Supporting Information

Three-dimensional Integration of CuO-Si Hierarchical Nanowires for Electrochemical Detection of N$_2$H$_4$

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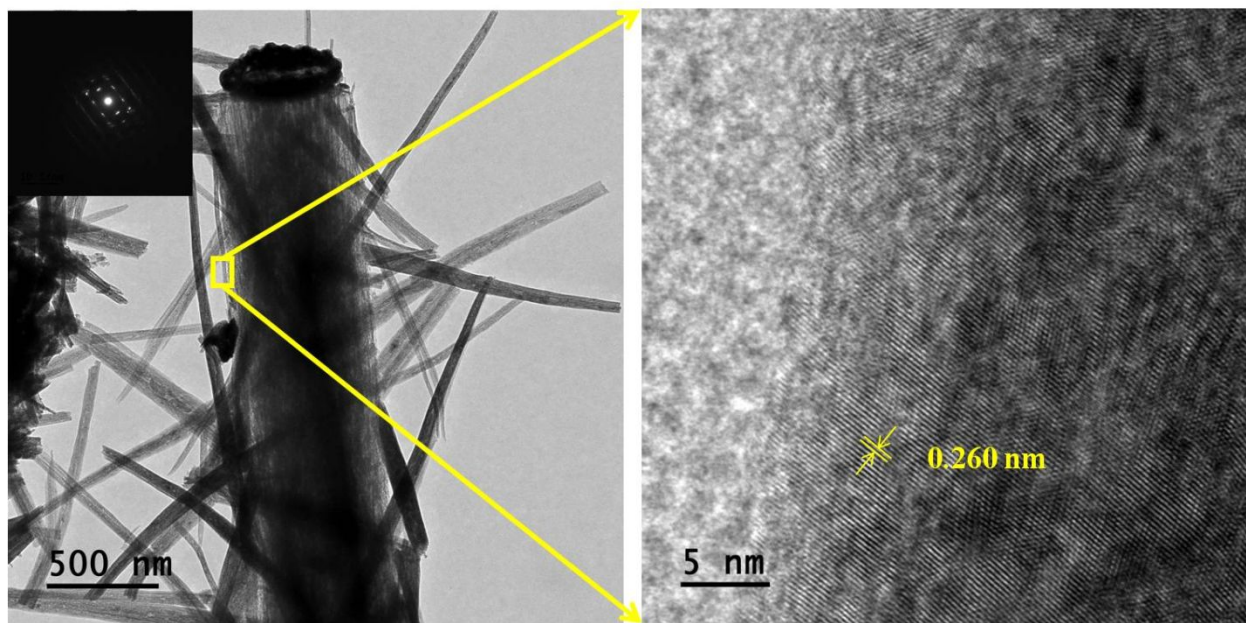**Supporting information 1: High resolution TEM**

Figure S1: High-resolution TEM of single CuO-Si HNW (Inset shows SAED pattern of Single CuO NW exhibiting monoclinic phase)

