

Electronic Supporting Information

Deep eutectic solvent assisted synthesis of poly(furfuryl alcohol) grafted carbon nanotubes: a metal free electrocatalyst for non-enzymatic glucose detection

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Experimental

Materials

Furfuryl alcohol (FA, 98%) was purchased from Merck. Choline chloride (ChCl, >98%) and anhydrous zinc chloride (ZnCl₂, >98%) were used as received from Alfa Aesar. Carbon nanotubes (CNTs, diameter 10-15 nm, length 10-20 mm, specific surface area 200 m²g⁻¹) were purchased from Hanwha Nanotech (Korea). The water in this study was used at the deionized grade. Other chemicals and solvents were obtained at high-purity grade and used as available.

Catalyst characterization

Fourier transform infrared (FTIR) spectra of the sample were obtained using a Bruker Tensor 27 (Germany) spectrometer with the wavenumber from 4000 to 500 cm^{-1} . Thermogravimetric analysis (TGA) was performed under nitrogen flow using a Setaram Labsys Evo S60/58988 thermoanalyzer (France) in a temperature range of 50-800 $^{\circ}\text{C}$ with heating rate of 10 $^{\circ}\text{Cmin}^{-1}$. The crystallographic state of materials was recorded by a Shimadzu 6100 X-ray diffractometer (Japan) in the 2-theta range of 10-80 $^{\circ}$. The morphologies of CNTs and PFA-*f*-CNTs materials were examined by scanning electron microscopy (SEM) connecting to an Energy Dispersive X-ray (EDX) spectrometer (Hitachi JEOL-JSM-6700F system, Japan). A LabRAM spectrometer (HORIBA Jobin Yvon, Edison, NJ) with a 785 nm diode laser was used to obtain Raman spectra of the samples.

Preparation of PFA-*f*-CNTs composites

FA (1.0 g) was dissolved in DES and sonicated at 60 $^{\circ}\text{C}$ for 20 min using an ultrasonic bath (GTSonic 150W) at the frequency of 40 kHz. Subsequently, CNTs (100 mg) were added to the same DES reaction mixture and the reaction was further continued for 30 min. Reaction mixture was diluted with water and centrifuge to separate PFA-*f*-CNTs composites which was later washed with solvents (deionized water, THF and methanol) and dried under vacuum at 50 $^{\circ}\text{C}$ until constant weight.

Electrochemical characterization

The electrochemical characters of the PFA-*f*-CNTs based electrodes were investigated at ambient conditions using a potentiostat-galvanostat (VSP, BioLogic-Science Instruments, France) in the absence and presence of glucose in alkaline media. A conventional three-electrode system with platinum wire and Ag/AgCl (3M NaCl) as the counter and reference electrodes, respectively, were

used for the measurements. For the electrode preparation, materials were dispersed in ethanol (10 mg/mL) followed by sonication for 30 min. Then, 20 μL of the solution mixture was dropped on a glass carbon electrode (GCE) and dried at room temperature resulting a uniform layer of PFA-*f*-CNTs with an active area of 7.07 mm^2 . The PFA-*f*-CNTs layer was coated in GCE using one drop of Nafion-117 binder solution.

Table S1: The effect of solvents on the grafted amount of PFA in PFA-*f*-CNTs composites.

SN	Sample	DES/FA feed ratio (w/w)		Grafted amount ^a (wt.%)
1.	PFA- <i>f</i> -CNTs-1	DES/FA	1.0	20
2.	PFA- <i>f</i> -CNTs-2		1.5	32
3.	PFA- <i>f</i> -CNTs-3		2.0	50
4.	PFA- <i>f</i> -CNTs-4		4.0	74
5.	PFA- <i>f</i> -CNTs-5		10	92

