Electronic Supplementary Information

A new stable Pd-Mn_3O_4 nanocomposite as efficient electrocatalyst for the hydrogen evolution reaction

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EXPERIMENTAL SECTION

Materials:

All reagents were of analytical grade and used without further purification. The glasswares were cleaned well with aqua-regia and double distilled water used throughout the course of experiment.

Instrumentations:

Phase purity of the synthesized samples are characterized by recording X-ray diffraction (XRD) data on a BRUKER-AXS-D8-ADVANCE defractometer equipped with Cu Kα radiation ($\lambda = 1.5418$ Å) with a scan range of 10 - 80° at a scanning rate of 0.5° min^{-1}. X-ray photoelectron spectroscopy (XPS) analysis is done with a SPECS GmbH, Phoibos 100 MCD Energy Analyzer equipped with an Mg Kα excitation source (1283.6 eV) and XPS spectra are corrected using the C 1s line at 284.6 eV followed by curve fitting and background subtraction. Raman spectra were recorded for the solid samples by using a fiber-coupled micro-Raman spectrometer (Horiba Jobin Yvon Technology) equipped with 488 nm (2.55 eV) of 5 mW air cooled Ar^+ laser as the excitation light source, a spectrometer (model TRIAX550, JY), optical microscope (Model BX 41, Olympus, Japan), and a Peltier-cooled CCD detector (Horiba scientific, France).Electron Microscopy (FESEM) is used with a (Supra 40, Carl Zeiss Pvt. Ltd.) microscope at an accelerating voltage of 20 kV. Transmission electron microscopic (TEM) analyses of the samples are performed on a FEI - TECNAI G2 20S – TWIN transmission electron microscope, operating at 200 kV and energy dispersive X-ray microanalyzer (OXFORD EDAX) has been attached to it for compositional analysis. Elemental area mapping analysis is done by AURIGA Compact Scanning Transmission Electron Microscopy (STEM) instrument. ICP-MS was conducted using an Agilent 7500c (Agilent Technologies, Tokyo, Japan). Here, Bi was used as an internal standard.

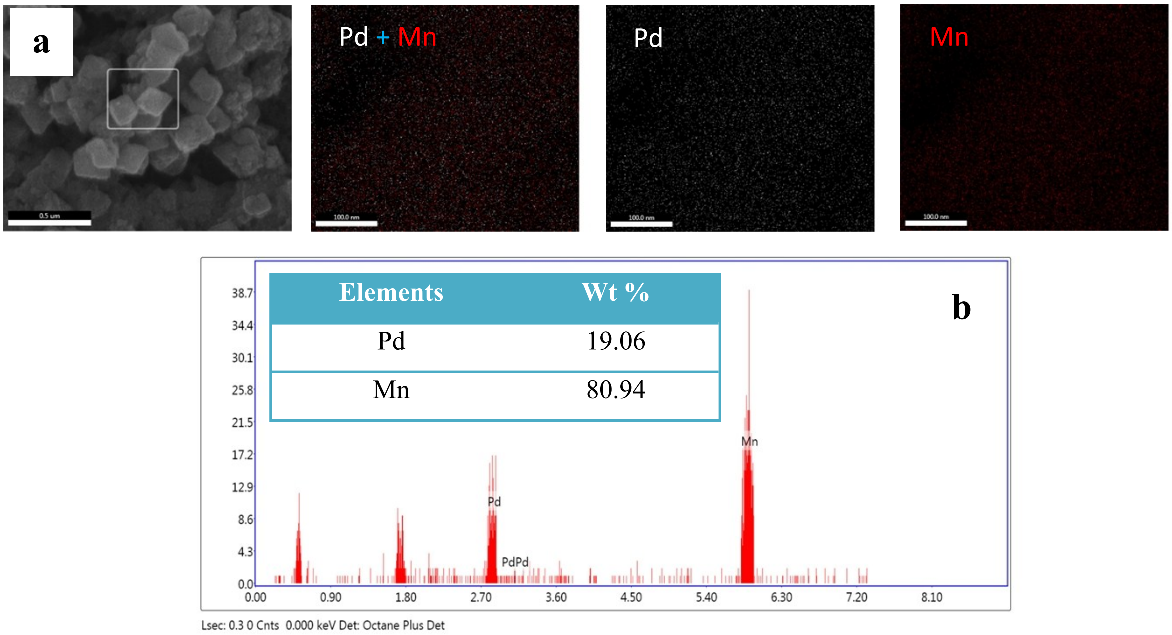
Synthesis of Pd-Mn_3O_4 nanocomposites (PMO):

