

Electronic Supplementary Information

Electrocatalytic Oxidation of Water at Polyoxometalate Nanoparticles Modified Gold Electrode

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Experimental Section

Chemicals and instruments: Sodium dodecyl sulfate (SDS) and poly(vinylpyrrolidone) (PVP) were purchased from Sigma-Aldrich. Molybdic acid and phosphoric acid were purchased from SD Fine Chemical Limited. All the chemicals and reagents were used as purchased without further purification. Phosphate Buffer Saline (PBS) solution (0.1M) was used to maintain the pH of the medium. All the solutions were made in double distilled water.

Infrared spectroscopic investigations were done by using Shimadzu Spectrometer IR Prestige 21 in the region 4000-400 cm^{-1} using KBr pellet. UV-Vis absorption spectroscopic data were obtained from JASCO V-670 spectrophotometer. Transmission electron microscopic (TEM) characterizations were performed using JEM-2100, Jeol microscope. Scanning electron microscopic characterizations along with the energy-dispersive X-ray spectroscopy (SEM-EDX) were performed using instrument JSM – 6360, Jeol. All the electrochemical measurements were executed using CHI 660C, Electrochemical workstation, a conventional three-electrode cell consisting of Au electrode (2 mm diameter) as working electrode, Ag/AgCl (3M KCl) as reference electrode and Pt-wire as auxiliary electrode. pH of the solution was measured by using pH meter from Macro Scientific Works (Regd), New Delhi. The amount of oxygen was measured by using a calibrated Ocean Optics FOXY probe. The Faraday efficiency was calculated by the relation: Faraday efficiency (%) = (Amount of $\text{O}_2 \times$ Number of electrons needed to produce O_2) / amount of charge passed to the solution.

Synthesis of Phosphomolybdic acid, $[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$ (HPMo): Phosphomolybdic acid (HPMo) was synthesized by using modified literature procedure [T. J. Hastings, H. A. Frediani, *Anal. Chem.* 1948, **20**, 382–383]. To an aqueous solution of molybdic acid (0.162 g, 1 mmol in 25 mL water), 0.5 ml of phosphoric acid (0.049 g, 0.5 mmol) was added drop wise with constant stirring. The colour of the solution was changed to light yellow. The mixture was refluxed for 2- 3 hours to yield a yellow precipitate of phosphomolybdic acid. The precipitate was filtered, washed and dried in vacuum.

Synthesis of [HPMo] nanoparticles: The nanoparticles of phosphomolybdic acid was prepared according to modified literature procedure [G. Maayan, R. P. Biro, R. Neumann, *J. Am. Chem. Soc.* 2006, **128**, 4968-4969]. An aqueous solution of sodium dodecyl sulphate (SDS) (0.0015 g, 0.1 M, 500 μL) was added drop wise to a mixture of aqueous solution of phosphomolybdic acid (0.0037 g, 0.01 M) and a solution of poly(vinylpyrrolidone) (PVP) (0.0002 g, 0.1 M). The solution mixture was kept in a sonicator bath for about 5 minutes and a greenish yellow amorphous solids was formed. In this process, PVP was used to prevent aggregation during the precipitation of phosphomolybdic acid onto the SDS micelle surface and to help anchoring [HPMo]NPs on electrode surface during gold electrode fabrication.

Electrode cleaning and modification: Before immobilizing the SDS-[HPMo] nanoparticle on gold electrode surface, the electrode was polished with 0.05 μm alumina slurry and sonicated in distilled water. After mechanical cleaning the gold working electrode was cleaned electrochemically. For that the electrode was taken in 1.0 M H_2SO_4 and scanned repetitively between potential – 0.47 to +1.77 V with respect to RHE. A reproducible cyclic voltammogram of characteristic features confirmed proper cleaning. The electrode was then washed with double distilled water and dipped in an aqueous solution of [HPMo] nanoparticle for 5-6 hours. The modified [HPMo] NPs/Au electrode was washed with double distilled water and used for further electrochemical studies.

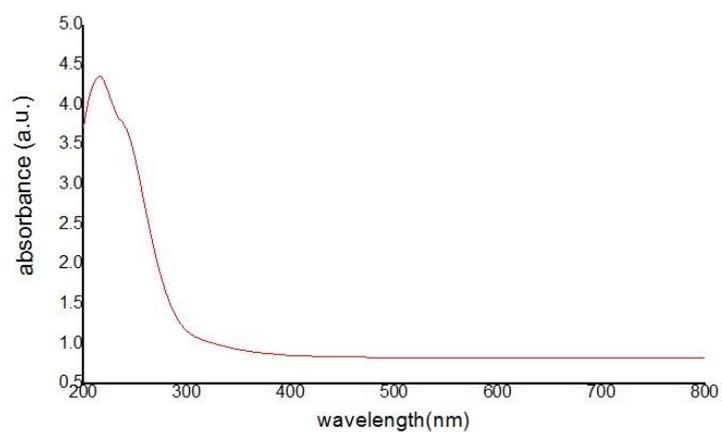


Figure S1 UV-Visible spectra of [HPMo] nanoparticles in water.

