

Supporting Information:

Photoelectrocatalytic Oxidation of NADH by Visible Light Driven Plasmonic Nanocomposites

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EXPERIMENTAL SECTION

Materials. Zn (CH₃COOH)₂ · 2H₂O and Urea were purchased from Merck, India. HAuCl₄ and Azure A chloride were obtained from Sigma-Aldrich. Other chemicals used in this investigation were of analytical grade and used without further purification. All solutions used during the experiments were prepared using deionised water obtained from Millipore system.

Characterization. The as-synthesized RB-ZnO and RB-ZnO/Au were characterized by a field emission scanning electron microscope (FE-SEM, ZEISS, Supra-55), X-ray diffraction (XRD), X'pert PRO (Pan Analytical) X-ray diffraction unit using Ni filtered CuK α ($\lambda = 1.54 \text{ \AA}$) radiation, transmission electron microscope (FEI, TECHNAI G2 transmission electron microscope operating at 200 kV), UV-Vis absorption Spectroscopy, SHIMADZU (UV-2600), X-ray photoelectron spectroscopy (Prevac, Poland), Raman Instrument (Renishaw in Via Raman microscope).

Synthesis of Raspberry shaped ZnO nanostructure (RB-ZnO). Synthesis of Raspberry shaped ZnO structure was carried out by adopting a facile microwave assisted solution phase approach. In a typical procedure, Zn (CH₃COOH)₂ · 2H₂O and urea were taken in stoichiometric amount. This mixture was then dissolved with minimum quantity of deionised water and then 50 ml of ethylene glycol was added to it. The mixed solution was placed in the microwave instrument at 900 W for about 10 min. After the completion of reaction, the product was thoroughly washed with copious amount of deionised water followed by absolute ethanol and dried at 85 °C in a hot air oven.

Synthesis of AuNPs decorated RB-ZnO hybrid nanostructures (RB-ZnO/Au): The Functionalization of the RB-ZnO structures was carried out by a simple wet chemical reduction method. In a typical procedure, 0.5 gm of the as synthesized RB-ZnO is dispersed in water via sonication and to it 5ml of certain percentage HAuCl₄ solution (0.01, 0.03, 0.05, 0.1 or 2%) was added. Then 800 μ l of 0.002M NaBH₄ was added by drop wise under stirring condition. After 10 min the suspension was filtered, washed and placed in a hot air oven to dry and stored in the desiccator prior to use.

Electrochemical Measurements. All the electrochemical measurements were carried out by taking a two compartment three electrode cell. Here glassy carbon electrode is taken as the working electrode, a bare Pt wire electrode as the counter and Ag/AgCl as the reference electrode. All the electrochemical measurements were recorded in an argon atmosphere. The electrochemical measurements are recorded by using a computer

controlled CHI660C electrochemical work station. The as-synthesized nanoparticles are dispersed over glassy carbon electrode with nafion and dried prior to electrochemical experiments.

The Photoelectric measurements were carried out by illuminating 1cm^2 of the working electrode at zero bias voltage against Ag/AgCl electrode in $0.01\text{M Na}_2\text{SO}_4$ as the supporting electrolyte. Here the Photocurrent action spectra was obtained with a 100W lamp (Luminous Intensity 530 (max) cd) and the generated photocurrent signals were measured by the CHI 660C electrochemical work station. Similarly the NADH Photoelectrocatalytic oxidation was carried out by taking 0.1M phosphate buffer (pH 7.2) solution as the supporting electrolyte. The photon to electron conversion was calculated using a monochromatic light (sodium low pressure vapor lamp, $\lambda = 589\text{ nm}$).

