Ni-Pd Bimetallic Catalysts for the Direct Synthesis of H\textsubscript{2}O\textsubscript{2} - Unusual Enhancement of Pd Activity in Presence of Ni

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Supplementary Information
Materials and Characterization Techniques:

Materials:

PdCl$_2$ (Sigma Aldrich), HAuCl$_4$.3H$_2$O (Sigma Aldrich), NiCl$_2$.6H$_2$O (S D Fine Chemicals), NaBH$_4$ (S D Fine Chemicals), KBr (S D Fine Chemicals), TiOSO$_4$ (Sigma Aldrich), H$_2$SO$_4$ (98%, AR grade), HCl (37%, AR grade) were used without any further purification.

Characterization Techniques:

Powder X-ray diffraction (PXRD) patterns were recorded using Bruker-D8 diffractometer using Cu K$_\alpha$ radiation, ($\lambda=1.54$ Å, step size: 0.02, current: 30 mA and voltage: 40 kV). Field-emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy (EDS) were obtained by using FEI (Nova-Nano SEM-600 Netherlands) equipment. Transmission electron microscope (TEM) imaging was done on a JEOL, JEM 3010 operated at 300 kV. Samples were prepared by putting a drop of very dilute dispersion in ethanol on a TEM grid (carbon polymer, 300 mesh). Electronic absorption spectra were recorded by Perkin Elmer Lambda 900 UV-Vis-NIR Spectrometer. 1 cm path length cuvette was used for recording the spectra. Inductive coupled plasma – atomic emission spectroscopy (ICP-AES) was carried out using a Perkin–Elmer Optima 7000 DV machine. Infra-red (IR) spectra were recorded on a Bruker IFS 66v/S spectrometer. X-ray photoelectron spectroscopy (XPS) has been performed using Omicron EA 125 spectrometer with Al K$_\alpha$ (1486.6 eV) source. The magnetic measurement was carried out by using Quantum Design SQUID VSM magnetometer at 298K. The composition of gas mixture was analysed by Gas Chromatography (Agilent 7890A) using MolSieve 5A 60-80 mesh column 40 ºC temperature.
Experimental Details:

Metal nanostructure and bimetallic nanostructures were prepared by the reduction of metal precursor(s) solution by NaBH₄ at room temperature.¹ PdCl₂, NiCl₂·6H₂O and HAuCl₄·3H₂O were used as metal precursors. The detailed procedure is given below:

(i) **Synthesis of Pd, Ni, and Au nanostructure:**

In the typical procedure, 10 mL of 0.1 M metal precursor solution (PdCl₂ in case of Pd, NiCl₂·6H₂O in case of Ni and HAuCl₄·3H₂O in case of Au) was rapidly added to a 50 mL of 0.1 M aqueous solution of freshly prepared NaBH₄ with vigorous stirring. The stirring was continued for 10 min. The solid product obtained was filtered and washed with distilled water for several times. Finally it was dried at 50 °C for overnight.

(ii) **Synthesis of Ni₀.₄Pd₀.₆ nanostructure:**

A mixture of 3.4 mL of 0.1 M NiCl₂·6H₂O solution (in aqueous medium) and 2.82 mL of 0.1 M PdCl₂ solution (in aqueous medium) was rapidly added to 31.1 mL freshly prepared 0.1 M aqueous solution NaBH₄ with continuous stirring. The reaction mixture was allowed to stir for 10 min. The solid product was filtered and washed several times with distilled water and dried at 50 °C for overnight.

(iii) **Synthesis of Au₀.₅Pd₀.₅ nanostructure:**

In the typical procedure, a mixture of 1.27 mL of 0.1 M HAuCl₄·3H₂O solution (in aqueous medium) and 2.35 mL of 0.1 M PdCl₂ solution (in aqueous medium) was rapidly added to 18.1 mL freshly prepared 0.1 M aqueous solution of NaBH₄ with vigorous stirring. The stirring was continued for 10 min. The solid product was filtered, washed with distilled water for several times and dried at 50 °C for overnight.
(iv) **Direct Synthesis of H₂O₂:**

Direct synthesis of H₂O₂ from gaseous H₂ and O₂ was carried out using a glass jacket reactor described elsewhere.² 5 mg catalyst (for Pd, Au₀.₅Pd₀.₅, Ni₀.₄Pd₀.₆ and 3 mg for Ni₀.₁Pd₀.₉) was dispersed by sonication in 30 mL aqueous solution containing 0.1 M HCl and 0.01 M Br⁻ (introduced as KBr) and added to the glass jacket reactor shown below. The individual gasses, H₂ and O₂ were allowed to bubble through the glass frit in a ratio of 1:4 with a total flow rate of 50 mL min⁻¹ using two separate Aera (Hitachi) mass flow controllers. To reduce the dead volume, the below portion of the glass frit was filled with 4 mm glass beads. The reaction temperature was maintained at 10 °C using Julabo water circulation unit.