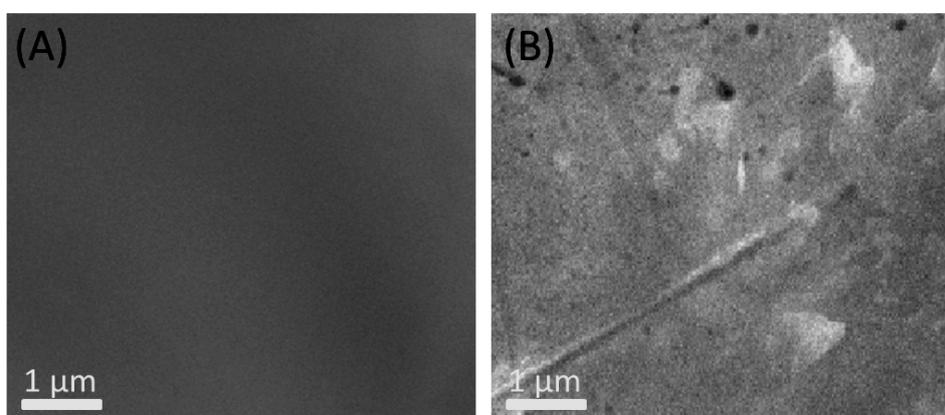


Figure S2 SEM images of bare (A) and [HPMo] nanoparticles (B) modified gold electrodes (scale bars are 1 μm).