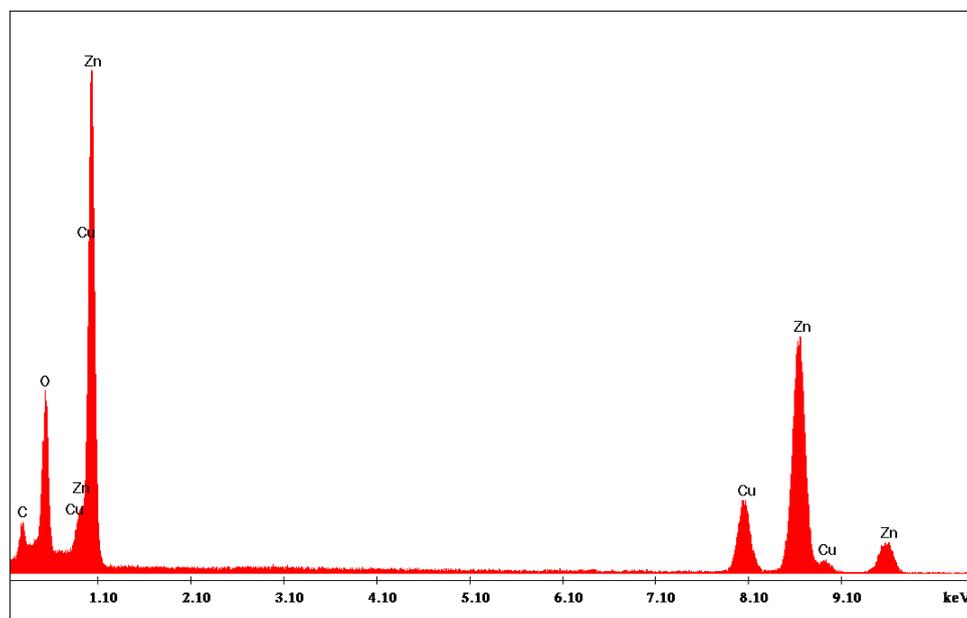


Figure S1. EDAX of RB-ZnOs

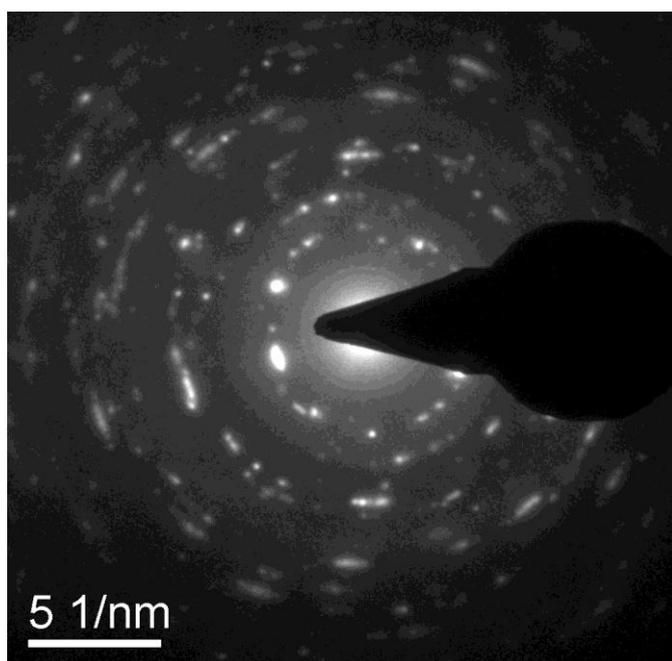


Figure S2. SAED pattern of RB-ZnOs

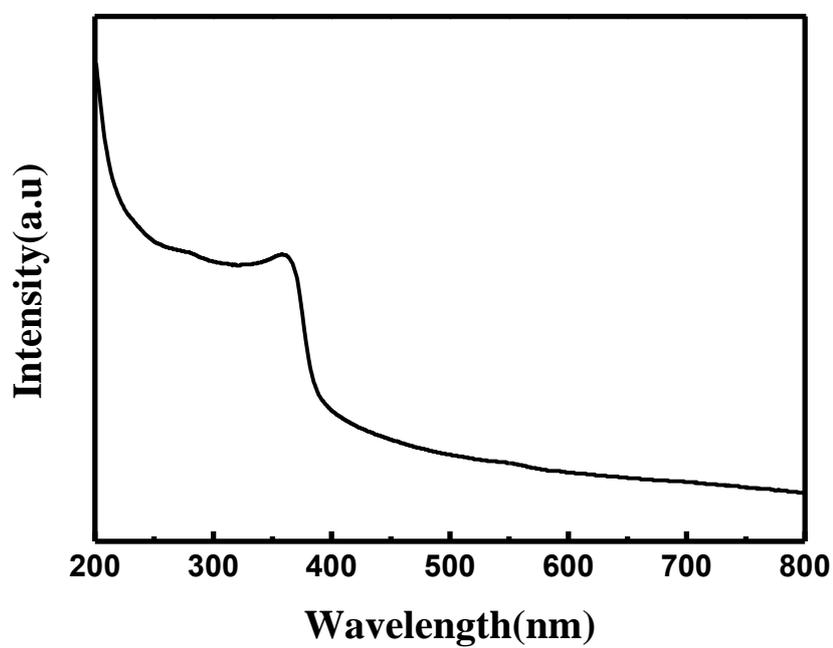


Figure S3. UV-Visible spectrum of RB-ZnOs

