Unusual neutral pH assisted electrochemical polymerization of aniline on MWCNT modified electrode and its enhanced electro-analytical features†

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Experimental Section

Materials and Reagents. Multiwalled carbon nanotubes (MWCNTs; >90% carbon basis, outer diameter: 10–15 nm; inner diameter: 2–6 nm; length 0.1–10 μm), from Aldrich, USA. Ascorbic Acid, Aniline (distilled before use) were purchased from Rankem, Sd-fine chemicals respectively were used without further purification. Aqueous solutions were prepared using deionized and alkaline $KMnO_4$ double distilled (DD) water. Unless otherwise stated pH 7 PBS of 0.1 M ionic strength was used as a supporting electrolyte.

Apparatus and Characterization. All voltammetric measurements were carried out using CHI 660C electrochemical work station, USA with 10 mL working volume. The three electrode system consists of Gold (Au) electrode of 0.0707 cm^2 geometrical surface area and its chemically modified electrode (CME) as a working electrode, Ag/AgCl with 3 M KCl as a reference electrode and Pt wire as a counter electrode. The bio-analytical system (BAS, USA) polishing kit was used to polish the GCE surface. Raman spectra were recorded using Peakseeker Pro Raman Spectrometer (Agiltron, USA) using 532 nm laser probe. Fourier transform-infrared (FT-IR) spectra (4000−400 cm^{-1}) measurements were done using IR Affinity-1 fourier transform Infrared spectrometer (Shimadzu, Japan) as KBr pellet. A V-670 spectrometer (JASCO, Japan) was used for the UV-Vis measurements. Morphology and microstructure of the MWCNT and MWCNT@PANI$_{pH7}$

were studied using a JEOL JEM 2100 transmission electron microscopy (TEM). Flow Injection Analysis (FIA) was performed using a L-2130 pump delivery system (Hitachi, USA) interconnected to a CC5e flow cell cabinet (BASi, USA) and a Rheodyne (Cotati, CA, USA) Model 7125 sample injection valve (20 µL loop). A glassy carbon electrode (GCE) of surface area $0.0707 cm^2$ was used as an underlying electrode.

Preparation of chemically modified electrodes. Prior to the modification, the surface of the gold electrode was cleaned both mechanically (polished with 1µ alumina powder in the BAS polishing kit, cleaned with acetone and followed by DD water) and electrochemically (by performing cyclic voltammetry (CV) for ten cycles in the potential window -0.2 V to 1.2 V vs. Ag/AgCl in pH 7 PBS at scan rate (v) 50 mV/s). Then 5 µL of MWCNT of 1 mg MWCNT dispersed in 500 µL ethanol was drop-casted on bare Au and kept for drying in room temperature (298 ± 2 K or $25\pm2^{\circ}C$) for $2(\pm0.5)$ min. The Au/MWCNT was then pretreated electrochemically by performing continuous CV for ten cycles (n = 10, n= no. of cycles) at $v = 50$ mV.s^{-1} in the blank pH 7 PBS in the potential window of -0.5 to 0.5 V vs. Ag/AgCl. Au/MWCNT@PANI$_{pH7}$ was prepared by continuous potential cycling of the Au/MWCNT in a freshly prepared 50mM aniline solution (50 µL aniline + 450 µL ethanol +9.5mL of pH7 PBS) in a potential window -0.5 to 0.5 V vs. Ag/AgCl at a $v = 50$ mV.s^{-1} (n = 10). Then the Au/MWCNT@PANI$_{pH7}$ modified electrode was electrochemically pretreated in a potential window of -0.5 to 0.5 V vs. Ag/AgCl in pH 7 PBS at a $v = 50$ mV.s^{-1} (n = 10).