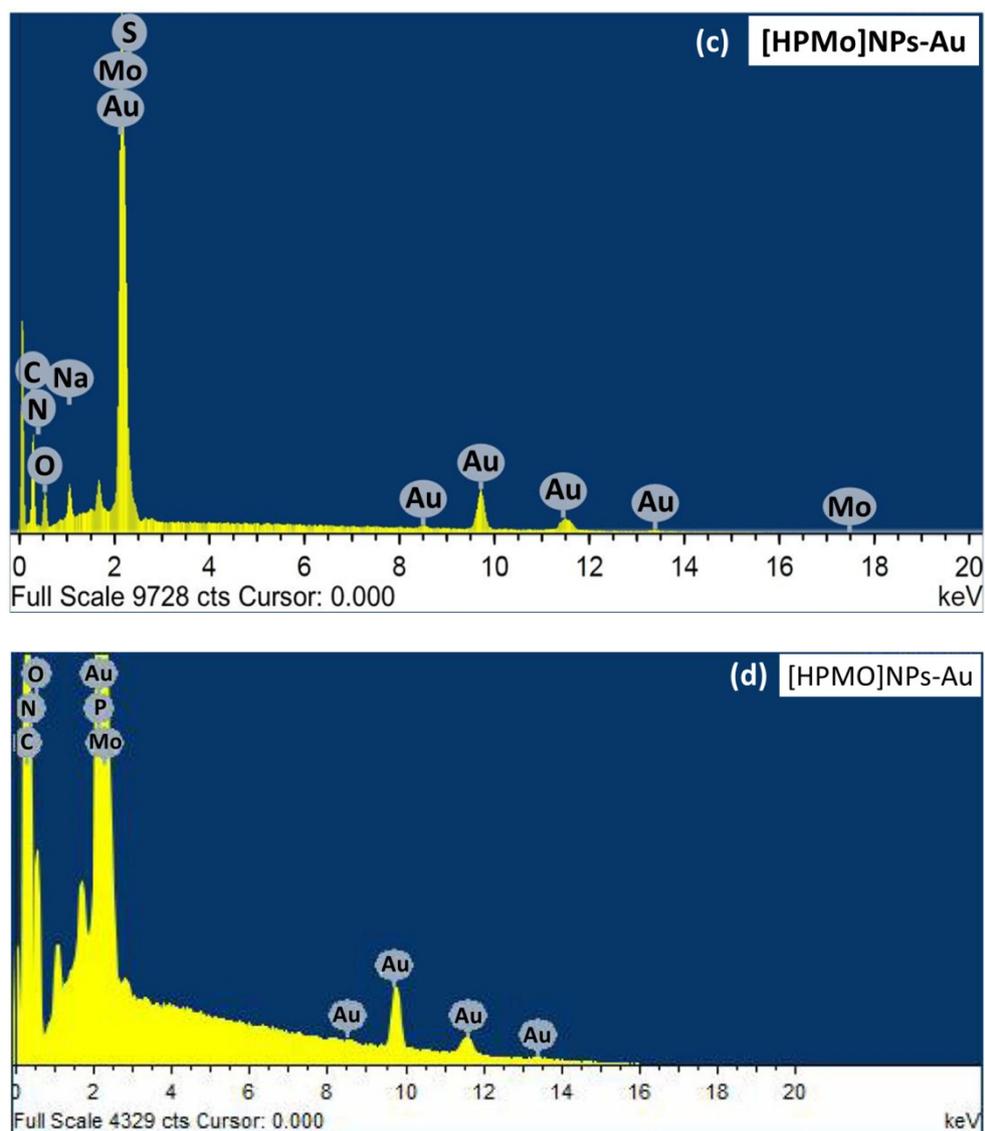
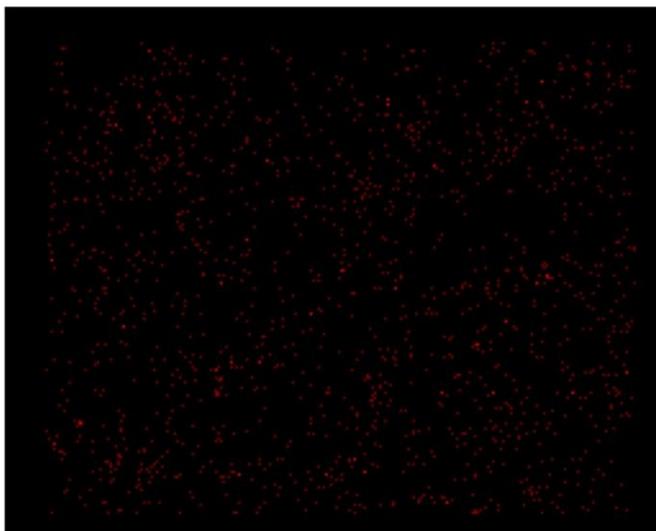
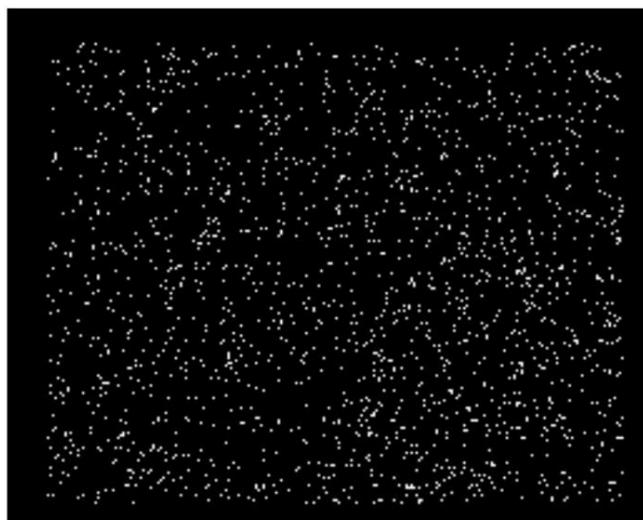


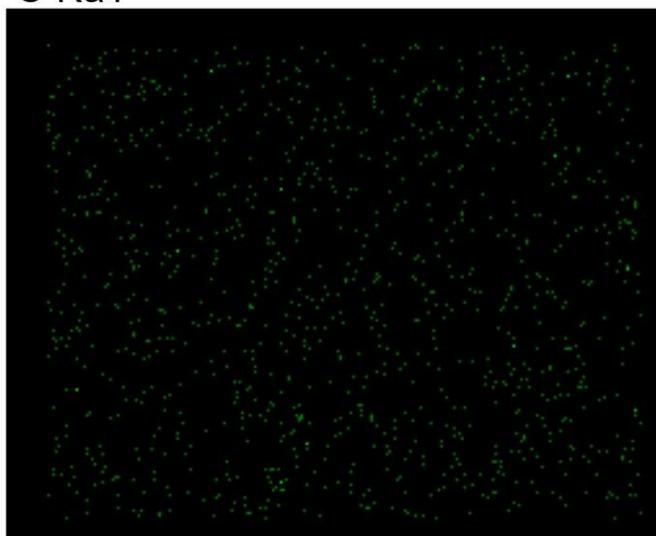
Figure S2 (c) and (d): EDX spectra of [HPMo] nanoparticles modified gold electrode surface