^aGrafted amount of PFA was calculated gravimetrically

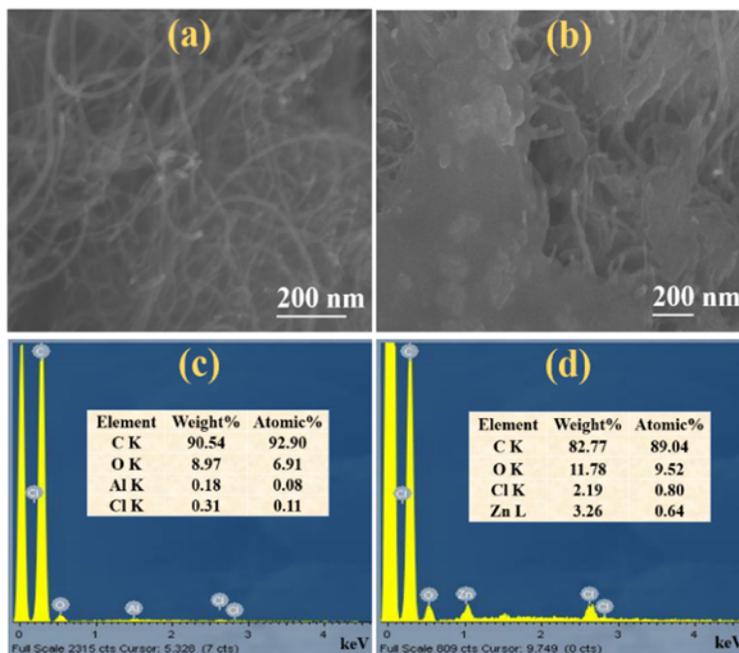


Figure S1. SEM-EDX analysis of CNTs (a, c) and PFA-*f*-CNTs (b, d)

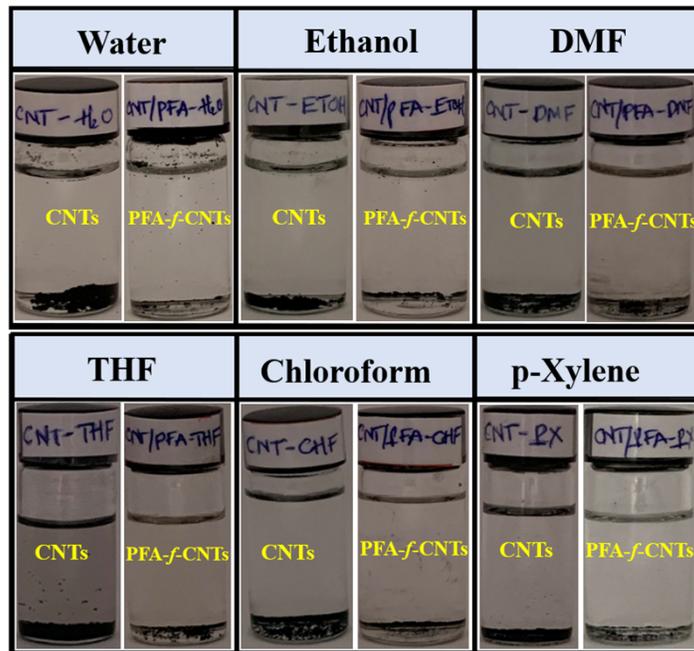


Figure S2. Digital images of CNTs and PFA-f-CNTs in different solvents

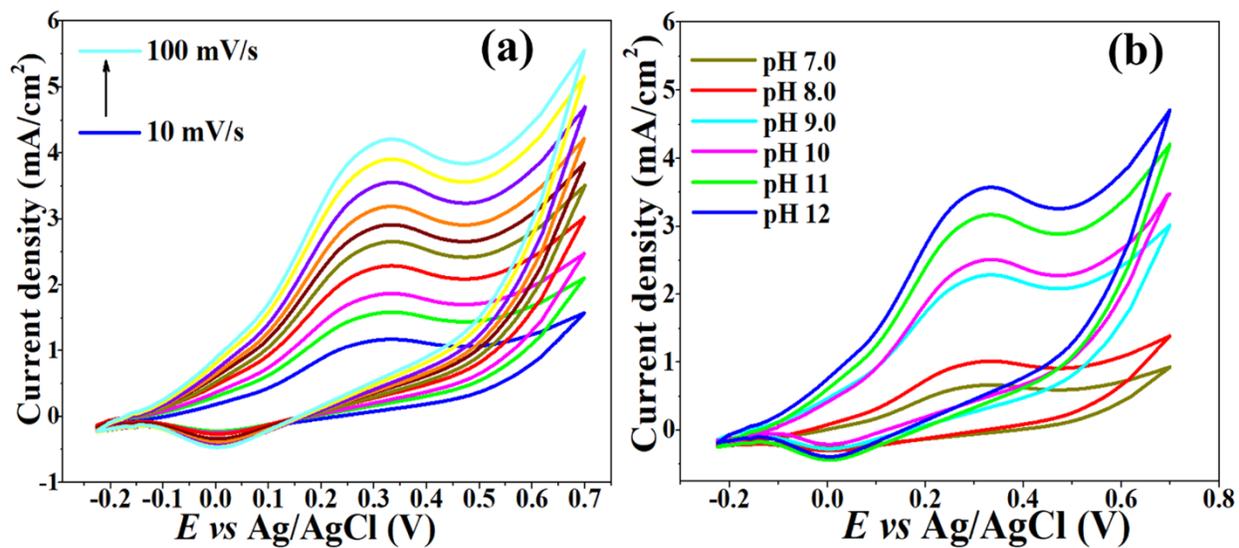


Figure S3. Electrochemical response plots in 0.1 M KOH at scan rate of 50 mV/s: PFA-f-CNTs-5 in 4.0 mM glucose solution at different scan rates (a) and PFA-f-CNTs-5 in 4.0 mM glucose at various pH values (b)

