Electronic Supporting Information

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Development of MoS_2-ZnO Heterostructures: An Efficient Bifunctional Catalyst for the Detection of Glucose and Degradation of Toxic Organic Dyes

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1. Experimental

1.1 Reagents and materials

Thioacetamide (TAA, CH_3CSNH_2, 98%), Sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$, 98%), and Nafion solution were purchased from Sigma Aldrich. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, 99%) and ammonia solution (NH_3) were purchased from Alfa Aesar. NaCl, NaOH, NaH_2PO_4 and Na_2HPO_4 were obtained from Alfa Aesar. Glucose and Ethanol (99.8%) were purchased from Scharlau (Spain). Cholesterol, ascorbic acid (AA), urea and citric acid were received from Sinopharm Chemical Regent Co., Ltd. methylene blue (MB) and rhodamine B supplied by MERCK (E. Merck, Darmstadt, F. R. Germany).Sandoz Yellow (SY) was obtained from local market. Phosphate buffer saline (PBS, 0.1 M) was prepared by mixing stock solutions of NaH_2PO_4 (0.2 M) and Na_2HPO_4 (0.2 M). Deionized water was used throughout the synthesis and measurements. For electrochemical measurements of glucose in human blood serum, fresh blood samples were collected from PAEC hospital, Nilore, Islamabad in blood collection tubes and used within 2 hours.

1.2 Synthesis of MoS_2

Synthesis of nanostructured MoS_2 was carried out by hydrothermal method. In the first step, 0.15 g $Na_2MoO_4.2H_2O$ and 0.5 g CH_3CSNH_2 were added in 20 mL aqueous solution under stirring. The prepared solution is poured into 40 mL Teflon-line stainless steel autoclave. The autoclave was maintained at 200^oC for 24 hours. After completing the reaction, the product was collected, washed with ethanol and deionized water several times and centrifuged at 2500 rpm for 20 min. Finally, the product was dried at 70^oC for 10 h in an oven.

1.3 Synthesis ofMoS_2-ZnO heterostructure

The hydrothermal method was also employed to synthesize MoS_2-ZnOheterostructure.The prepared 0.2g MoS_2 is dispersed in 20 mL deionized water by sonication for 30 min. In a separate beaker 0.378g $Zn(NO_3)_2.6H_2O$ was also prepared in 30 mL aqueous solution. The pH of the solution was adjusted to 9-10 by dropping NH_3solution. The dispersion of $MoS_2$was also added in the prepared solution. The whole mixture was kept under stirring for further 30 min.

Finally, the mixture was added into 40 mL autoclave and kept at 180ºC for 6 hours. After completing the reaction, the product was washed three times with ethanol and water. The obtained MoS_2-ZnO heterostructure was dried at 60^{o}Cfor 10 h in an oven.

1.4 Characterization

The phase and purity of the products were examined using Bruker Model D8 Advance X-ray powder diffractometer (XRD) with Cu-Kα radiation (λ = 1.54060 Å). The Raman spectrum was recorded using Horiba Xplora microscope at 532 nm laser. The morphology of the products were analyzed by field-emission scanning electron microscopy (FE-SEM, TESCAN MIRA A-3) equipped with an energy dispersive X-ray (EDX) system and high transmission electron microscope (HRTEM, JEOL JEM-2100 F, 200 kV). UV-Vis diffuse reflectance spectra of pristine MoS_2 and MoS_2-ZnO heterostructures were measured by UV- Vis spectrometer.The BET specific surface area of the synthesized products was measured by using N_2 adsorption–desorption isotherms. The photocatalytic performance of the catalyst were carried out by collecting absorption spectra of dyes methylene blue (MB), rhodamine B (RhB) and sandoz yellow (SY).