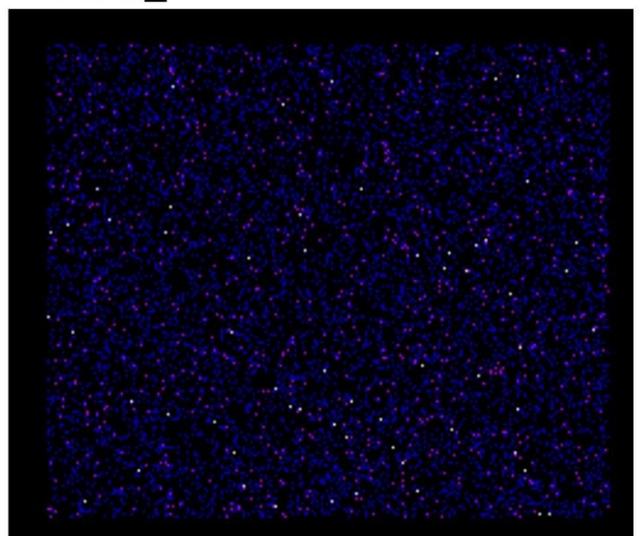
O Kα1



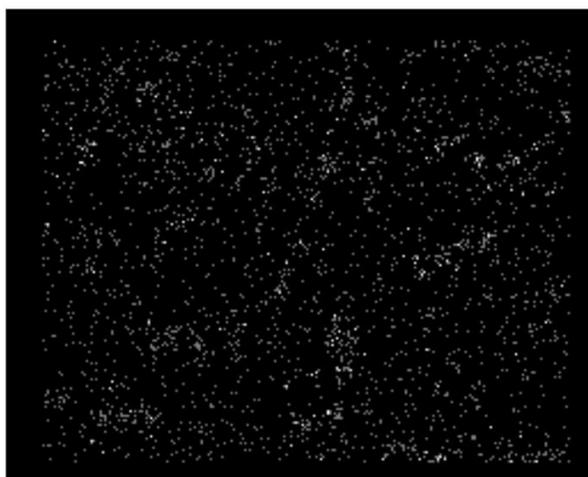
Na Kα1_2



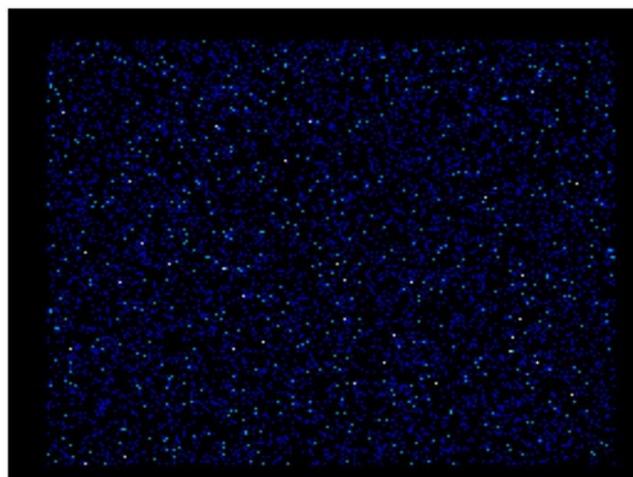
N Kα1_2



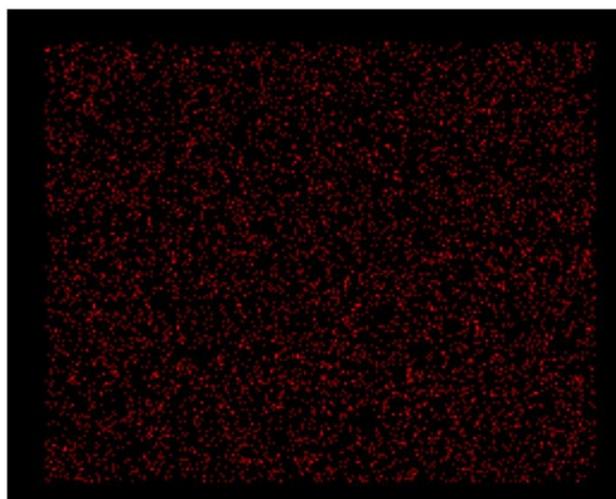
Mo Lα1



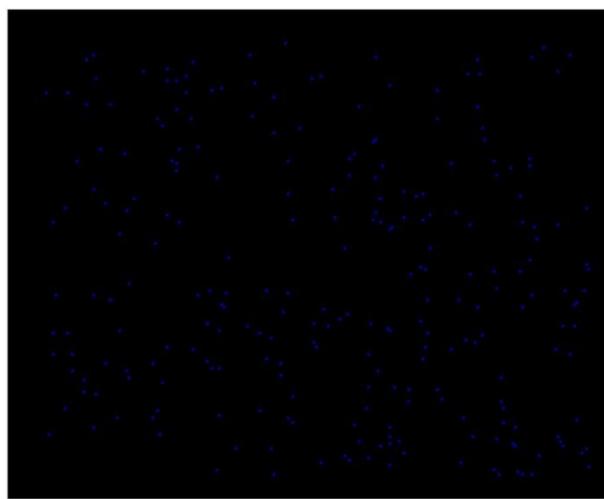
C Kα1_2



Au Lα1



P Ka1



S Ka1

Figure S3 (a-h) Elemental mapping images of oxygen, nitrogen, carbon, phosphorus, sulphur, sodium molybdenum and gold corresponding to the SEM image of [HPMo]NPs modified gold electrode.