[Image: Reaction set up for direct synthesis of hydrogen peroxide.]
H₂O₂ was analysed by TiOSO₄/H₂SO₄ method using UV-vis spectroscopy.³ 20 μL of aliquot from the reaction solution was withdrawn at different time interval and diluted with 1.98 mL of previously prepared TiOSO₄/H₂SO₄ solution. TiOSO₄/H₂SO₄ solution was prepared by dissolving 4.6 gm of TiOSO₄ and 20 gm of ammonium sulphate in 100 mL of concentrated H₂SO₄ followed by dilution with 350 mL H₂O. The concentration of H₂O₂ was determined from the calibration curve of absorption at 407 nm by UV-vis spectroscopy after complexation with a TiOSO₄/H₂SO₄ solution. The H₂ and O₂ gases were analysed using MolSieve 5A 60-80 mesh column 40 °C temperature. For selectivity measurement, to get better accuracy, the outlet gas was well diluted with N₂. The selectivity of H₂O₂, S₉₂O₂ was calculated from the following equation²:

\[
S_{\text{H}_2\text{O}_2} = \left( \frac{\text{Rate of hydrogen peroxide production (mmol/min)}}{\text{Rate of hydrogen consumption (mmol/min)}} \right) \times 100.
\]

(v) Dissolution Study (Synthesis of Ni₀.₁Pd₀.₉ from Ni₀.₄Pd₀.₆):

50 mg of Ni₀.₄Pd₀.₆ catalyst was soaked in aqueous solution containing 0.1 M HCl, 0.01 M Br⁻ and 0.3 M H₂O₂ in total volume of 30 mL in presence of H₂ flow (20 mL min⁻¹) at 10 °C for different time (0.5h, 1h and 72h). H₂ flow is necessary to avoid the dissolution of Pd as PdCl₄²⁻ in presence of chloride ions. The remaining solid product after dissolution at desired time interval was separated, washed with water and dried. The Ni:Pd ratio after dissolution of different time was found to be 10:90 analyzed by inductive coupled plasma (ICP).

(Vi) Decomposition of H₂O₂:

5 mg of catalyst (Pd and Ni₀.₄Pd₀.₆) was dispersed in 30 mL aqueous solution of 275 mM H₂O₂ and was stirred using magnetic stirrer. The decomposition of H₂O₂ was determined
by analyzing the H$_2$O$_2$ concentration using UV-vis spectroscopy as described above at different time interval. To study the stability of H$_2$O$_2$ in presence of HCl and Br$^-$, the same reaction was carried out in presence of 0.1 M HCl and 0.01 M Br$^-$ in 30 mL aqueous solution of 275 mM H$_2$O$_2$ using Pd and Ni$_{0.4}$Pd$_{0.6}$ catalysts and the H$_2$O$_2$ concentration was monitored at different time. The results are shown in the Figure S3A.

(Vii) Hydrogenation of H$_2$O$_2$:  

5 mg of catalyst (Pd and Ni$_{0.4}$Pd$_{0.6}$) was dispersed in 30 mL aqueous solution of 250 mM H$_2$O$_2$ at 10 °C and H$_2$ gas was bubbled in the dispersion with a flow rate of 10 mL min$^{-1}$. The H$_2$O$_2$ concentration of was analyzed at different time by UV-vis spectroscopy as described above. The same reaction was carried out in presence of 0.1 M HCl and 0.01 M Br$^-$ with same flow rate of H$_2$. The results are given in the Figure S3B.
List of Supplementary Figures:

(A) X-ray diffraction patterns for \( \text{Ni}_{0.4}\text{Pd}_{0.6} \) and Pd. The peaks at 20°, 40°, and 60° correspond to the (111), (200), and (220) planes, respectively.

(B) TEM image showing a 200 nm scale.

(C) TEM image with a 50 nm scale showing the 0.225 nm feature.

(D) TEM image with a 200 nm scale.

(E) TEM image with a 50 nm scale showing the 0.225 nm feature.
Figure S1: Characterization of Pd and Ni$_{0.4}$Pd$_{0.6}$ nanostructures. (A) PXRD pattern of Pd and Ni$_{0.4}$Pd$_{0.6}$ nanostructures prepared by NaBH$_4$ reduction method. Ni$_{0.4}$Pd$_{0.6}$ shows peaks for Pd and there is no peak shift associated with NiPd bimetallic nanostructure. (B) FESEM and (C) TEM images of Pd nanostructure show network morphology formed by the fusion of nanoparticles of size varying from 5 to 8 nm (calculated from the histogram determined over 200 particles). HRTEM (inset of (C)) shows the lattice spacing, 0.225 nm of Pd. (D) FESEM and (E) TEM images of assynthesized Ni$_{0.4}$Pd$_{0.6}$ nanostructure show fused network morphology interconnected with each other. HRTEM image in the inset of (E) shows the lattice spacing, 0.225 associated with Pd.
**Figure S2:** Formation of H$_2$O$_2$ by Ni$_{0.4}$Pd$_{0.6}$ catalyst without HCl and Br$^-$. Reaction conditions: 10 °C, 5 mg Ni$_{0.4}$Pd$_{0.6}$ catalyst, 30 mL water, 1 atm pressure, H$_2$:O$_2$ (1:4) gas mixture was bubbled with a flow rate, 50 mL min$^{-1}$.