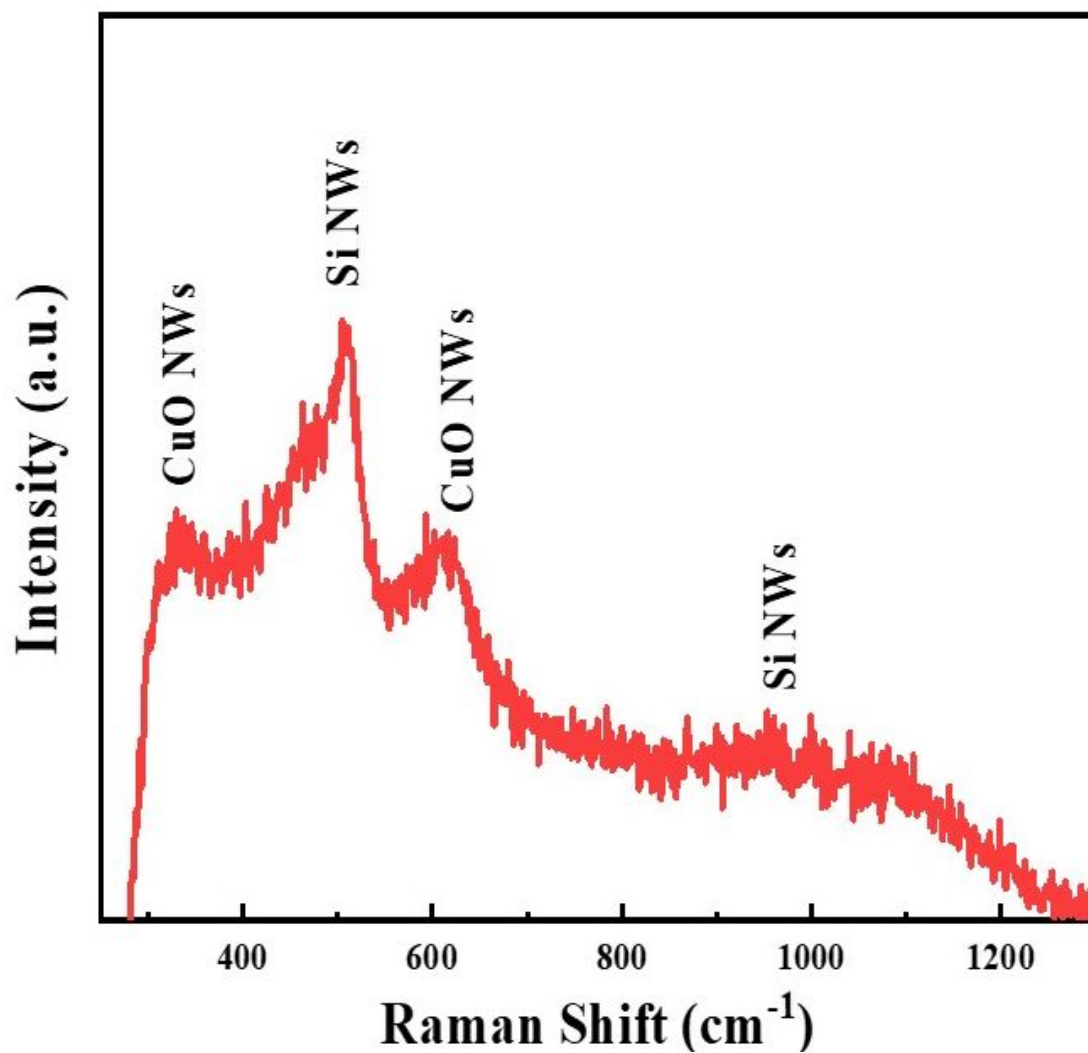**Supporting Information 2: Raman Spectra of CuO-Si HNWs structure**

Figure S2: Raman spectrum of CuO-Si HNWs.

Supporting Information 3: XPS survey spectrum of CuO-Si HNW and narration of core-level Si and O
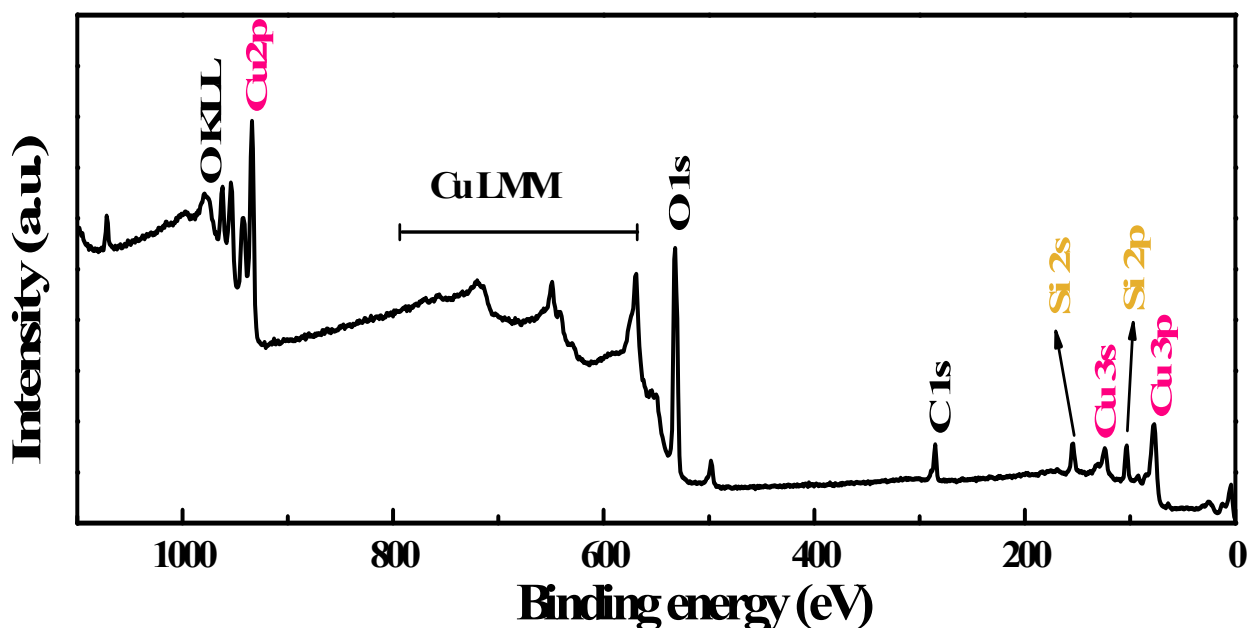

