Electronic Supplementary Information

Enzyme–free uric acid electrochemical sensors using β–cyclodextrin modified carboxylic acid functionalized carbon nanotubes.

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Contents:

Instrumentation/Procedural Details of Microscopy and Spectroscopic Characterization of Films

Transmission Electron Microscopy (TEM). COOH–MWCNT structure was supported visually with TEM (JEOL 1010) characterization. Samples of COOH–MWCNT were dispersed in ethanol before casting on a TEM grid. Fourier transform infrared (**FTIR**) spectroscopy was conducted using a Thermo Scientific Nicolet Model iS10 FTIR equipped with a diamond SMART iTX HATR sample accessory. UV–vis spectroscopic analysis was conducted using Agilent 8453 Ultraviolet–Visible Spectrophotometer.

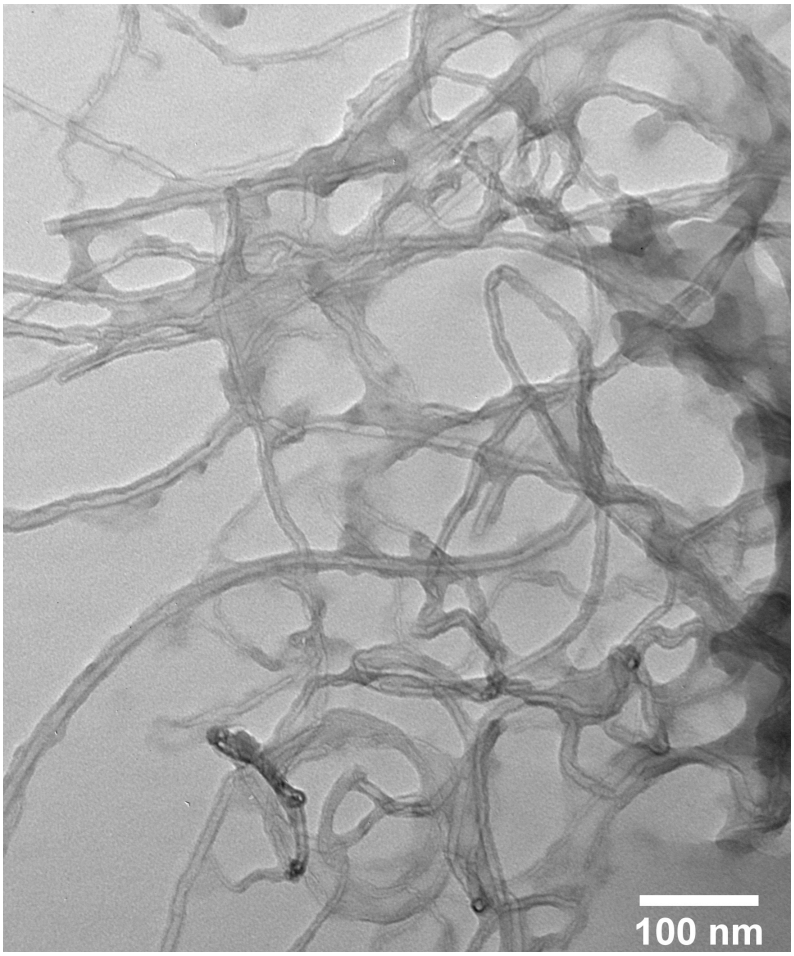


Figure S1. Typical TEM images of the as purchased carboxylic acid functionalized multi–walled carbon nanotubes (COOH–MWCNT); 0.4 mg/mL of COOH– MWCNT in ethanol was drop casted on the TEM grids prior to scan.