Real sample analyses. Ascorbic acid containing two commercially available fruit juices, #1 (grape), #2 (orange) and one pharmaceutical tablet #3 were obtained from a local super market and VIT health centre respectively, and stored in refrigerator until it use. Displayed AA contents in the sample #1 and #3 are 2.96 and 163.5 µM respectively. Prior to the FIA, the fruit juices were filtered using syringe filters and suitably diluted with pH 7 PBS. Similarly, the tablet sample was first crushed as powder using mortar and pestle and then dissolved in pH 7 PBS. Standard addition method was adopted for real sample analysis.

Table S1 A comparison of various types of PANI based ascorbic acid electrodes

Chemically Modified Electrode	pH (medium) of preparation	E_{pa} for AA	pH (medium) for AA oxidation	D_L	Ref No.[#]
1. GCE/PANI	~0 (0.5 M H_2SO_4)	350 mV[1]	~5 (0.1 M $NaClO_4$)	1μM[a]	19
2. Pt/PANI/Asc. Oxid.	~0 (1 M HCl)	400 mV[1]	~7 (0.2 M PBS)	--	17
3. Ni/PANI	~0 (0.5 M H_2SO_4)	220 mV[3]	~1 (0.1 M H_2SO_4)	--	22
4. Pt/PANI-camphor sulfonic acid	~0 (0.5 M H_2SO_4)	340 mV[1]	~7 (0.1 M PBS)	--	24
5. Pt/PANI/Cu	~0 (0.5 M H_2SO_4)	320 mV[2]	~6 (0.1 M PBS)	1mM[a]	13
6. GCE/PEDOT+PANI	< 0 (pTSA)	420 mV[1]	~6 (Cit-PBS)	--	25
7. Au/PANI/MWCNT/Asc. Oxid.	~0 (1 N HCl)	600 mV[1]	~6 (EDTA-PBS)	0.9μM[b]	27
8. Pt/MWCNT-Nf/PANI+PAA	< 0 (1 M H_2SO_4)	300 mV[1]	~6 (1M H_2SO_4, 0.1 M PBS)	0.25 μM[c]	28
9. Au/MWCNT@PANI$_{pH7}$	7 (0.1 M PBS)	-15 mV[1]	7 (0.1 M PBS)	42 nM[a]	Our work

*is optimal, 1 is vs. Ag/Agcl, 2 is vs. Hg/HgSO$_4$ and 3 is vs. SCE;

a=By FIA, b=Amp i-t, c=DPV

[#] = Manuscript reference numbers

Table S2 Flow injection analysis (FIA) of ascorbic acid in real samples using GCE/MWCNT@PANI$_{pH7}$-FIA detector.

Real sample	Linear expression	Regression (R)	Detected (μM)	Labelled (μM)	Recovery (%)
#1	0.0080+0.0023x	0.997	3.04	2.96	101 ± 0.0048
#2	0.0714+0.0055x	0.999	69.2	-Nil-	99.0 ± 0.0018
#3	0.2347+0.0015x	0.983	156	163.5	95.7 ± 0.1161