1.5 Electrochemical measurements

The electrochemical experiments were performed at room temperature using electrochemical workstation (CHI660E, China) with three-electrode configuration. A small amount of ZnO, MoS_2 and MoS_2-ZnO were dispersed in Nafion via sonication for 30 minutes. The suspension was then immobilized on glassy carbon electrode (GCE) via dropcasting. The fabricated electrodes (ZnO/GCE, MoS_2/GCE and MoS_2-ZnO/GCE) were served as the working electrodes for cyclic voltammetry and amperometric measurements whereas Hg/Hg_2Cl_2 and Pt used as the reference and counter electrode respectively. Cyclic voltammetry (CV) was performed in the potential range +0.8 to -0.5 V at scan rate of 50 mV/s and amperometric response was carried out at -0.35 V in 0.1M PBS (7.0 pH) under the mild stirring.

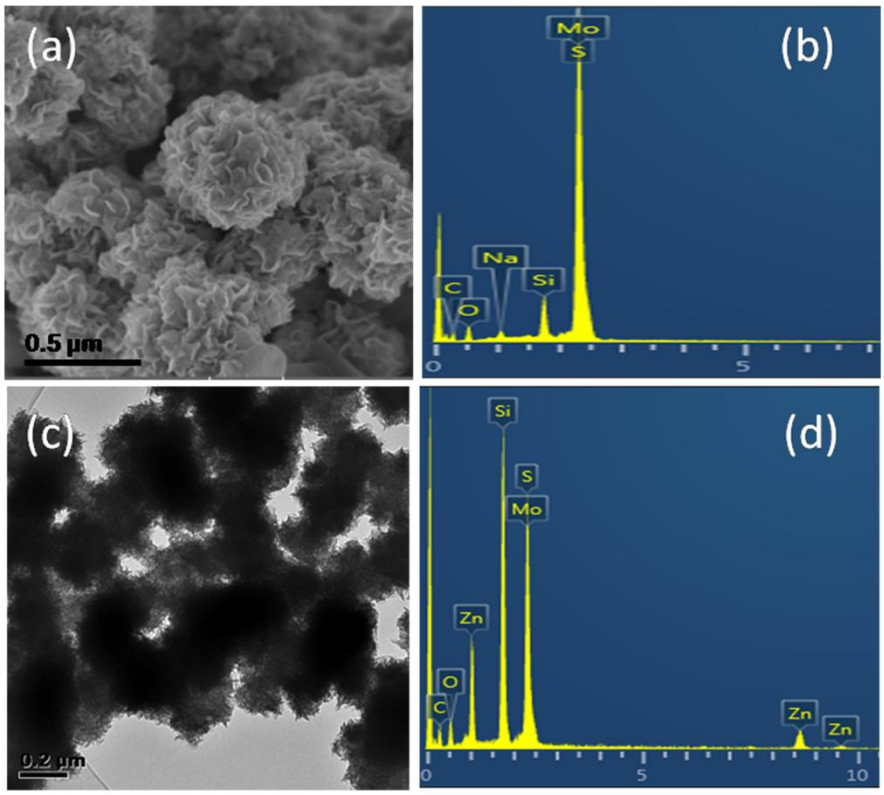

Figure S1: FESEM image of (a) MoS_2 nanoflowers (c) MoS_2-ZnO heterostructure. The corresponding EDS spectrum of (b) MoS_2 nanoflowers and (d) MoS_2-ZnO heterostructure.