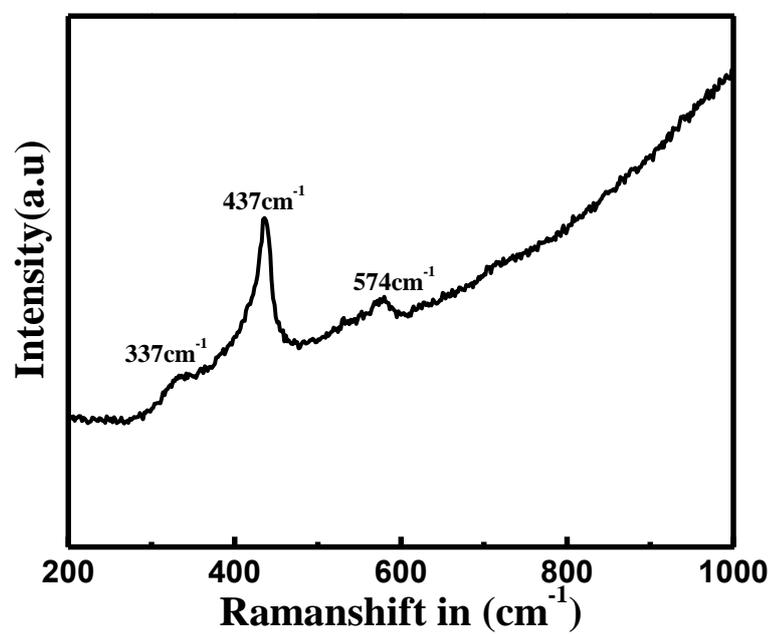


Figure S4. Raman spectra of RB-ZnOs

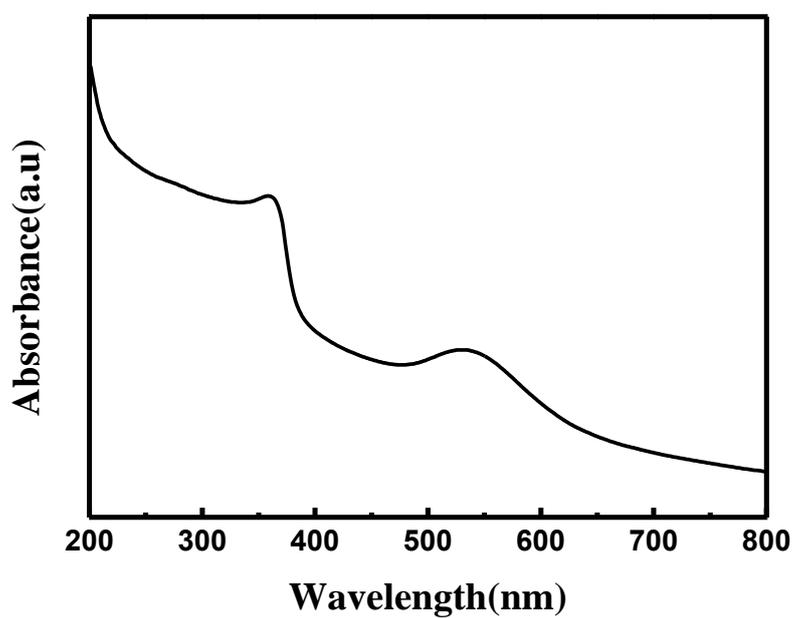


Figure S5. UV-Visible spectrum of RB-ZnO/Au NCs

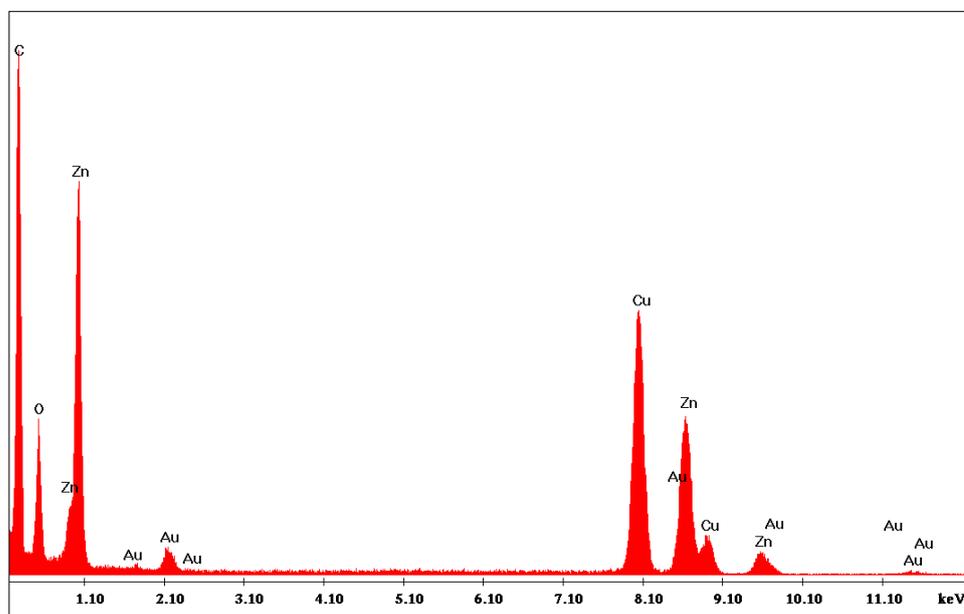


Figure S6. EDAX of RB-ZnO/Au