FIA conditions: hydrodynamic flow rate (H_f) = 700 μL.min^{-1}, applied potential = -15 mV vs. Ag/AgCl, sample injection volume = 20 μL and carrier solution = pH 7 PBS.
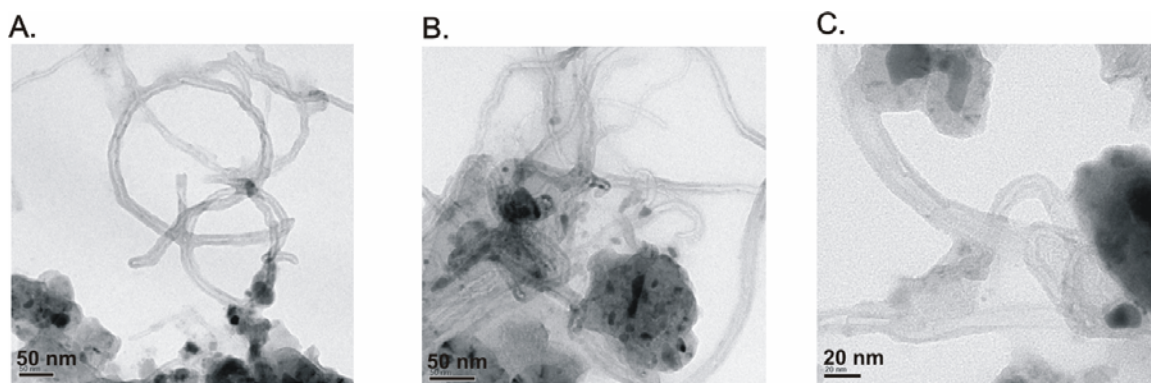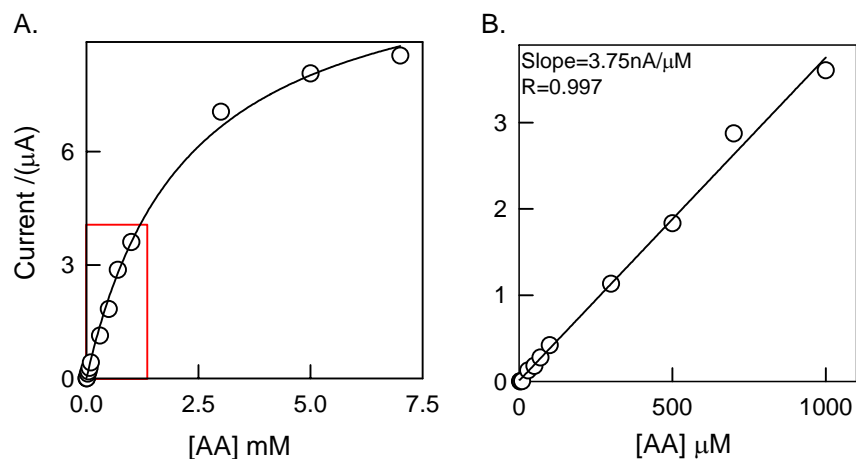
Fig. S1 TEM images of MWCNT@PANI $_{pH7}$

Fig. S2 Plot of FIA peak currents vs. concentration of AA from 3 to 7000 μM (A) and 3 to 1000 μM (B)

Note: Linear response is observed from 3μM to 1000 μM with a slope = 3.75 nA.μM^{-1}, R=0.997
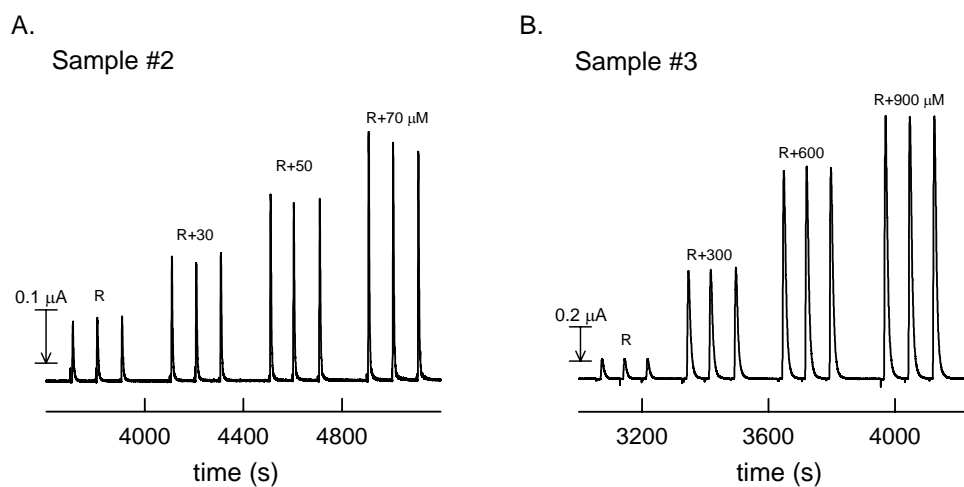
A.