In the typical synthesis of Pd-Mn_3O_4 nanocomposites, firstly 0.1 mmol manganese acetate tetrahydrate ($C_4H_6MnO_4.4H_2O$) was dissolved in a 10 mL double distilled water. In that solution 1 mL 10^{-2} M aqueous palladium chloride (H_2PdCl_4) solution was incorporated. The pH of the solution was maintained at 7 by addition of 1 M aqueous anhydrous sodium acetate (NaOAc) solution. After that the mixture solution was heated in a 20 mL screw-capped test tube at 160 °C for 6 h under modified hydrothermal (MHT) condition. The product of the redox transformation reaction was washed with water repetitively and finally with ethanol before dried at 60°C. We have also varied the amount of introduced 10^{-2} M H_2PdCl_4 solution e.g., 0.5, 1 and 2 mL and the obtained products were labelled as PMO-0.5, PMO-1 and PMO-2 respectively.

Similarly, Mn_3O_4 nanooctahedrons were also synthesized by following exactly above mentioned procedure except the addition of H_2PdCl_4 solution in reaction mixture.

Measurements of electrocatalytic activities of hydrogen evolution reaction:

The electrochemical characterization and catalytic activity of Pd-Mn_3O_4 nanocomposites (PMO) were investigated using a three electrode cell in CHI 660E taking catalyst coated glassy carbon (GC) electrode (geometric area 0.07 cm^2) as a working electrode, a platinum wire with a diameter of 1 mm as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. To prepare working electrode, at first GC electrode was cleaned by polishing with 1, 0.3, 0.05 μm alumina powder consecutively. Then under ultrasonic condition the electrode was cleaned with distilled water and absolute ethanol respectively for 3 minutes and completely dried in air at room temperature. For hydrogen evolution reaction process 7 μL of as-prepared PMO, Mn_3O_4 and commercial Pt/C catalysts dispersion (1 mg/mL concentration) was drop casted on GC and dried in air for 3 h, which results in a catalyst loading of 7 μg. 7 μL aqueous Nafion solution (0.01%) was applied as a binder of catalyst on GC. 0.5 M H_2SO_4 aqueous solution was used as the supporting electrolyte. Linear sweep voltammetry (LSV) was conducted within the potential range from 0.05 to -0.3 V (vs. RHE) at a scan rate of 2 mVs^{-1} in 0.5 M H_2SO_4 solution under magnetic stirring at 1000 rpm. Electrochemical impedance spectroscopy (EIS) was performed in a frequency range of 0.1Hz – 10^5 Hz with 5 mV amplitude at a bias potential of 0.02 V (vs. RHE). Chronoamperometry curve was recorded at -0.011 V (vs. RHE), resulting in a current density of 10 mA cm^{-2} .All potentials reported in this paper were normalized with respect to the reversible hydrogen electrode (RHE) by adding a value of $(0.242 + 0.059 \times pH)$ V.



Elements	Wt %
Pd	19.06
Mn	80.94

Fig. S1: (a) Elemental area mapping and (b) EDXS analysis of PMO-1 nanocomposite.