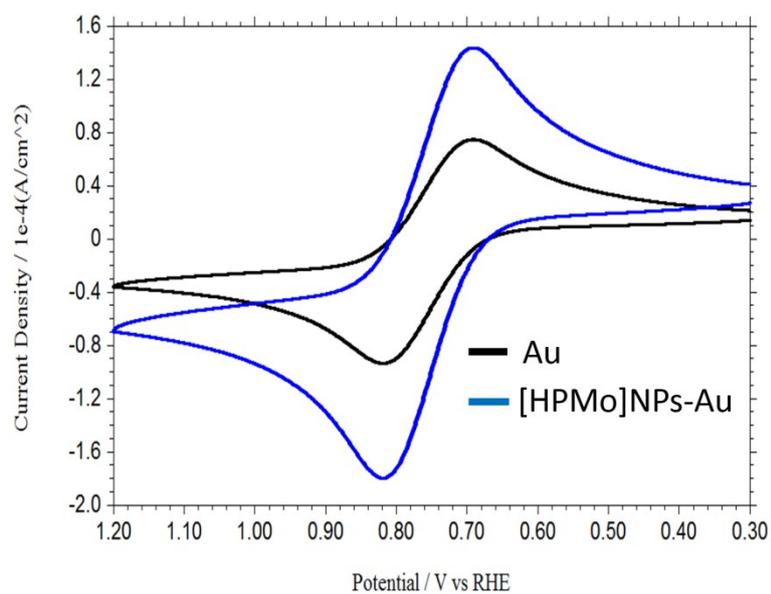


Figure S4 Overlaid cyclic voltammogram of 0.5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M PBS solution at pH 7.0 using bare (black curve) and [HPMo]NPs (blue curve) modified gold electrode.

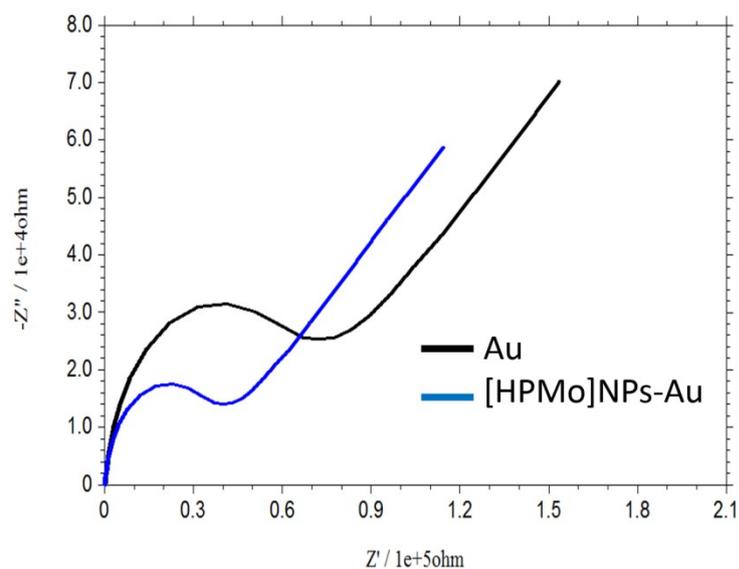


Figure S5 Overlaid Nyquist plot ($-Z''$ and Z') of 0.5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M PBS solution at pH 7.0 using bare (black curve) and [HPMo]NPs (blue curve) modified gold electrode.