Figure S3: the survey spectrum of core-shell CuO-Si HNW

Description of core-level Si and O spectra of CuO-Si HNW

Figure 5c depicts the high-resolution Si 2p peak deconvoluted with two peaks at binding energies of 98.87 eV and 103.1 eV. The peak at 98.87 eV appeared as a result of the contribution from metallic Si, while the peak at 103.1 eV was due to SiO_2.[1,2]The slight shift in the binding energy is attributed to the air exposure of the SiNWs, the wet chemical process to fabricate $Cu(OH)_2$-Si HNWs and the air annealing of the hierarchical nanostructure of the CuO-Si HNWs. It is worth mentioning here that the intensity of $SiO_2$was higher than that of Si. This result is because XPS is a surface phenomenon that gives information up to 10 nm only. The CuO-Si HNWs were synthesized by using a Si substrate, which upon further treatment, was exposed to the ambient conditions, and hence, the oxidation of Si took place. However, due to the surface sensitivity of

XPS, the only electrons probed were from a depth of up to 10 nm, wherein most of the Si was in the oxidized form. It is also important to mention here that a slight shift in the position of the binding energy of SiO_2 was observed which corresponds to the interactions between Si and CuO. To confirm the presence of CuO and Cu_2O and the interaction of these oxides with Si, the high-resolution O 1s peak was analyzed.

Figure 5d reveals the high-resolution O 1s peak deconvoluted with five fitted peaks at binding energies of 529.68, 530.20, 530.99, 531.57, and 532.60 eV. The peaks at 530.20 eV and 531.57 eV were attributed to lattice and defective oxygen from Cu_2O, while those at 529.68 eV and 530.99 eV were due to lattice and defective oxygen from CuO, respectively.[3] Furthermore, another peak at 532.9 eV arose due to the contribution of oxygen from Si.[1]

References:

(1)   Zhao, X.; Scott, S. A.; Huang, M.; Peng, W.; Kiefer, A. M.; Flack, F. S.; Savage, D. E.; Lagally, M. G. Influence of Surface Properties on the Electrical Conductivity of Silicon Nanomembranes. *Nanoscale Res. Lett.* **2011**, *6* (1), 402. https://doi.org/10.1186/1556-276X-6-402.

(2)   Jensen, D. S.; Kanyal, S. S.; Madaan, N.; Vail, M. A.; Dadson, A. E.; Engelhard, M. H.; Linford, M. R. Silicon (100)/SiO 2 by XPS. *Surf. Sci. Spectra* **2013**, *20* (1), 36–42. https://doi.org/10.1116/11.20121101.

(3)   Biesinger, M. C. Advanced Analysis of Copper X-Ray Photoelectron Spectra. *Surf. Interface Anal.* **2017**, *49* (13), 1325–1334. https://doi.org/10.1002/sia.6239.

Supporting Information 4: Calculation of LOD and LOQ

The LOD and LOQ has been calculated from the well known formulae as follows

$$LOD = 3s_b/S$$

$$LOQ = 10s_b/S$$

Where s_b is the standard deviation of the blank signal and S represents sensitivity (slope) of the electrode.