Growth Mechanism: To obtain a well-defined Pd NPs decorated Mn_3O_4 nanocomposite, 0.1 mmol of manganese acetate ($Mn(OAc)_2$) and 0.01 mmol H_2PdCl_4 stands to be ideal. Alter mol ratio leads to nanocomposite with inefficient electrocatalytic performance. Fig. S2 represents stepwise evolution of PMO-1 nanocomposite from the reaction between H_2PdCl_4 and $Mn(OAc)_2$ precursors under the experimental reaction conditions. In neutral pH under heating condition formation of Mn_3O_4 from $Mn(OAc)_2$ is thermodynamically feasible.[1] After 1 h of heating in 160°C under our laboratory developed modified hydrothermal reaction condition FESEM image shows formation of some ill-defined tiny Mn_3O_4 nanoparticles (Fig. S2a). After 2 h heating the freshly evolved tiny particles have undergone self assembly and produced Mn_3O_4 nanoocathedrons (NOs) as shown in Fig. S2b. The smooth surface of the NOs has confirmed that Pd NPs formation has not started yet. After prolong heating for 4 h, small nanosphere-like Pd NPs deposition over Mn_3O_4 NOs has been started (Fig. S2c). In neutral pH condition the formal reduction potential of Pd^{2+}/Pd couple increases as well as formal potential of Mn^{3+}/Mn^{2+} couple decreases.[2] As a result, Pd^{2+} to Pd reduction has started slowly with cooperative redox reaction path way. Further heating for 6 h produced completely Pd NPs decorated Mn_3O_4 NOs (Fig. S2d). The smooth surface of Mn_3O_4 becomes roughened by the blister like deposition of Pd(0).

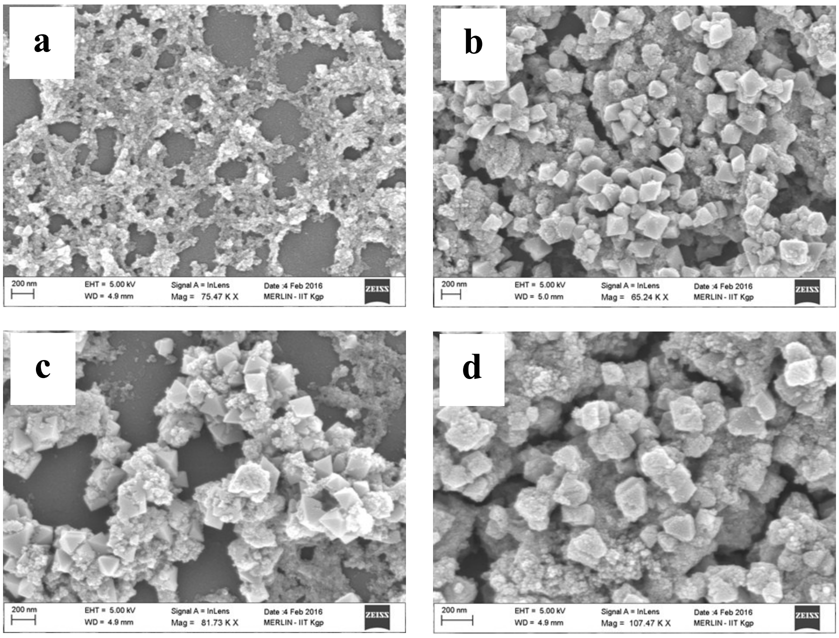


Fig. S2: FESEM images of time dependent synthesis of PMO-1 nanocomposite at (a) 1 h, (b) 2 h, (c) 4 h and (d) 6h.

1. S. Mann, N. H. C. Sparks, G. H. E. Scott, and E. W. De Vrind-De Jong, *Appl Environ Microbiol.*, 1988, **54**, 2140.
2. K. W. Kim, S. M. Kim, S. Choi, J. Kim and I. S. Lee, *ACS Nano*, 2012, **6** , 5122.