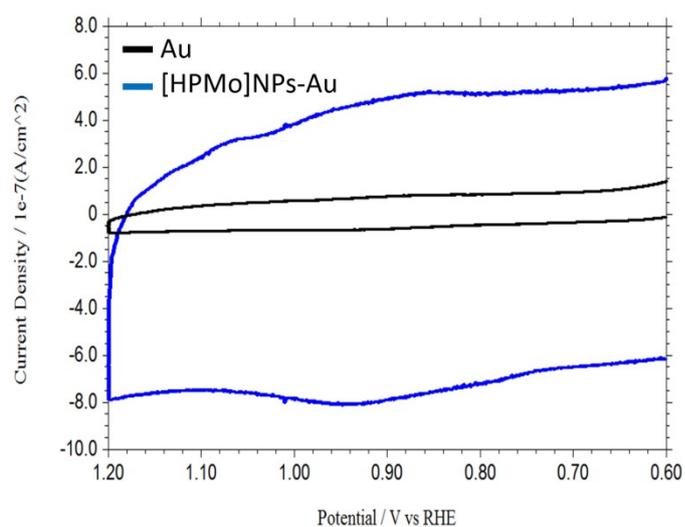


Figure S6 Cyclic voltammograms obtained in 0.1 M PBS solution (pH 7.0) using bare gold (black) and [HPMo]NPs (blue) modified gold electrode.

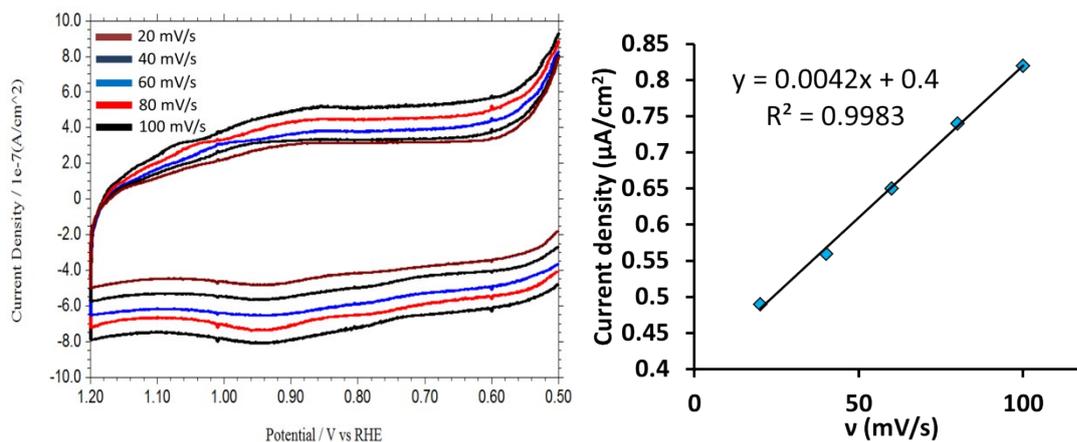


Figure S7 Cyclic voltammograms obtained in 0.1 M PBS solution (pH 7.0) using [HPMo]NPs modified gold electrode at different scan rate (20-100mV/s). Plot of current density *versus* scan rate.

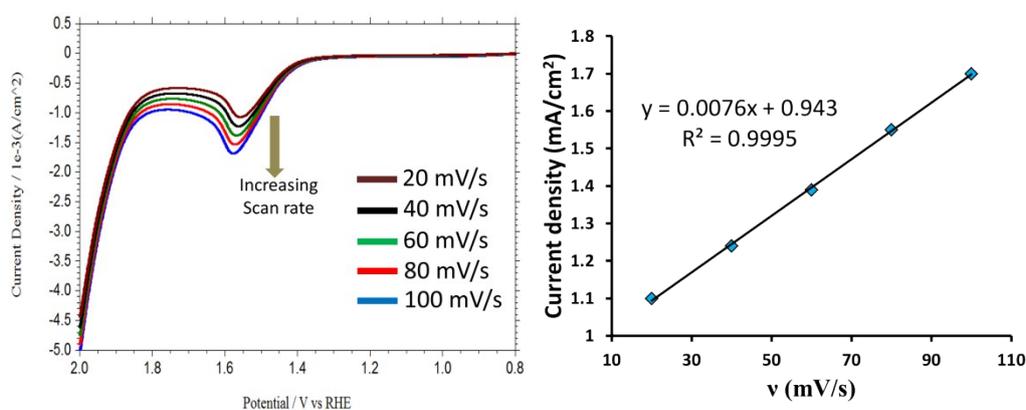


Figure S8 Overlaid LSV obtained in 0.1 M PBS solution (pH 7.0) using [HPMo]NPs modified gold electrode at different scan rate (20-100 mV/s). Plot of current density *versus* scan rate.