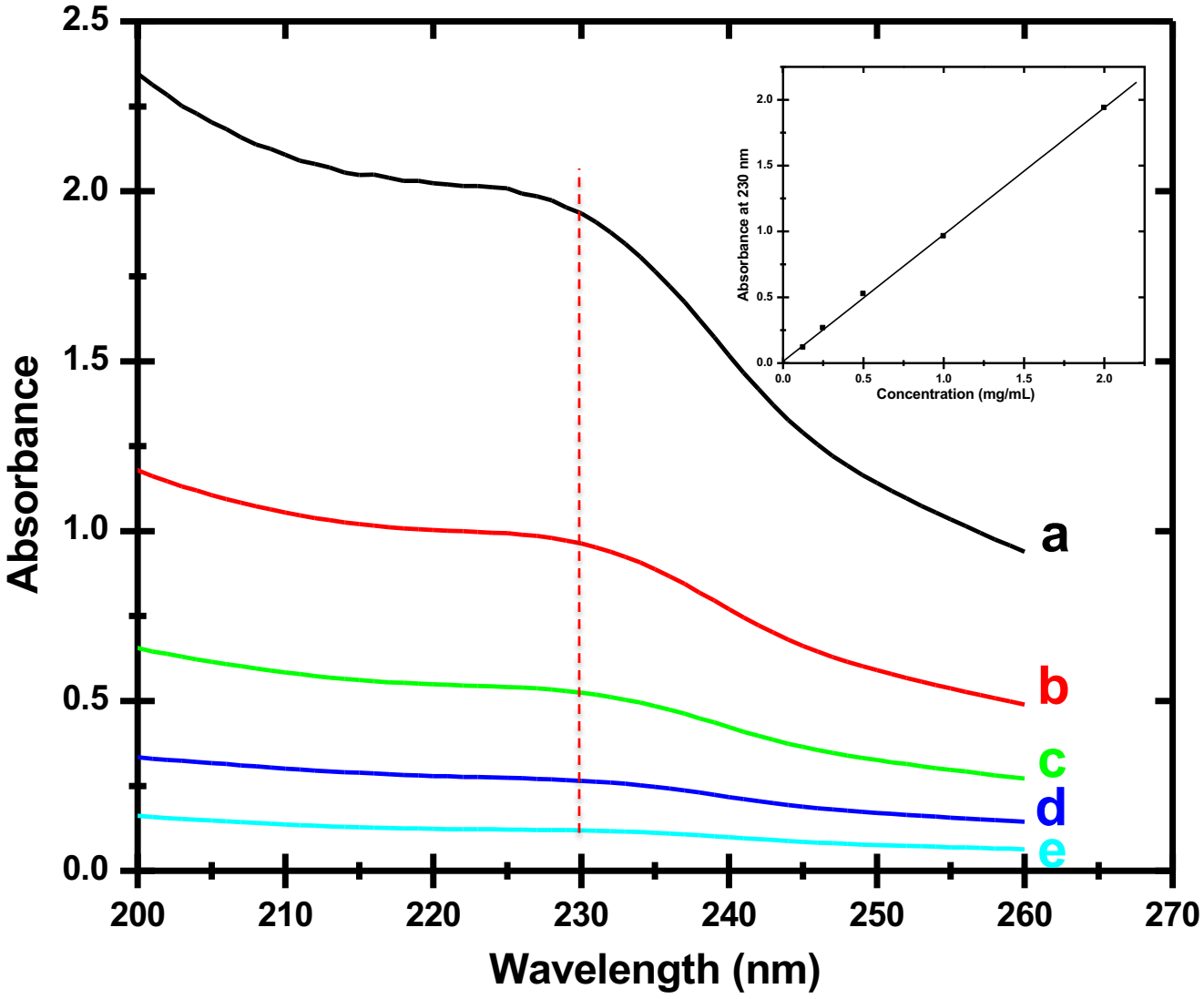


Figure S2. UV–vis absorption spectra of as purchased carboxylic acid functionalized multi–walled carbon nanotubes (COOH–MWCNT) in aqueous solutions with a) 2.0, b) 1.0, c) 0.5, d) 0.25 and e) 0.125 mg/mL concentrations. **Inset**: Calibration curve of absorbance vs concentration at 230 nm.