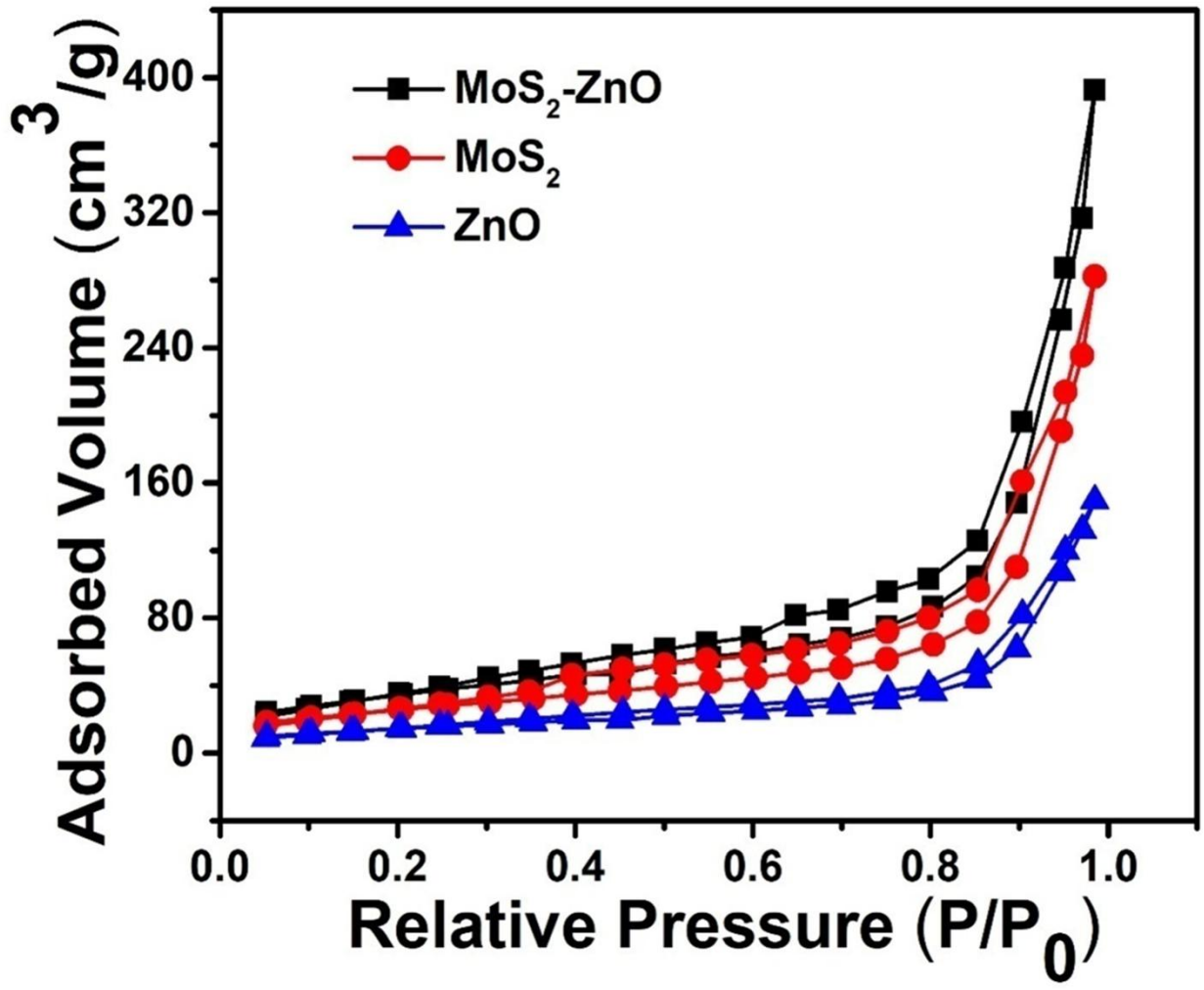

Figure S2: BET surface area nitrogen adsorption-desorption isotherms of MoS_2-ZnO heterostructure, pristine MoS_2 and ZnO.