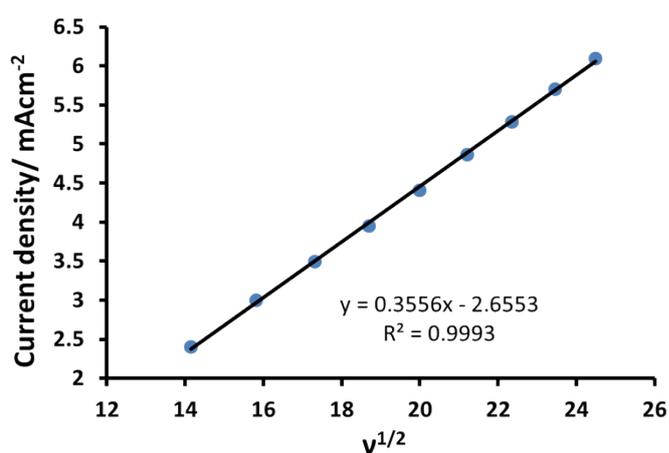


Figure S9 Plot of current density *versus* square root of scan rate (scan rate, 200 - 600 mV/s).

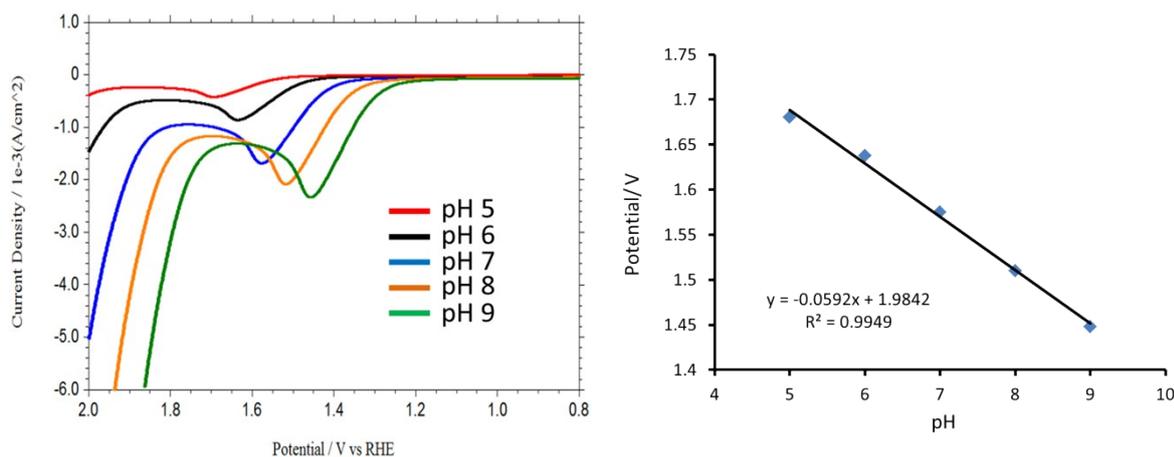


Figure S10 LSV obtained from [HPMo]NPs modified gold electrode at different pH values (5.0 to 9.0) of 0.1 M PBS, Scan rate: 100 mV s^{-1} . A plot of potential *versus* pH of the medium.

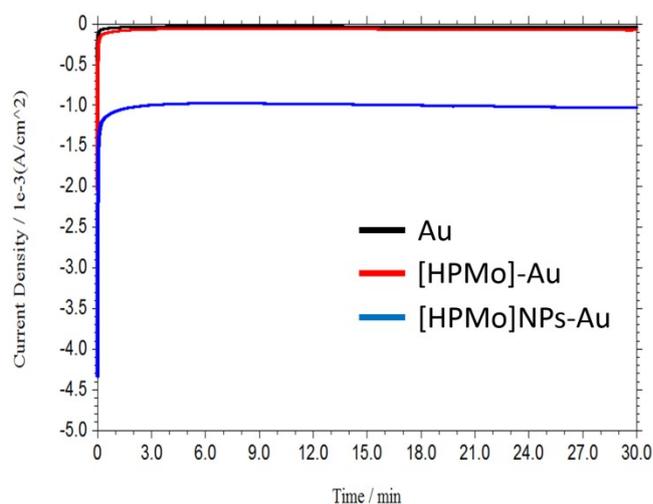


Figure S11 Controlled potential electrolysis at +1.58 V in 0.1 M PBS (pH 7.0) using bare Au, [HPMo]-Au and [HPMo]NPs-Au electrodes.