Temperature Effect: To study the effect of temperature for redox transformation reaction the reaction mixture was kept at room temperature, 80°C and 160°C for 6 h. At room temperature no product formed, i.e. the reaction does not proceed in forward direction. But after heating at 160°C under MHT condition the reaction proceeds favourably. So, activation energy of this reaction has to be supplied in form of heat out of MHT. The reaction goes in forward direction even on a water bath (80°C). However, the morphology of PMO-1 composite becomes ill-defined (Fig. S3).

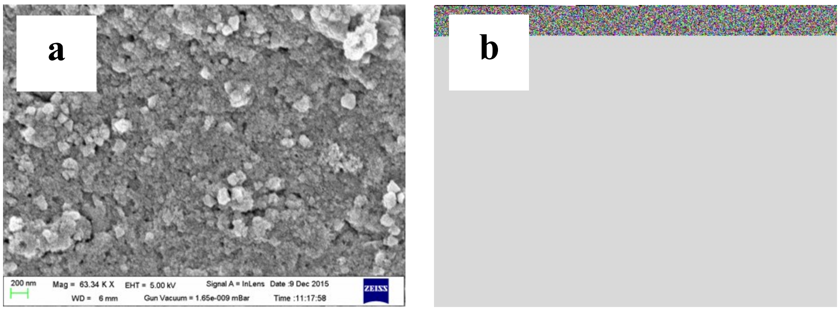


Fig. S3: Synthesis of PMO-1 nanocomposite at (a) 80 °C and (b) 160 °C.

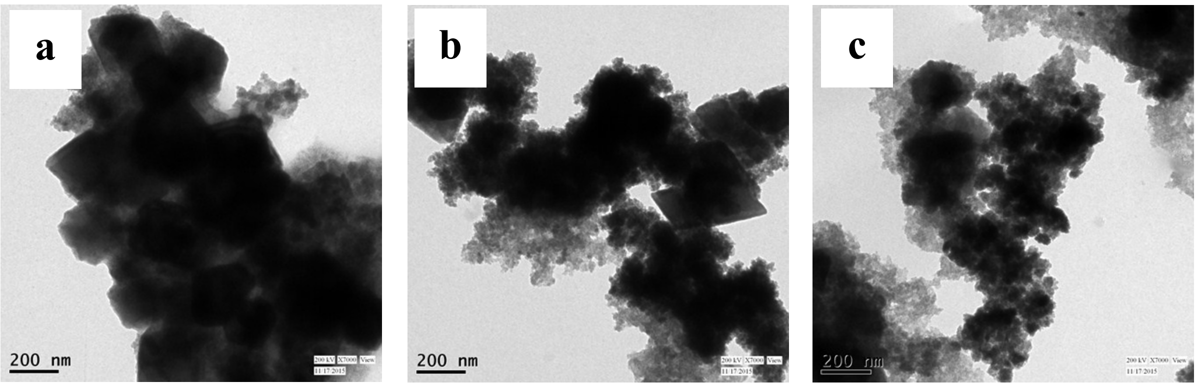


Fig. S4: TEM images of (a) PMO-0.5, (b) PMO-1 and (c) PMO-2 nanocomposites.

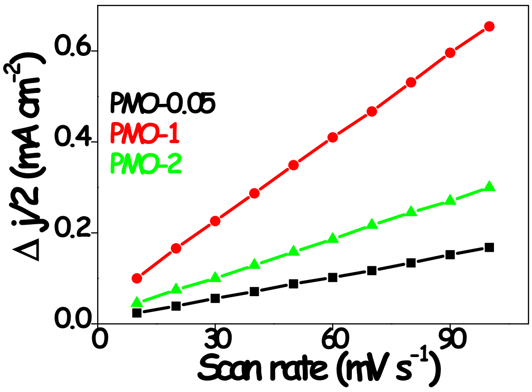


Fig. S5: Charging current density differences plotted against scan rates. The linear slope, equivalent to the double-layer capacitance C_{dl}, was used to represent the ECSA.