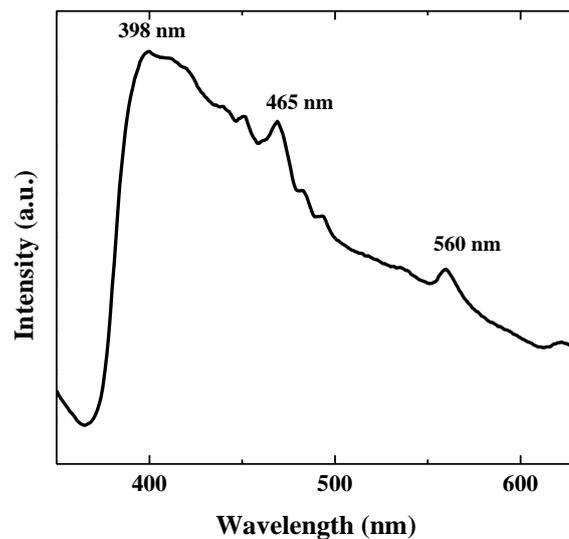


Figure S7. The photoluminescence spectra of as synthesized RB-ZnO. Excited at 320 nm

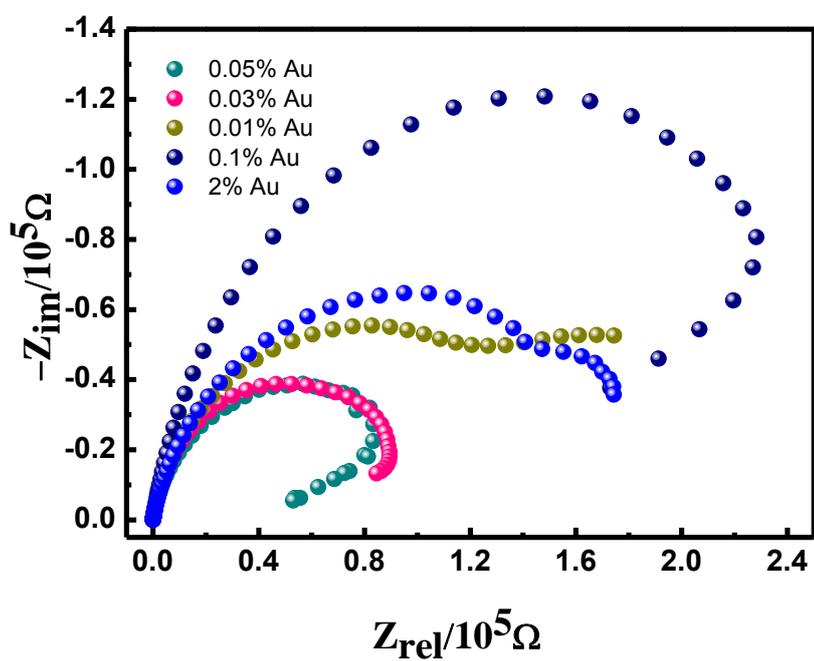


Figure S8. Impedance plot (Nyquist) for RB-ZnO/Au at different percentage of Au loading.