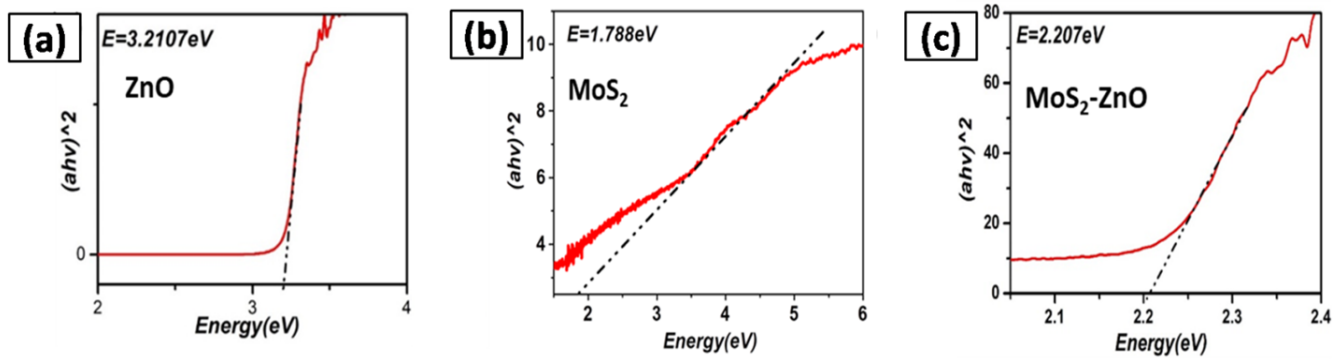

Figure S3: Band gaps of ZnO, MoS_2 and MoS_2-ZnO estimated by $(\alpha h\upsilon)^2$ vs. photon energy curve.

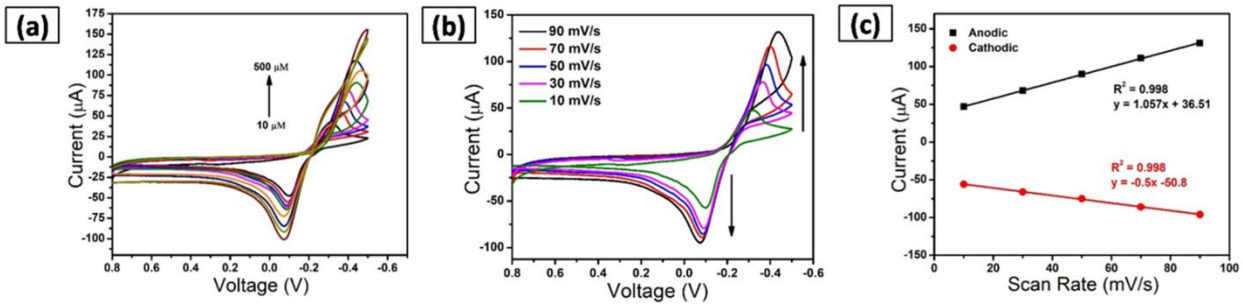

Figure S4: (a) CV response of MoS_2-ZnO/GC electrode in the presence of glucose concentrations in the range 10-500 µM glucose. (b) CV response of MoS_2-ZnO/GC electrode at different scan rates in the presence of 100 µM glucose. (c) Peak current versus scan rate.