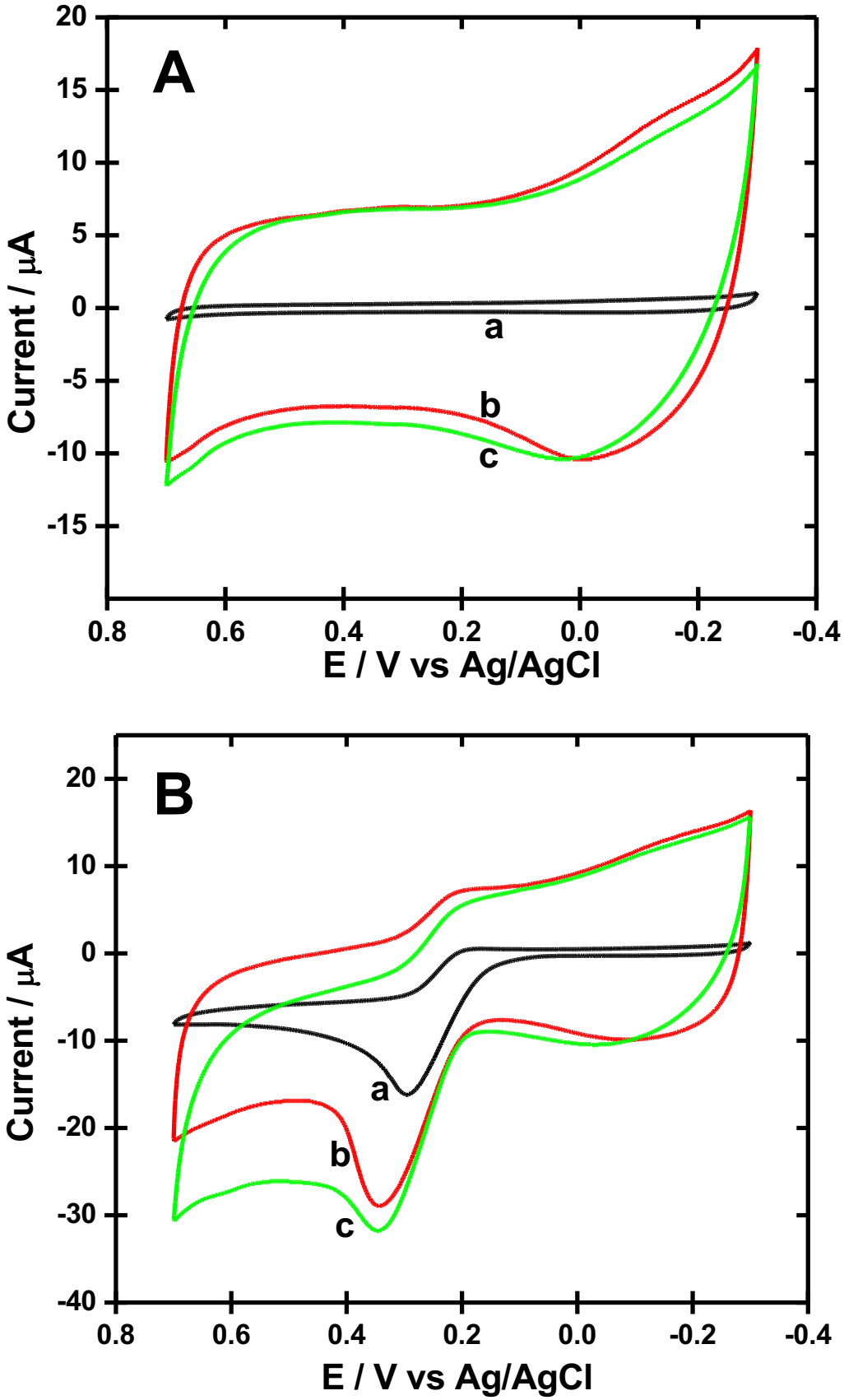


Figure S3: Cyclic Voltammograms of a) bare GCE, b) GCE/COOH–MWCNT*/Nafion, c) GCE/(COOH–MWCNT:β–CD)*/Nafion electrochemical sensors in 65.55 mM PBS (pH = 7.0) **(A)** without (background) and **(B)** with 1 mM UA. * indicates sonicated.

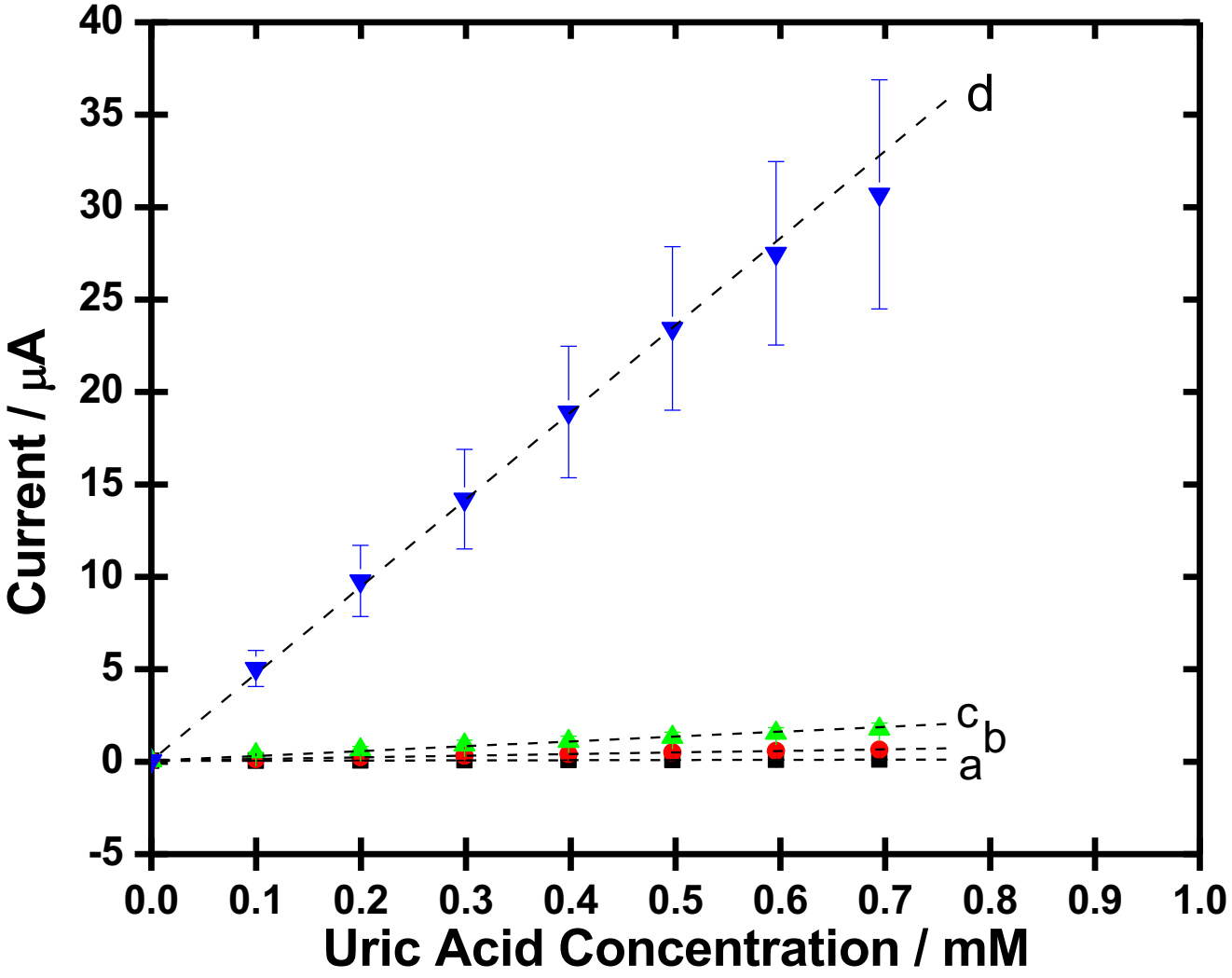


Figure S4: Calibration curves obtained from successive 0.1 mM injections of uric acid at **(a)** GCE/Nafion, **(b)** GCE/β–CD/Nafion, (**c**) GCE/COOH–MWCNT/Nafion and (**d**) GCE/COOH–MWCNT (1:1) β–CD/Nafion. Note: In some cases, standard error bars are smaller than markers for average value (n = 2).