Supporting Information 5: Evaluation of various interferents on the surface of the CuO-Si-HNW-modified electrode

To investigate the possibility of the presence of various other molecules coexisting with N_2H_4 the interference study was carried out under optimized conditions (section 3.3 in the manuscript). In 0.1 M NaOH containing a predetermined amount of N_2H_4, 5-fold higher concentrations of ascorbic acid, dopamine, serotonin, formaldehyde, hydrogen peroxide, NH_4^+ and NO_3^- were added (**Figure S4**). No apparent response was observed upon the addition of all aforementioned interfering species. This result suggests the excellent specificity of the CuO-Si HNW catalyst towards the electrooxidation of N_2H_4.
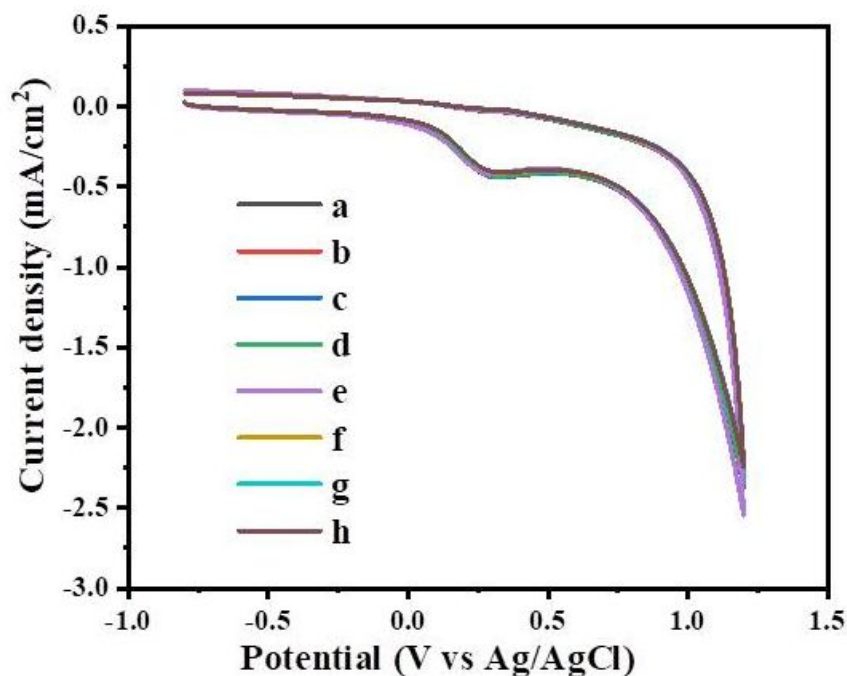

Figure S4: The CV response of the CuO-Si-HNW-modified electrode in 0.1 M NaOH with **a)** 5 $\times 10^{-3}$ M Hydrazine and the addition of 5-fold higher concentrations of various interfering molecules with 5×10^{-3} M Hydrazine:**b)** Dopamine, **c)** Serotonin, **d)** Formaldehyde, **e)** Ascorbic acid and **f)** Hydrogen peroxide, **g)** NH_4^+, and **h)** NO_3^-

Supporting Information 6: Evaluation of the repeatability and storage stability of the CuO-Si HNW nanostructure

The repeatability and storage stability are the parameters of prime importance in analytical studies. Herein, the aforesaid parameters were studied for the CuO-Si HNW catalyst using cyclic voltammetry in 0.1 M NaOH containing 5.0×10^{-3} M N_2H_4. For the case of repeatability, the CVs were obtained for 30 consecutive cycles (**Figure S5a**). In contrast, the storage stability was assessed on a daily basis over a period of one month (**Figure S5b**). The responses obtained from both studies were remarkable with an SD of 0.061 and 0.14 (inset, **Figure S5a and b**), respectively.
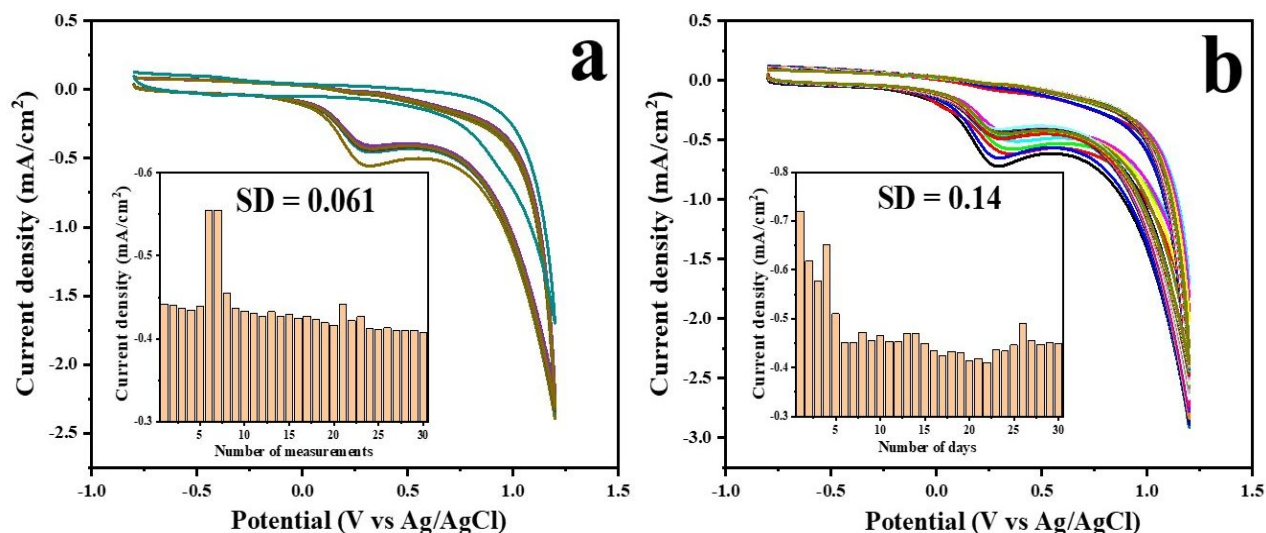