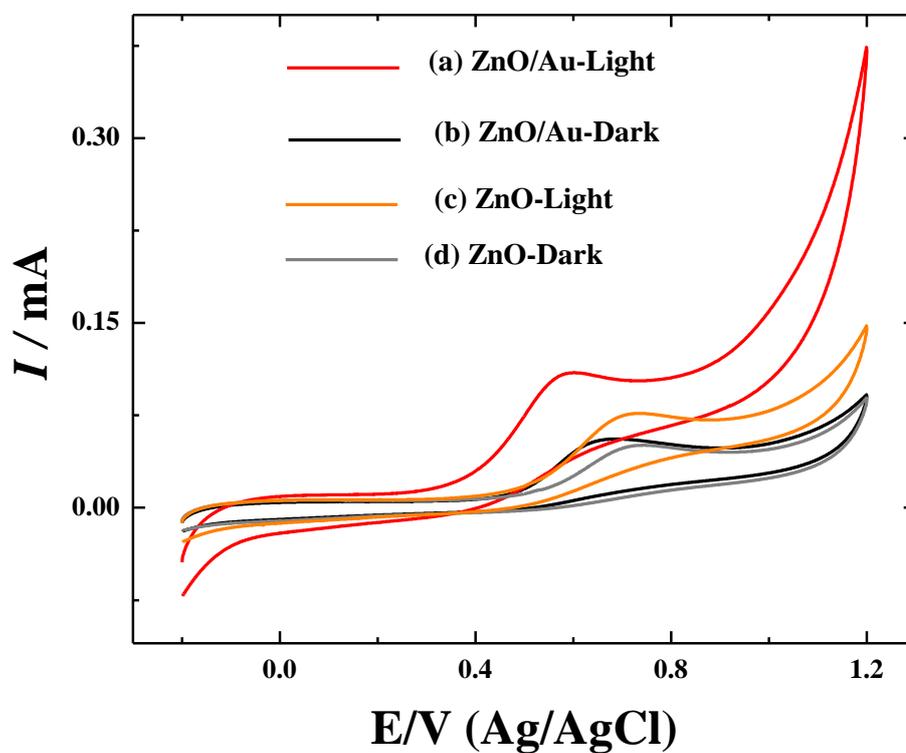


Figure S9. The CV for oxidation of NADH (0.5mM) at (a, b) RB-ZnO/Au and (c, d) RB-ZnO modified electrodes in the presence (a, c) and absence (b,d) of light respectively. Electrolyte: PBS medium (pH: 7.2). Scan rate: 10 mV/s

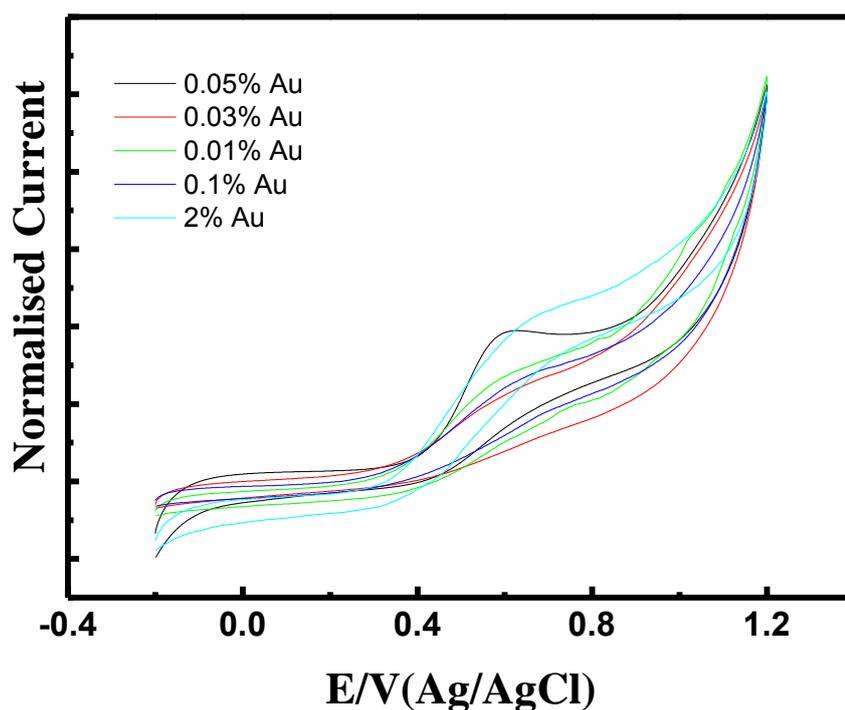


Figure S10. The CV for oxidation of NADH (0.5mM) at different percentage of Au loaded RB-ZnO/Au in the presence of light. Electrolyte: PBS (pH: 7.2). Scan rate: 10 mV/s. Table 1 shows the summarized oxidation potential of NADH at different electrodes.

Table 1

Photocatalysts	Oxidation Potential for NADH
RB-ZnO	0.73V
ZnO-Au(2%Au)	0.72V
ZnO-Au(0.1%Au)	0.69V
ZnO-Au(0.01%Au)	0.66V
ZnO-Au(0.03%Au)	0.64V
ZnO-Au(0.05%Au)	0.60V