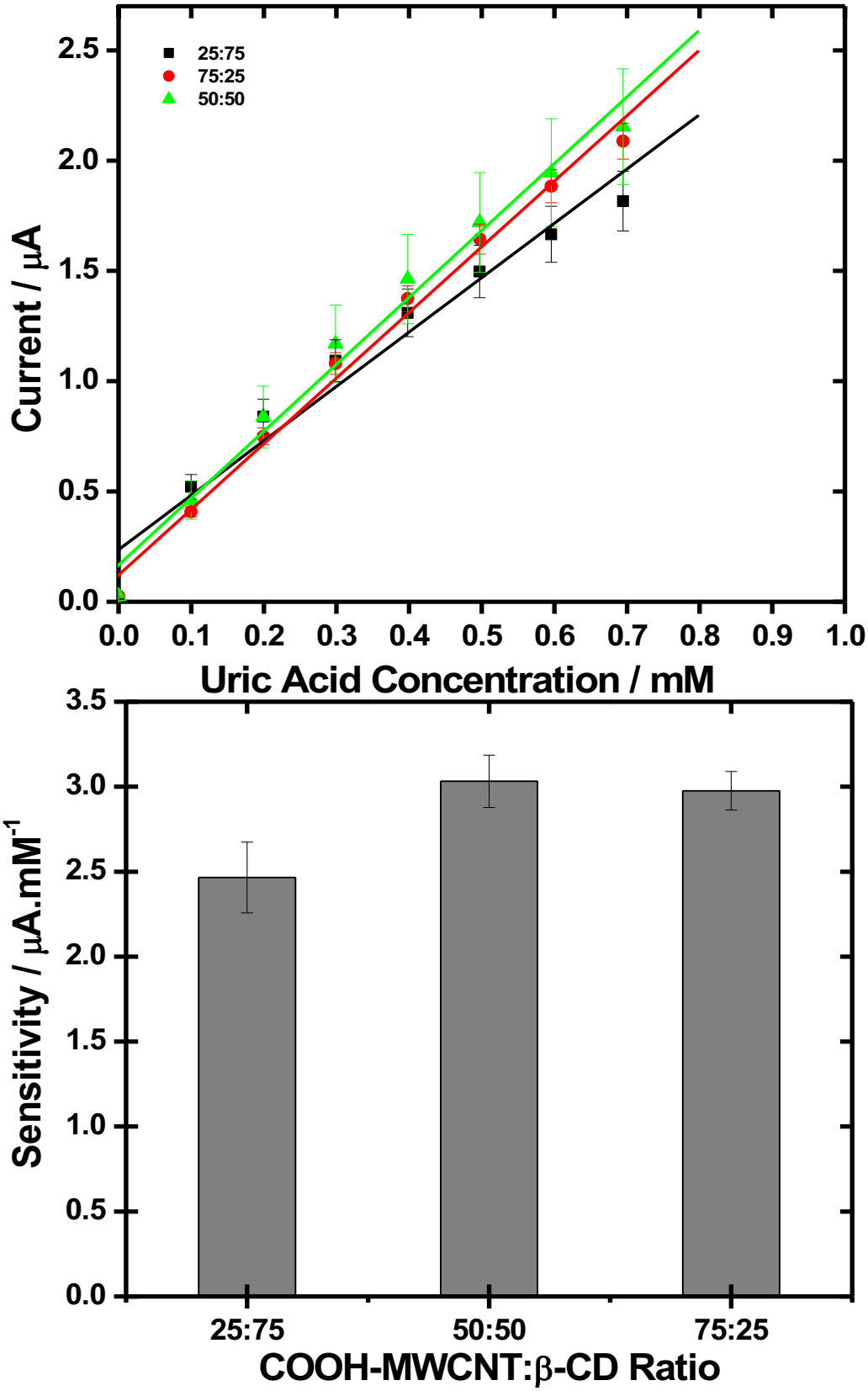
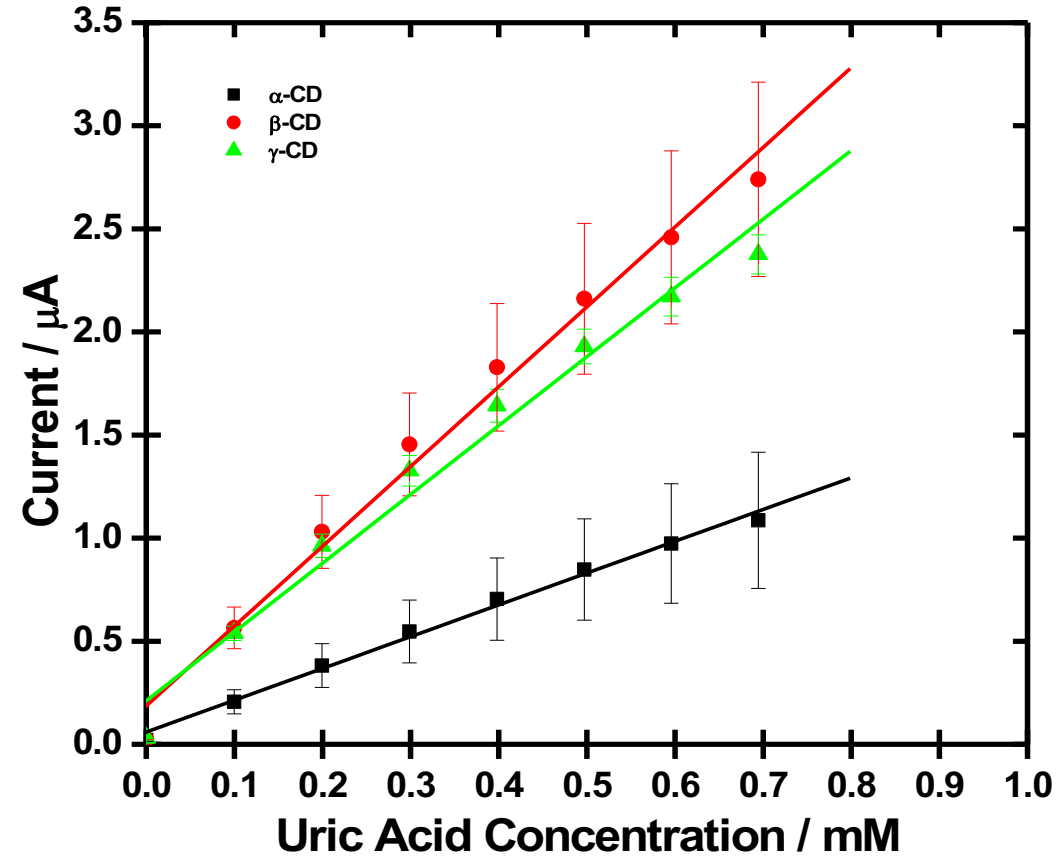