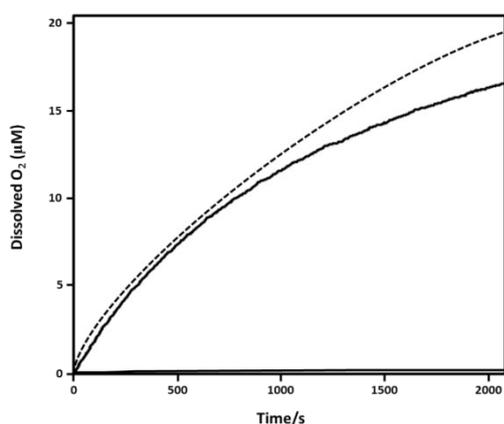


Figure S12 Oxygen evolution during controlled potential electrolysis of water in a gas-tight electrochemical cell in nitrogen atmosphere with and without [HPMo]NPs as measured with a fluorescence probe. Dotted line shows the theoretical oxygen evolution with 100% efficiency.

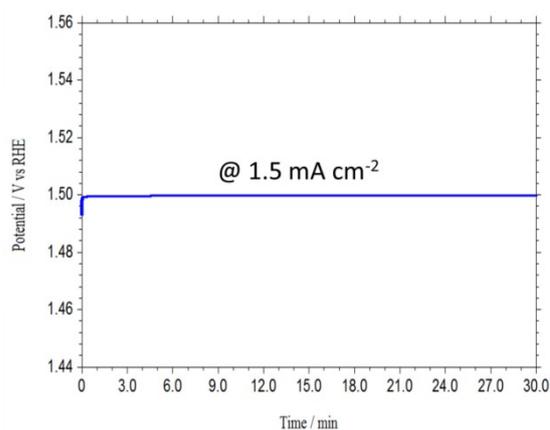


Figure S13 Chronopotentiogram obtained by using [HPMo]NPs-Au electrode in 0.1 M PBS (pH 7.0) at constant current 1.5 mA Cm⁻².

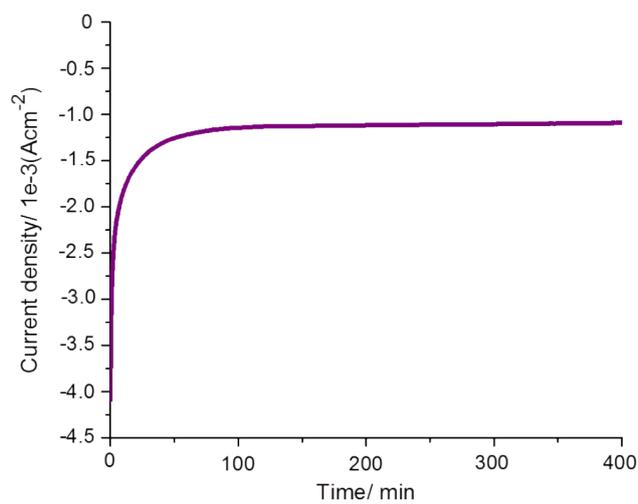


Figure S14 Controlled potential electrolysis using [HPMo]NPs-Au electrode at + 1.58 V *versus* RHE in stirred 0.1 M PBS solution (pH 7.0).

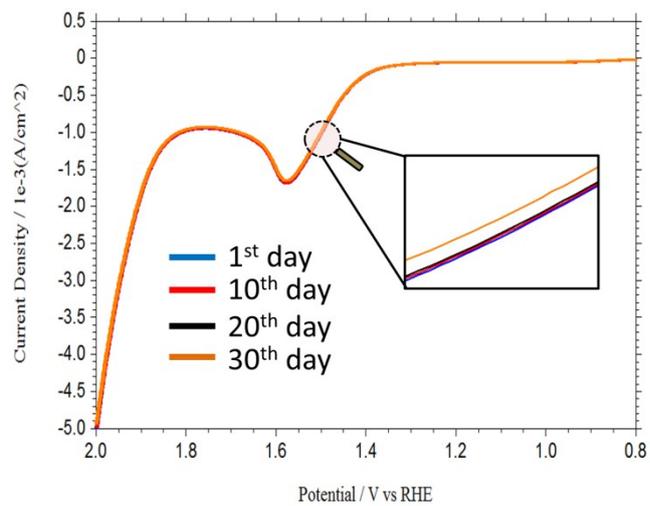


Figure S15 Overlaid LSV taken in ten days interval by using a [HPMo]NPs-Au electrode in 0.1 M PBS solution at pH 7.0.