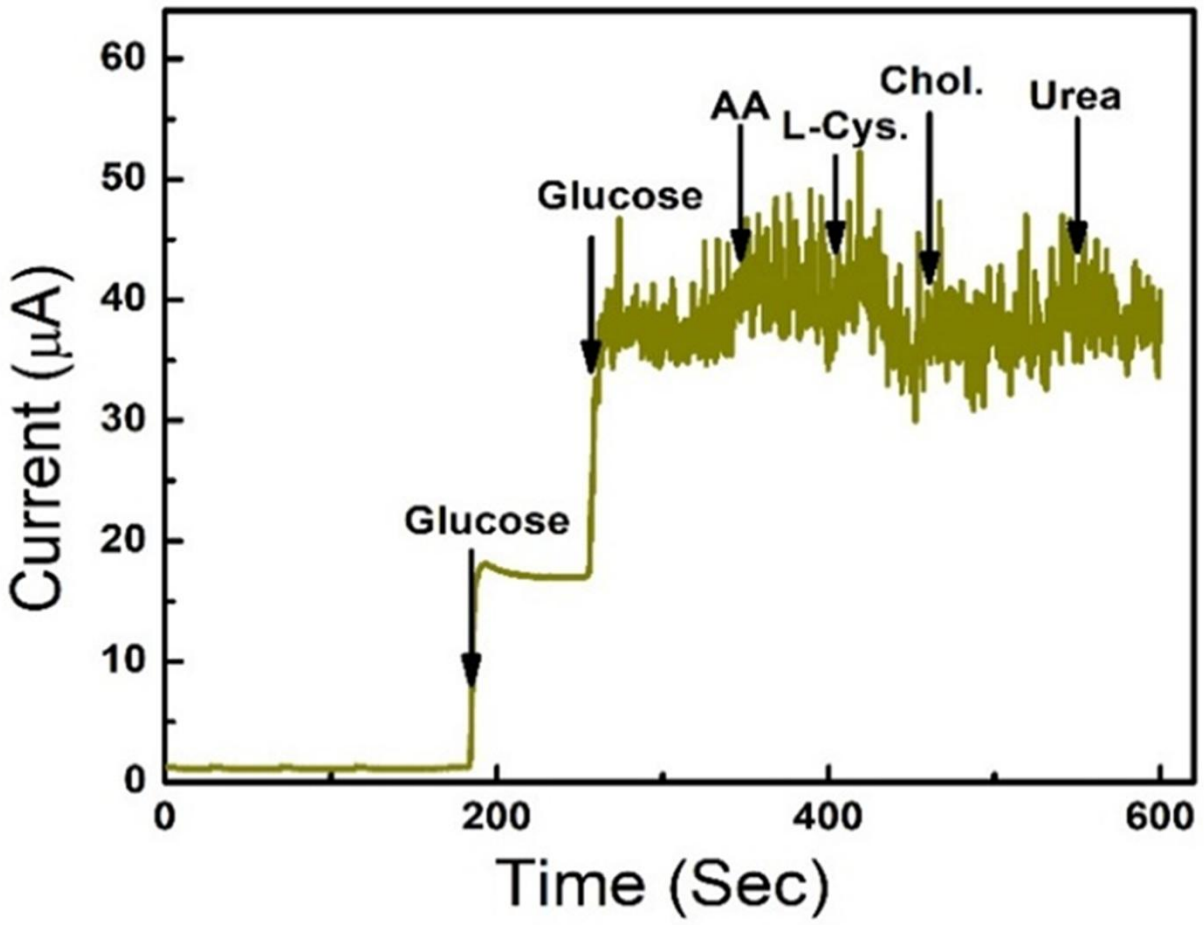

Figure S5: Selectivity of the MoS_2-ZnO/GC electrode adding different electroactive species.