Figure S5: The effect of varying the (wt/wt) ratio of COOH–MWCNT to β–CD in GCE/(COOH–MWCNT:β–CD)*/Nafion/HPU UA electrochemical sensor. Note: In some cases, standard error bars are smaller than markers for average value (n = 3). * indicates sonicated.



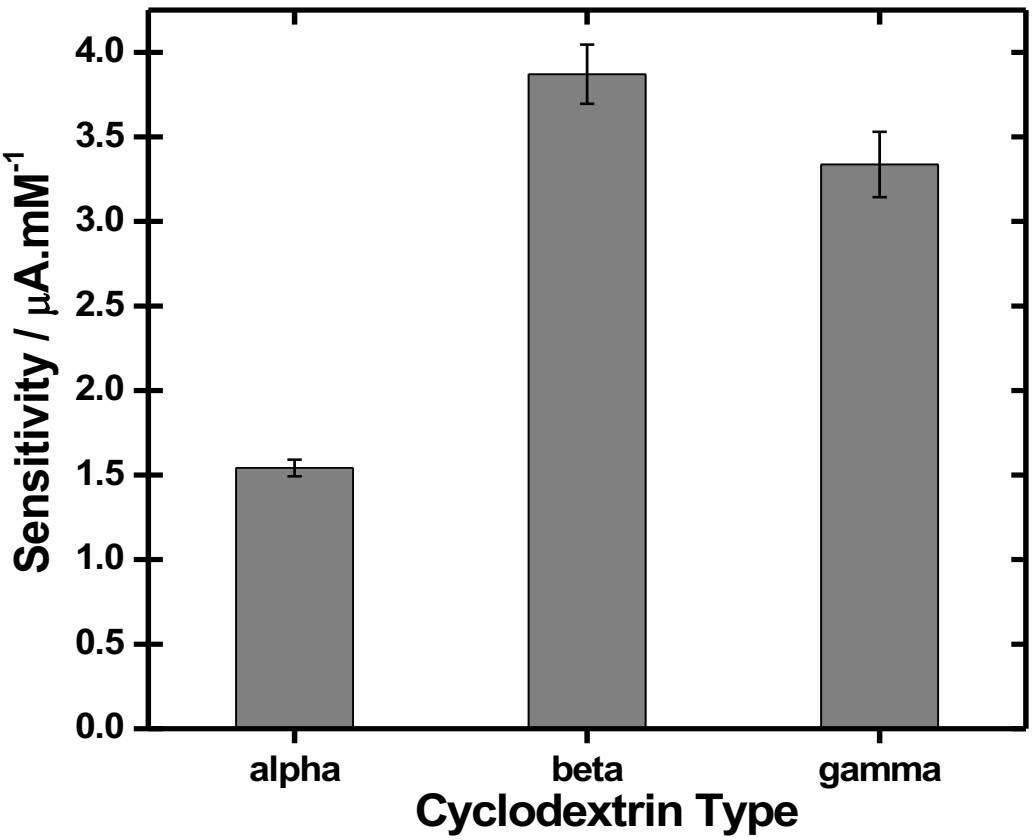


Figure S6: The effect of varying the types of CD in GCE/(COOH–MWCNT:CD)*/Nafion/HPU UA electrochemical sensor. Note: In some cases, standard error bars are smaller than markers for average value (n = 3). * indicates sonicated.