Table S1: A comparative account of HER activity

Catalyst	j^a (mA cm^{-2})	η^b(mV)	j_0^c (mA cm^{-2})	Mass activity (mA mg^{-1})	Reference
Pt−TiO$_2$−N−rGO	126	300	0.22	3110	*J. Phys. Chem. C*, 2015, **119**, 19117.
Pt–Pd–rGO I	791	300			*Angew. Chem. Int. Ed.,* 2014, **53**, 12120.
Pt−SiO$_2$	200	500			*RSC Adv.*, 2014, **4**, 50114.
Pt−SnO$_2$	40	300	0.46		*Catal. Lett.,* 2012, **142**, 809.
Pt−W$_2$C	15.8	10	2	476	*Int. J. Hydrogen Energy*, 2008, **33**, 6865.
Cu$_c$−Pt$_s$	5	800		275	*Energy Environ. Sci.*, 2014, **7**, 1461.
MoS$_2$-Pd		248	4.57×10^{-3}		*J. Power Sources*, 2015, 284, 68.
Pd ND/DR-MoS$_2$	83	103	0.426		*J. Mater. Chem. A*, 2016, DOI: 10.1039/C5TA10337A
PMO-1	186	14	7.74	9930	This work

^{a} Cathodic current density (j) was recorded at η = 300 mV; ^{b} Overpotential (η) was recorded at j = 10 mA cm^{-1}; ^{c} Exchange current density (j_0) was recorded at η = 0 mV.

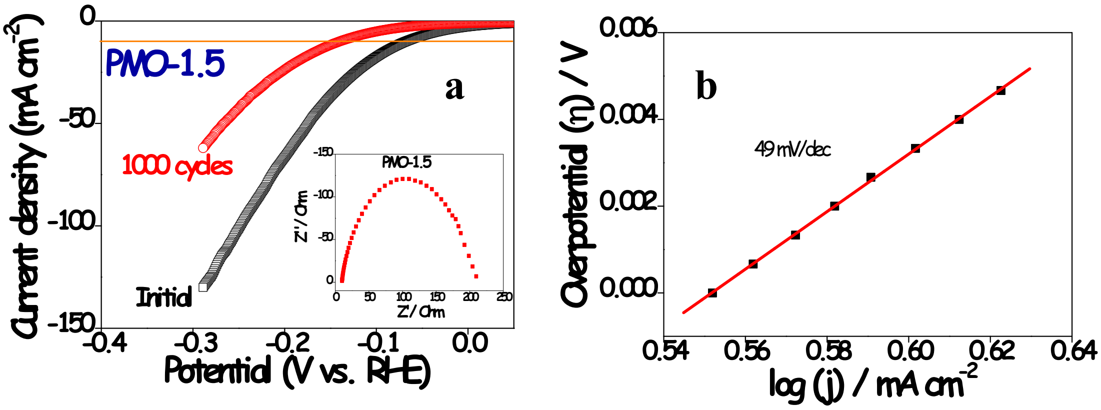


Fig. S6: (a) HER polarization curve of PMO-1.5 before and after 1000 cycles. The inset shows Nyquist plot of PMO-1.5. (b) Tafel plot recorded on the corresponding catalyst.

Table S2: A comparative account of HER activity of as-synthesized various PMO nanocomposites.

Catalysts	**j^a (mA cm^{-2})**	**η^b(mV)**	**j_0^c (mA cm^{-2})**	**Tafel slope (mV/dec)**	**R_{ct} (Ω)**
PMO-0.5	78	101	1.83	69	365.1
PMO-1	186	14	7.74	42	11.35
PMO-1.5	130	51	3.44	49	209.4
PMO-2	113	66	2.49	51	261.3

[a] Cathodic current density (j) was recorded at $\eta = 300$ mV; [b] Overpotential (η) was recorded at $j = 10$ mA cm^{-1}; [c] Exchange current density (j_0) was recorded at $\eta = 0$ mV.