Figure S5: **a)** The cyclic voltammetric response of the CuO-Si-HNW-modified electrode in 0.1 M NaOH at 50 mV/s for 1.0×10^{-3} M N_2H_4 [30 repetitive measurements on the same day (the inset shows the current response of N_2H_4 vs. the number of measurements)], **b)** the response obtained over a period of one month; a single measurement recorded each day (the inset shows the current response of N_2H_4 vs. the number of days).

Supporting Information 7: Table S1 showing change in current density with sequential addition of N_2H_4 at different voltages

Table S1: Variation of current density of 3-D CuO-Si HNW electrode at different applied voltages vs Ag/AgCl upon sequential addition of N_2H_4 .

N_2H_4 concentration (μM)	Current density obtained at 0.5 V (mA/cm²)	Current density obtained at 0.6 V (mA/cm²)	Current density obtained at 0.7 V (mA/cm²)	Current density obtained at 0.8 V (mA/cm²)
10	-0.0023±2E-5	-0.00511±5E-5	-0.01147±1E-5	-0.0104±1E-5
30	-0.00857±8E-5	-0.01684±8E-5	-0.02365±2E-5	-0.02873±2E-5
50	-0.02797±2E-4	-0.03414±2E-4	-0.03877±3E-4	-0.04967±4E-4
100	-0.04525±4E-4	-0.05261±4E-4	-0.05858±5E-4	-0.06805±6E-4
200	-0.12112±1E-3	-0.10555±1E-3	-0.11121±1E-3	-0.13537±1E-3
300	-0.18268±1E-3	-0.17452±2E-3	-0.1848±1E-3	-0.22009±2E-3
400	-0.24896±2E-3	-0.25331±3E-3	-0.25835±2E-3	-0.31648±3E-3
500	-0.31134±3E-3	-0.31199±3E-3	-0.32875±3E-3	-0.43887±3E-3
600	-0.39037±4E-3	-0.39773±5E-3	-0.41038±3E-3	-0.53064±4E-3
700	-0.47021±5E-3	-0.48861±7E-3	-0.49554±4E-3	-0.63524±5E-3

800	-0.55547±5E-3	-0.59208±8E-3	-0.55745±5E-3	-0.738±7E-3
900	-0.6281±6E-3	-0.67188±8E-3	-0.63927±6E-3	-0.85067±7E-3
1000	-0.70706±9E-3	-0.74573±9E-3	-0.73277±7E-3	-0.95853±8E-3
2000	-1.20696±2E-2	-1.17343±1E-2	-1.31398±7E-2	-1.24282±2E-2
3000	-1.35828±3E-2	-1.38754±3E-2	-1.41592±3E-2	-1.40786±4E-2
4000	-1.53715±5E-2	-1.60651±6E-2	-1.57396±4E-2	-1.59272±3E-2
5000	-1.68541±6E-2	-1.87507±8E-2	-1.71732±3E-2	-1.72485±5E-2
7000	-1.91653±7E-2	-2.12487±9E-2	-1.92757±5E-2	-1.90954±8E-2
10000	-2.23213±8E-2	-2.52845±9E-2	-2.23362±3E-2	-2.30075±8E-2
15000	-2.83369±6E-2	-3.17481±9E-2	-2.70771±7E-2	-2.70488±9E-2
20000	-3.32201±1.5E-2	-3.90658±2E-1	-3.09427±1.9E-1	-3.27247±0.5E-1