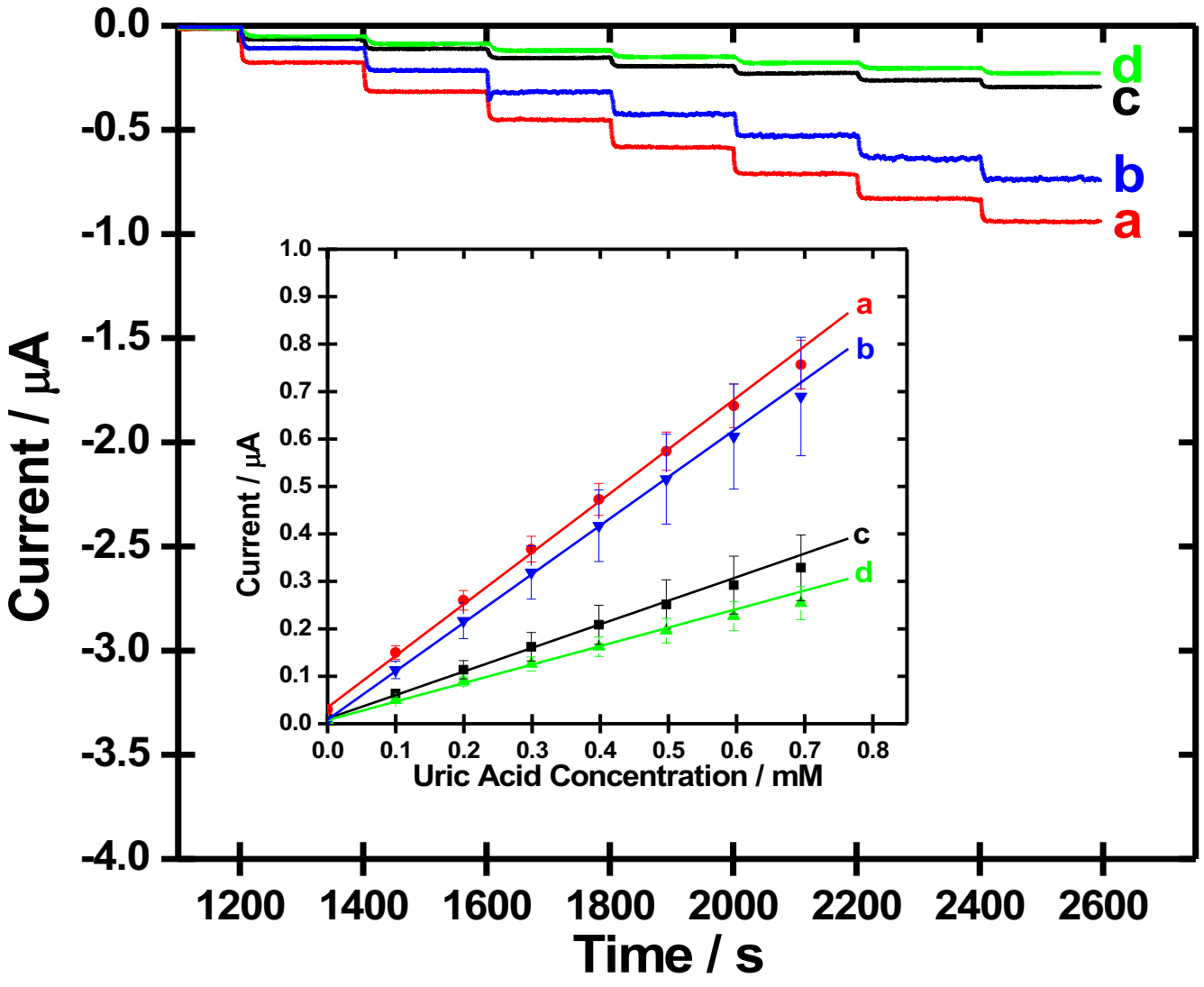


Figure S7: Representative amperometric I-t curves and corresponding calibration curves (**inset**) during successive 0.1 mM injections of uric acid at a) GCE/COOH–MWCNT*/β–CD/Nafion/HPU, b) GCE/COOH–MWCNT/β–CD/Nafion/HPU, c) GCE/β–CD*/COOH–MWCNT/Nafion/HPU and d) GCE/β–CD/COOH–MWCNT/Nafion/HPU. The sonication time was 30 min. Note: In some cases, standard error bars are smaller than markers for average value (n = 3). * = sonicated.

Table S1: Comparison of Amperometric Uric Acid Biosensor Performance Parameters – Literature Comparison (References listed next page)

