# Enhanced Amperometric Detection of Tumor Biomarker Vanillylmandelic Acid Using NiMoO<sub>4</sub>@C<sub>3</sub>N<sub>5</sub> Hybrid Nanostructures

Nirmal Kumar Sakthivel<sup>1,2</sup>, Sakthivel Kogularasu<sup>3,4</sup>, Yung-Lung Chen<sup>5,6</sup>, Wan-Ching Lin <sup>7,8</sup>, Guo-Ping Chang-Chien<sup>3,4\*</sup>, Hisham S.M. Abd-Rabboh<sup>9</sup>, Mani Govindasamy, <sup>1,2\*</sup>

<sup>1</sup>International Ph. D program in Innovative Technology of Biomedical Engineering & Medical Devices, Ming Chi University of Technology, New Taipei City, Taiwan.

<sup>2</sup> Research Center for Intelligence Medical Devices, Ming Chi University of Technology, New Taipei City, 243303, Taiwan.

<sup>3</sup>Institute of Environmental Toxin and Emerging-Contaminant, Cheng Shiu University, Kaohsiung 833301, Taiwan.

<sup>4</sup>Center for Environmental Toxin and Emerging-Contaminant Research, Cheng Shiu University, Kaohsiung 833301, Taiwan.

<sup>5</sup>Division of Cardiology, Department of Internal Medicine, Kaohsiung Chang Gung Memorial Hospital, College of Medicine, Chang Gung University, Kaohsiung 833, Taiwan.

<sup>6</sup>Graduate Institute of Clinical Medical Sciences, College of Medicine, Chang Gung University, Taoyuan 333, Taiwan.

<sup>7</sup>Department of Neuroradiology, E-da Hospital, I-Shou University, Kaohsiung 84001, Taiwan.

<sup>8</sup>Department of Neurosurgery, E-da Hospital, I-Shou University, Kaohsiung 84001, Taiwan.

<sup>9</sup>Chemistry Department, Faculty of Science, King Khalid University, PO Box 9004, Abha 62223, Saudi Arabia.

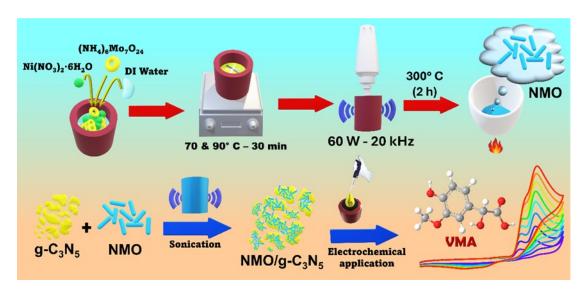
## \*Corresponding authors:

Prof. Guo-Ping Chang-Chien (guoping@gcloud.csu.edu.tw)

Prof. Mani Govindasamy (govindasamy 420700@gmail.com)

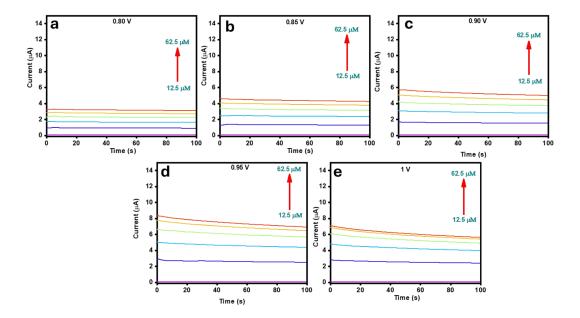
#### S1. Materials and instrumentations

For crystal structure confirmation was done by wielding XRD (Bruker D8 Advance Eco, China) instrument. The morphological studies of the composite were characterized by FESEM (JSM-7610F, Taiwan) and High-Resolution TEM (JEM-2100, Taiwan) instrument. The electron impedance spectroscopy (EIS) studies (t equilibration = 2s; Fixed potential (0.2 V; Number of frequencies, 56 = 9.2/dec; Frequency range from 0.1 Hz to 100000 Hz) was taken by using Palmsens4 FRA device. All voltammetry studies (CV & i-t) were grabbed by using Palmsens4 FRA electrochemical analyzer device. For electrochemical studies, common three electrode system was used where, glassy carbon electrode and rotating disk electrode as a working electrode, platinum wire as a counter electrode and Ag/AgCl (3M KCl) as a reference electrode.



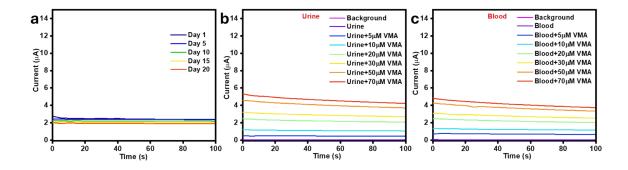
**Scheme S1.** Diagrammatic illustration for the synthesis of NMO nanorods.

#### **S2.** Current Response for Potential Ranges



**Figure S1.** Amperometric response of different potentials in electrolyte solution pH 3.0. (a) 0.80 V, (b) 0.85 V, (c) 0.90 V, (d) 0.95 V, (e) 1.0 V.

# S3. Long-Term Stability and Real Sample Analysis



**Figure S2.** (a) Amperometric curve of NMO@C<sub>3</sub>N<sub>5</sub>-1:2 for different days, real sample analysis with various spiked concentrations of VMA in (b) urine sample and (c) blood sample.

### S4. Mechanism

Scheme S2. Electron transfer in electrochemical mechanism of VMA oxidation.

**Table S1.** Real sample analysis using NMO@ $C_3N_5$ -1:2 /GCE in human blood and urine samples.

Added (μM)	Blood		Urine	Urine	
	Found (µM)	Recovery(%)	Found (µM)	Recovery(%)	
0	0	-	0	-	
5	4.84	96.8	4.79	95.8	
10	9.76	97.6	9.68	96.8	
20	18.81	94.04	18.66	93.3	

30	28.96	96.43	28.53	95.09
50	47.82	95.64	47.14	94.28
70	67.48	96.36	66.93	95.57