Sample #2

B.

Sample #3

Fig. S3 FIA (R) real sample analyze using the GCE/MWCNT@PANI$_{pH7}$ detector by standard addition approach. Other FIA conditions are: E_{app} = -15 mV vs. Ag/AgCl; hydrodynamic flow rate (H_f) = 700 µL.min^{-1} and carrier buffer solution = pH 7 PBS.

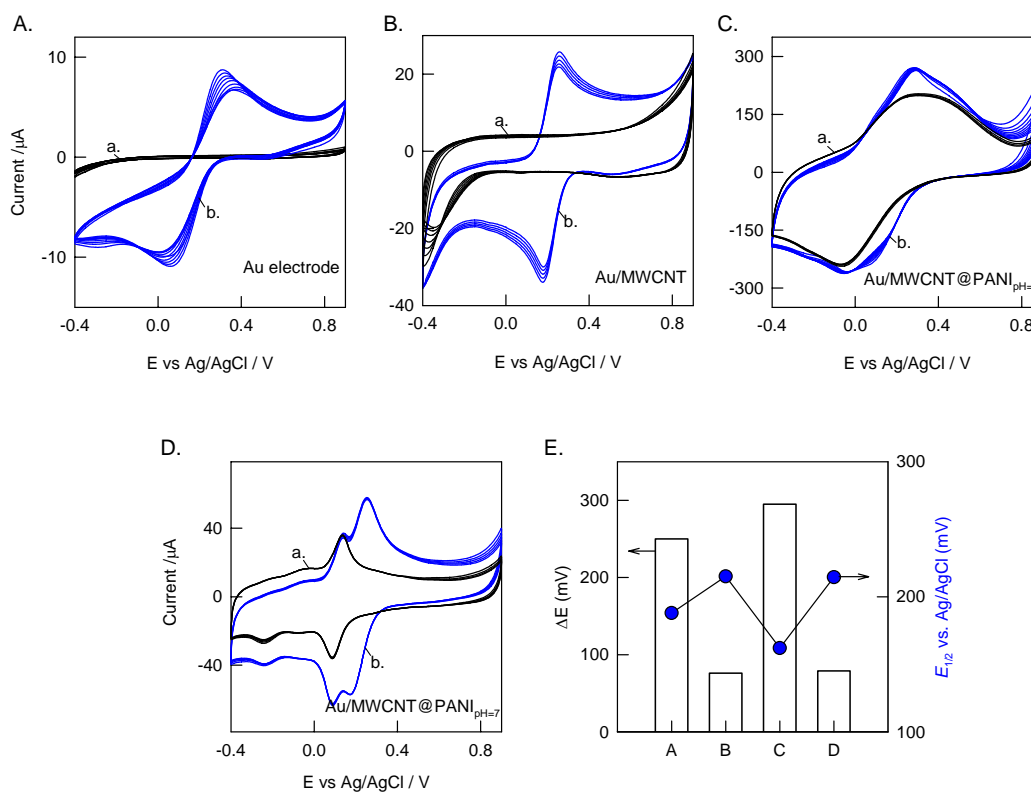**Other Supplementary information (not included in the manuscript)**

Fig. S3 CV responses of Au (A), Au/MWCNT (B), Au/MWCNT@PANI$_{pH2}$ (C) and Au/MWCNT@PANI$_{pH7}$ (D) without (a) and with (b) 5 mM potassium ferricyanide in pH 7 PBS (n=20 seg, v = 50 mV.s^{-1} vs. Ag/AgCl and (E) Plot of ΔE_p and $E_{1/2}$ against various modified electrodes.

Note: Au/MWCNT@PANI$_{pH7}$ electrode (70±3 mV) has lesser ΔE_p than that of the Au/MWCNT@pH$_2$ (300±5 mV). This observation indicates superior conductive nature of the pH 7 prepared PANI electrode in this work!