System	Type	WE	Sensitivity (nA/μM)	Response Time (s)	Linear Range [a] (μM)	Dynamic Range [a] (μM)	LOD $x10^{-6}$ (μM) [b]	Stability	Ref [c]
COOH-MWCNT/β-CD/Nafion/HPU	Direct	GCE	$4.28_{\pm 0.11}$	$4.0_{\pm 0.5}$	700	700	2	12 days	d.
Nafion-MWCNT/β-CD/HPU	Direct	GCE	$2.11_{\pm 0.29}$	$5.38_{\pm 0.33}$	700	700	12	2 weeks	*1.*
Pt/PtB/MPC-HMTES*/HMTES/PL-A/HPU	1st G	Pt	$0.97_{\pm 0.11}$	15	700	700	15	5 days	*2.*
Pt/HMTES*/HMTES/PL-A/PU	1st G	Pt	$0.78_{\pm 0.11}$	$10.0_{\pm 5.3}$	700	700	$5.0_{\pm 2.4}$	>10 days	*3.*
Selected Multi-walled Carbon Nanotubes Based UA Sensors From Literature									
Au/c-MWCNT/AuNP/UOx	1st G	Au	-	7	800	-	0.01 mM	120 days	*4.*
Au/MWCNTs	Direct	Au	92.19	2	1800	-	0.1 μM/mM	2 weeks, 10% decrease	*5.*
ITO/MWCNT/PANI/UOx	1st G	ITO	-	8	600	600	5	90 days	*6.*
Au/MWCNT/AuNP/UOx	1st G	Au	-	7	800	800	10	120 days	*7.*
GCE/PVF/GEL/c-MWCNT/UOx	2nd G	GCE	-	40	710	-	$2.3x10^{-8}$ M	Day 1-10; 30% decrease; Day 11-35; 50% decrease	*8.*
GCE/MWCNT-HoFNPs	Direct	GCE	-	-	0.2-500	0.2-500	0.16	6 months	*9.*
β-CD/CNT/GE	Direct	GE	2.7	-	0.5-50	0.5-50	0.2	4 days	*10.*

Notes: * indicates UOx doped layer; **a.** Typical upper limit of range listed; **b.** Limit of detection (L.O.D.) is the concentration required to elicit a sensor response ($3\sigma_{BI}/\beta_1$); **c.** Comparative references (examples) listed next page with (**d.**) current work; **Additional notes:** MWCNT: multi–walled carbon nanotubes; β–CD: beta cyclodextrin; HPU: hydrothane polyurethane; GCE: glassy carbon electrode; PtB: Platinum black; MPC: monolayer–protected cluster; HMTES: hydroxymethyltriethoxysilane; PL–A: polyluminol/polyaniline; 1st G: 1st generation (indirect); ; ITO: indium tin–oxide; 2nd G: 2nd generation (mediated);PANI: polyaniline; AuNP: Gold nanoparticles; PVF: Poly(vinylferrocene); HoFNPs: holmium Fluoride nanoparticles; GE: graphite electrode.

Table S1 References

1. Wayu MB, DiPasquale LT, Schwarzmann MA, Gillespie SD, Leopold MC (2016) Electropolymerization of β-cyclodextrin onto multi-walled carbon nanotube composite films for enhanced selective detection of uric acid. J. Electroanal. Chem. 783:192-200.
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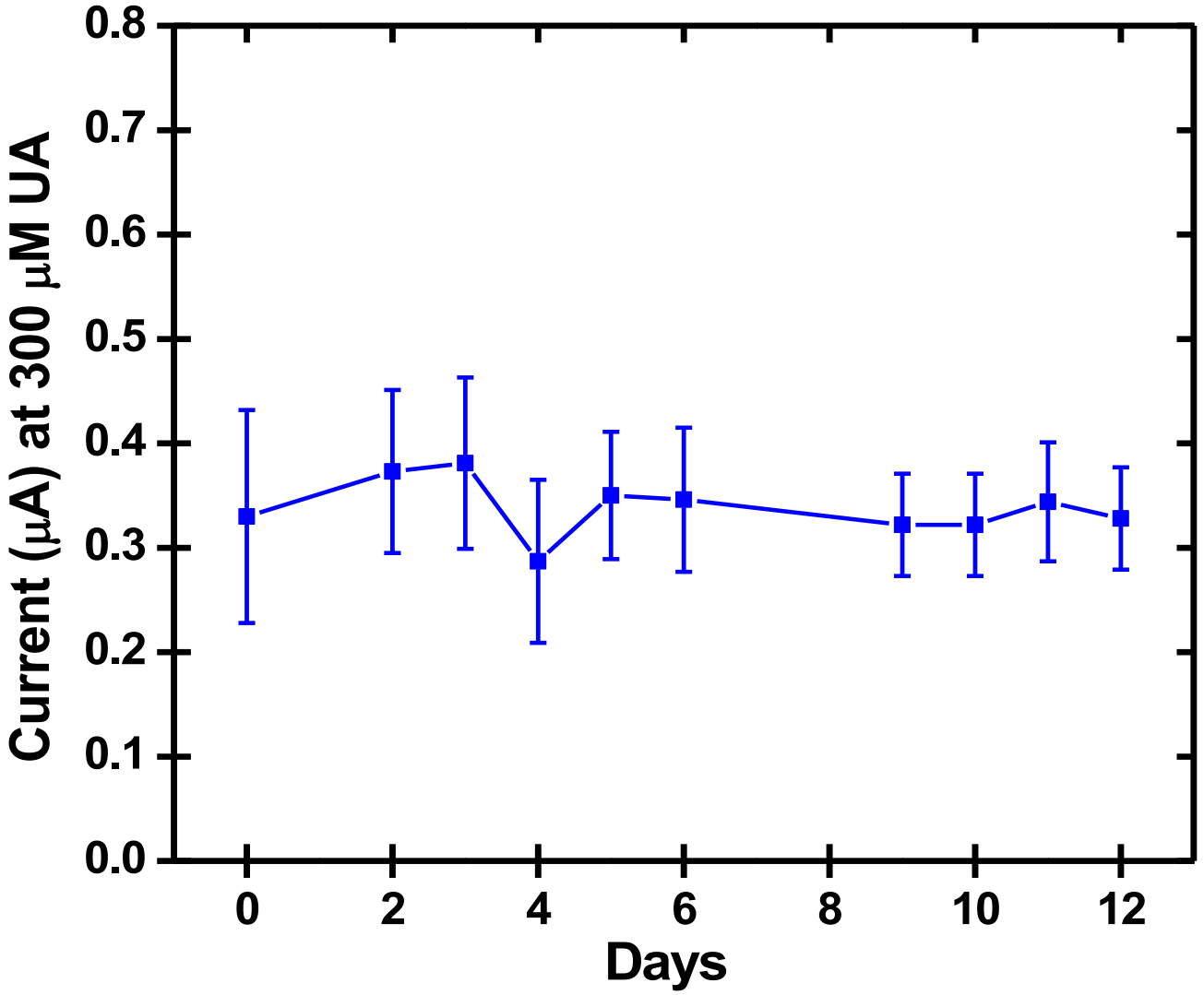