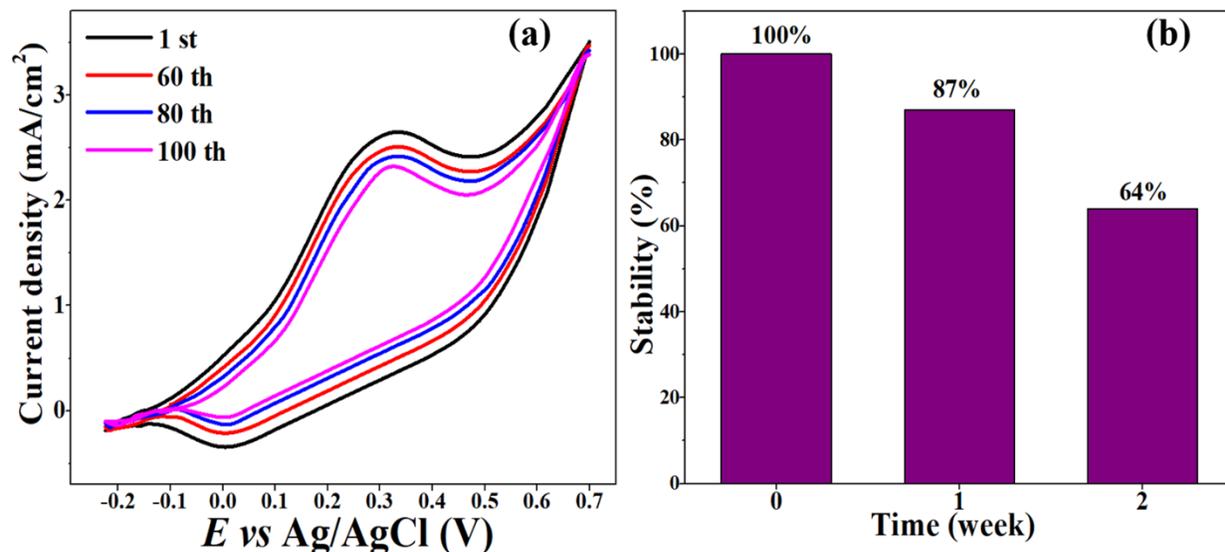


Figure S4. CV curves of PFA-*f*-CNTs-5 after 60, 80, and 100 cycles in 4.0 mM glucose (a) and stability of PFA-*f*-CNTs-5 electrodes during electrochemical detection of glucose (b). Condition: 0.1 M KOH, scan rate of 50 mV/s

Table S2. Comparison of electro catalytic activity of PFA-*f*-CNTs

SN	Electrodes	Glucose concentration (mM)	Current density (mA/cm ²)	Potential vs Ag/AgCl (V)	Refs.
1.	GOx-Chit-CNT85/ITO	20	0.27	-0.431	[1]
2.	Glucose oxidase-graphene-chitosan/GCE	12	0.455	-	[2]
3.	Well-aligned MWNTs	11	0.048	+0.2	[3]
4.	G-IL/CNTs/(GOD+HRP)/GCE	5	0.269	-	[4]
5.	Redox polymer/Enzym film/MWCNTs	5	0.8	+0.1	[5]
6.	[P20-Os(2,20-bipyridine)2(4-aminomethylpyridine)Cl].PF ₆ /MWCNTs/GOx	5	0.215	+0.2	[6]
7.		100	0.56	+0.45	
8.	[Os(2,2-bipyridine)2(4-aminomethyl pyridine)Cl].PF ₆ /Gox/MWCNT	5	1.0	+0.45	[7]
9.	AuNBP/MWCNTs	36.7	3.71	+0.15	[8]
10.	GOx/MnO ₂ /MWCNT	3.2	0.077	-0.55	[9]
11.	PFA- <i>f</i> -CNTs-5	4	2.64	0.3	This work
12.	PFA- <i>f</i> -CNTs-5	9	5.88	0.3	This

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