HNT. (B) Silver Nano particles. (C) rGO-HNT-AgNPs hybrid-composite. (D) EDX analysis and pie representation of rGO-HNT-AgNPs hybrid-composite.

#### S.2. Real sample preparation:

Silver pompfret fish is obtained from Zhnongshan fish market, Taipei, Taiwan. A weighed silver pompfret fish of about 6g is taken and been homogenized with 3.0 mL of 0.1 mol L-1 EDTA merged with 2.0 ML of pH 7.0 Mclvaine buffer solution by using a HY-4 homogenizer model instrument, at a speed of 5000 rpm for 30 mins. Later, the sample is shake vigorously for 10 mins with 3 mL of acetonitrile. Continuing, it is centrifuged at a speed of 5000 rpm for 10 mins, transferred to a clean polypropylene tube. Moreover, using 3.0 mL of aliquot acetonitrile fish residues were extracted. Later, both the extracts are combined further evaporated by drying in nitrogen atmosphere.<sup>5,6</sup> Obtained dried extract is re-formed in 200 µL of methanol, centrifuged in 5000 rpm for 5 mins and then stored for further use in 4<sup>0</sup>C dark area.



**Fig.S4.** Nyquist plot of various rGO-HNT-AgNPs hybrid-composites inset(a): Bare SPCE plot inset(b) diagram of Randles equivalent circuit model.



**Fig.S5.** CV curves of red-bare SPCE, green HNT-AgNPs, blue rGO-AgNPs in 0.05 M (pH7.0) at a scan rate of 50 mV s<sup>-1</sup>.



**Fig.S6.** Stability studies of rGO-HNT-AgNPs electrode consisting of 4-NP with the foremost possible interfering compounds a. catechol, b. hydroquinone, c. Resorcinol, d. Ascorbic acid, e. uric acid, f. Dopamine and g. nitrobenzene.

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