Figure S8: Current response obtained from the third injections of 0.1 mM uric acid at GCE/COOH–MWCNT*/β–CD*/Nafion/HPU over a period of 12 days. The sonication time was 30 min. Note: In some cases, standard error bars are smaller than markers for average value (n = 6). * indicates sonicated.

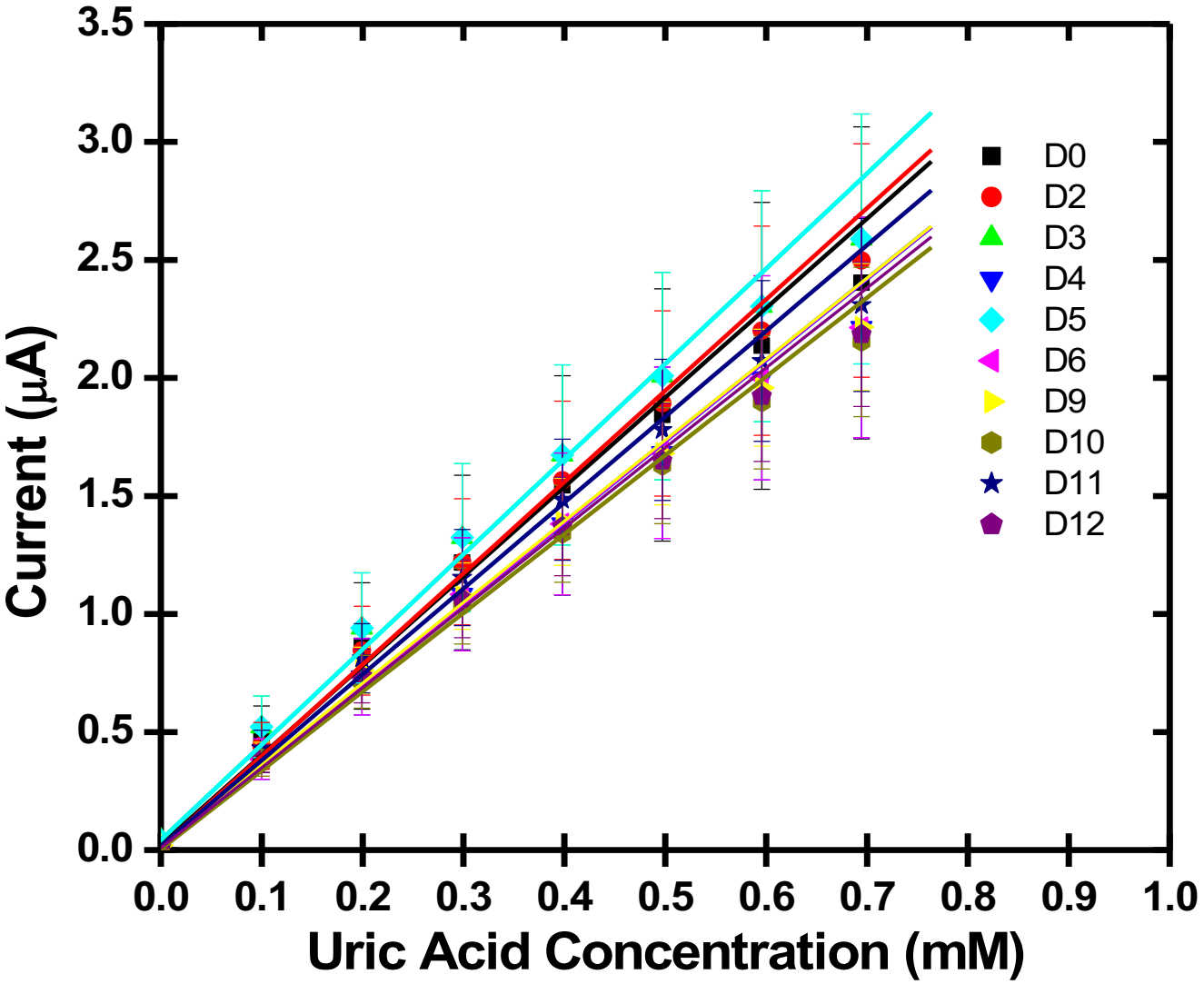

Figure S9: Calibration curves obtained from successive 0.1 mM injections of uric acid at GCE/COOH–MWCNT*/β–CD*/Nafion/HPU over a period of 12 days. The sonication time was 30 min. Note: In some cases, standard error bars are smaller than markers for average value (n = 6). * indicates sonicated.