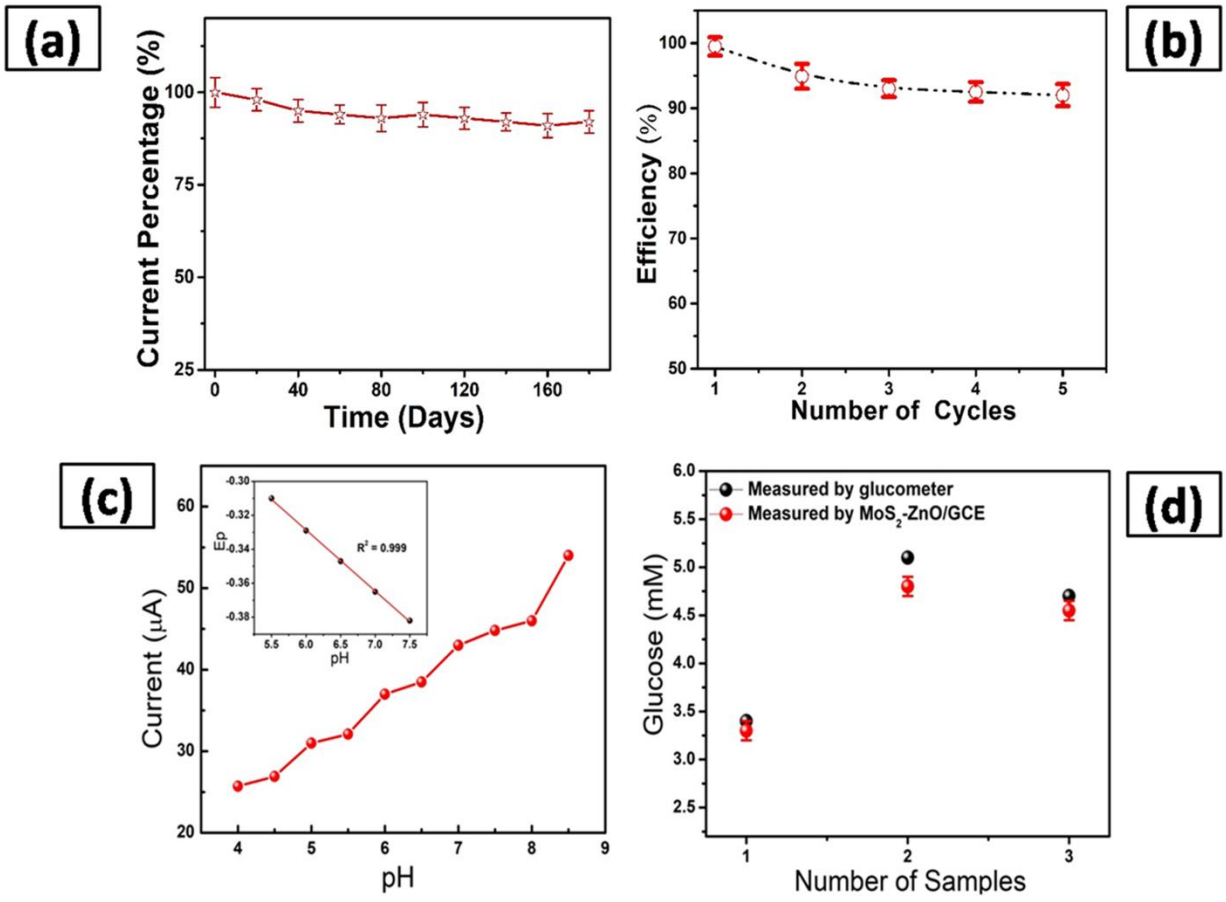

Figure S6: (a) Efficiency of MoS_2-ZnO/GC electrode for 150 days. (b) Repeatability and stability of the MoS_2-ZnO/GC electrode for 5 cycles in the presence of 50 µM glucose.(c) Effect of pH of 0.1 M PB solution on the performance of MoS_2-ZnO/GC electrode for glucose detection: inset is the Ep vs pH from the linear part. (d) Performance of the MoS_2-ZnO/GC electrode for the measurement of glucose in human blood serum.

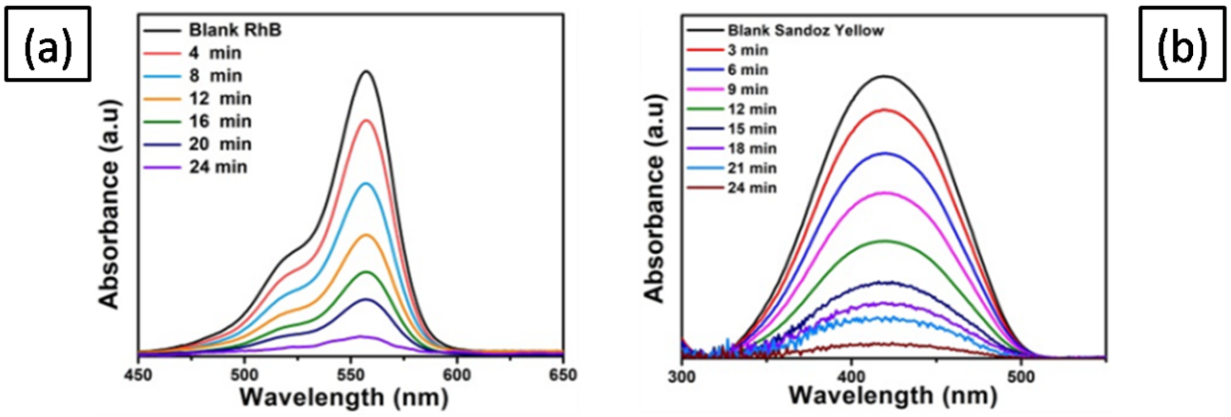

Figure S7 : Time dependent UV-Vis absorption spectral changes of (a) RhB and (b) SY in the presence of MoS_2-ZnO heterostructure.