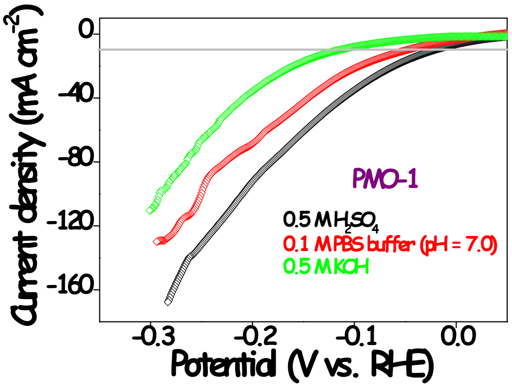


Fig. S7: HER polarization curve of PMO-1 nanocomposite at different pH.

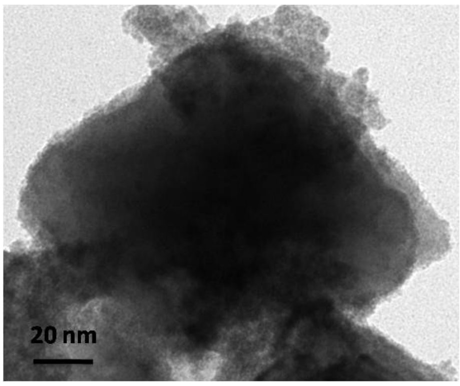


Fig. S8: TEM image of PMO-1 nanocomposite after catalysis.

Generally, manganese oxides do not have good stability in acidic medium as is true for our prepared free Mn_3O_4 nanooctahedrons. However, the designed PMO nanocomposites exhibit extremely high stability in 0.5 M H_2SO_4 medium even after 36 h of electrochemical process.

To confirm the stability of as-synthesized PMO nanocomposites, the Mn_3O_4 nanoparticles and PMO-1 nanocomposite were separately incubated in 0.5 M H_2SO_4. After some time the clear acid extract was tested with $NaBiO_3$. As shown in following Fig. S9 after 1 h in case of Mn_3O_4 the color of solution becomes pink. However, even after 24 h the supernatant solution of PMO-1 nanocomposite extract does not show any color development with $NaBiO_3$

treatment. Thus it can be concluded that, in case of PMO nanocomposites no leaching of Mn^{2+} has really occurred, i.e., as–synthesized PMO nanocomposites attain high stability in acidic medium owing to Pd NPs deposition.

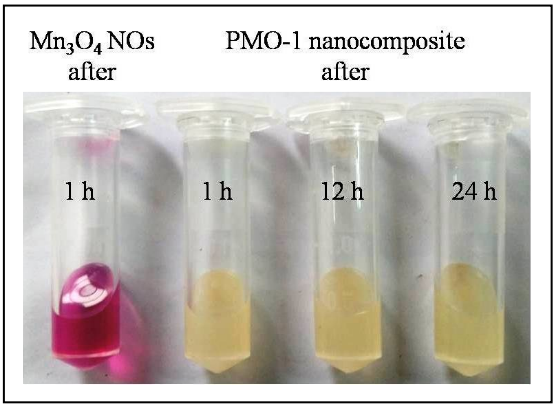


Fig. S9: Extract of incubated solids (Mn_3O_4 NO and PMO-1) with 0.5 M H_2SO_4 showing the reaction with $NaBiO_3$.

This remarkable stability of PMO electrocatalyst under acidic condition may attributable to the interaction between Pd NPs and Mn_3O_4 nanooctahedrons, which hinders dissolution of Mn_3O_4 during electrocatalysis. Various reports of Mn_3O_4 based nanocomposite as electrocatalyst have been reported in the literatures which show good stability in acidic medium.[3-5]

3. S. Themsirimongko, N. Promsawan and S. Saipanya, *Int. J. Electrochem. Sci.,* 2016, **11**, 967.

4. K. W. Kim, S. M. Kim, S. Choi, J. Kim and I. S. Lee, *ACS Nano*, 2012, **6**, 5122.

5. A. Ejigu, M. Edwards and D. A. Walsh, *ACS Catal.*, 2015, **5**, 7122.