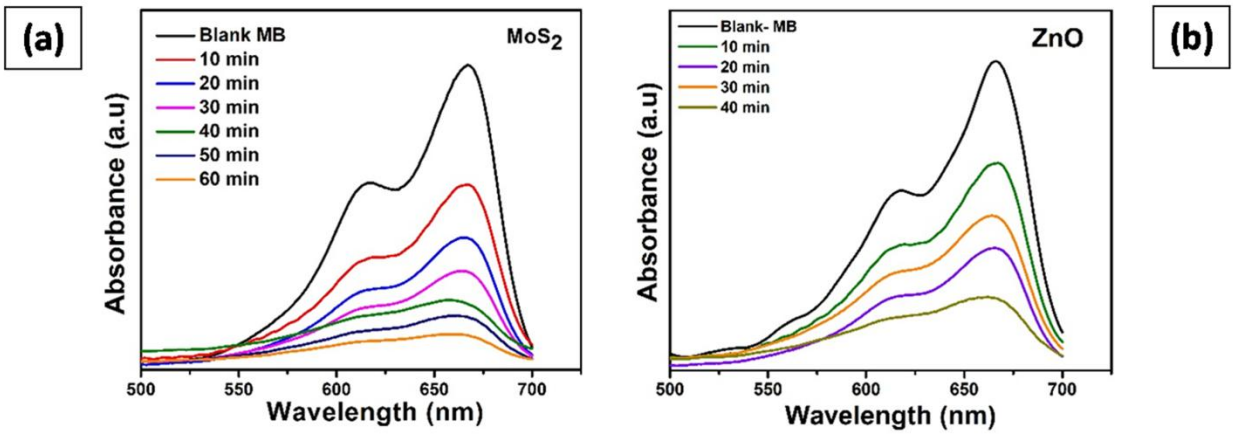

Figure S8: (a) Time dependent UV-Vis absorption spectral changes of MB in the presence of (a) MoS_2 and (b) ZnO structure

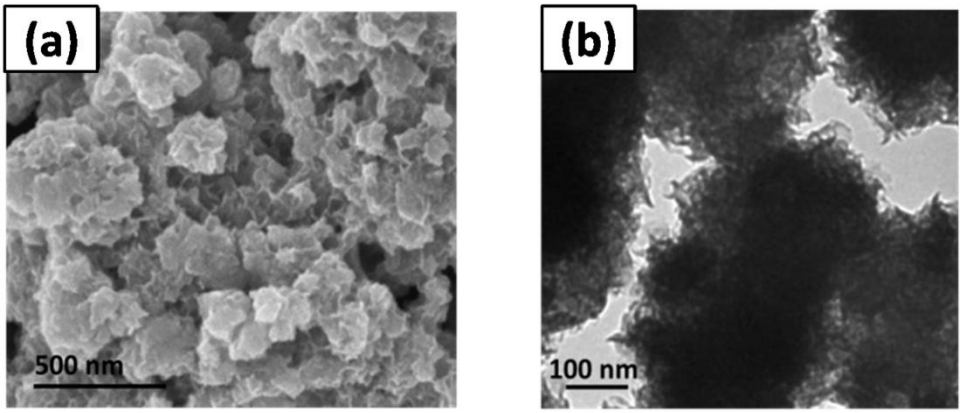

Figure S9: (a, b) FESEM and TEM images after five cycles of operation.

Table S1. Comparison of glucose detection by glucometer and retrieval of glucose in real blood samples using MoS_2-ZnO/GC electrode.

Blood serum Samples	**Glucose measured by glucometer (mg/dL)**	**Glucose measured by MoS_2-ZnO/GCE (mg/dL)**	**Recovery (%)**	**RSD (%)**
Sample # 1	91.8	86.4	94.1	1.05
Sample # 2	115.2	113.4	98.4	2.36
Sample # 3	84.6	81.9	96.8	1.21

Table S2. EIS fittings

Sample ID	**R_s(Ω)**	**R_{ct}(Ω)**
MoS_2	6.524	337.9
MoS_2-ZnO	1.747	123.5

Table S3. Comparison of k-values

Dye	**RHB**	**MB**	**S.Y**
K value (1/s)	0.035772	0.07458	0.076016