**Figure S3:** (A) Decomposition of H$_2$O$_2$ by Pd and Ni$_{0.4}$Pd$_{0.6}$ with and without HCl and Br$^-$. (B) Hydrogenation of H$_2$O$_2$ over Pd and Ni$_{0.4}$Pd$_{0.6}$ catalysts with and without HCl and Br$^-$. 
Figure S4: Selectivity of $\text{H}_2\text{O}_2$ (with respect to $\text{H}_2$) and conversion of $\text{H}_2$ for Pd and Ni$_{0.4}$Pd$_{0.6}$ catalysts.

(A) 
Normalized Intensity vs. 2θ (degree)

(B) 
SEM image of catalysts with scale bar 200 nm.
**Figure S5:** Characterization of Au$_{0.5}$Pd$_{0.5}$. (A) PXRD pattern of Au$_{0.5}$Pd$_{0.5}$ shows the formation of AuPd alloy and (B) FESEM image of Au$_{0.5}$Pd$_{0.5}$ shows the network morphology.

**Figure S6:** H$_2$O$_2$ productivity rate in terms of mmol gm$^{-1}$ Pd h$^{-1}$, for all the catalysts after 72h reaction in terms of absolute amount of Pd present in the catalysts.
**Figure S7:** Formation of H$_2$O$_2$ over 5 mg Ni$_{0.4}$Pd$_{0.6}$ and 3 mg Pd catalysts. Reaction conditions: 10 °C, 30 mL water containing 0.1 M HCl and 0.01 M Br$^{-}$, 1 atm pressure, H$_2$:O$_2$ (1:4) gas mixture was bubbled with a flow rate, 50 mL min$^{-1}$.

![Graph showing concentration of H$_2$O$_2$ over time](image)

**Figure S8:** Formation of H$_2$O$_2$ after removing the solid catalyst, Ni$_{0.4}$Pd$_{0.6}$ at 72h. No H$_2$O$_2$ formation was observed after removing the solid catalyst at 72h. Reaction conditions: 10 °C, 30 mL water containing 0.1 M HCl and 0.01 M Br$^{-}$, 1 atm pressure, H$_2$:O$_2$ (1:4) gas mixture was bubbled with a flow rate, 50 mL min$^{-1}$.
Figure S9: Characterization of as-synthesized Ni nanostructure. (A) Infra-red spectra of as-synthesized Ni nanostructure prepared by NaBH₄ reduction method. The presence of absorption band at 3556 cm⁻¹ associated with O-H stretching confirms the existence of Ni(OH)₂. (B) PXRD pattern of (i) as-synthesized Ni nanostructure shows amorphous nature and (ii) on heating in Ar at 500 ºC for 12h. The appearance of peaks for NiO after heating supports the presence of Ni(OH)₂ in as synthesized Ni nanostructure. (C) Magnetization (M) vs magnetic field (H) curve of as-prepared Ni, Pd and Ni₀.₄Pd₀.₆ nanostructure at 298 K. The relatively higher value of magnetization for Ni₀.₄Pd₀.₆ in compared to Pd confirms the presence
of metallic Ni nanoparticles which are not detected by PXRD. Higher magnetization value for assynthesized Ni nanostructure confirms the presence of more metallic Ni nanoparticles than that in Ni$_{0.4}$Pd$_{0.6}$.

**Figure S10:** XPS spectra of Ni$_2$p$_{3/2}$ in as-prepared Ni and Ni$_{0.4}$Pd$_{0.6}$ nanostructures. Appearance of Ni$_2$p$_{3/2}$ peaks at 855.9 eV and 861.8 eV (satellite peak) in both Ni and Ni$_{0.4}$Pd$_{0.6}$ nanostructures confirms the existence of Ni$^{2+}$ in the form of Ni(OH)$_2$ in the samples.
**Figure S11:** FESEM image of (A) Pd bulk and (B) Ni_{0.4}Pd_{0.6} bulk. Bulk samples were prepared by heating the as-synthesized samples at 500 °C for 12h in presence of 5% H\textsubscript{2} in N\textsubscript{2}. Both images show the micron sized particles fused together. (C) Formation of H\textsubscript{2}O\textsubscript{2} by bulk catalysts which do not show any activity towards direct synthesis of H\textsubscript{2}O\textsubscript{2}. For reference, the activity of Pd nanostructure is shown here. Reaction conditions: catalyst (5 mg), 10 °C, 30 mL water containing 0.1 M HCl and 0.01 M Br\textsuperscript{-}, 1 atm pressure, H\textsubscript{2}:O\textsubscript{2} (1:4) gas mixture was bubbled with a flow rate, 50 mL min\textsuperscript{-1}.
**Figure S12:** TEM image of assynthesized Ni$_{0.4}$Pd$_{0.6}$ and the corresponding elemental mapping of Pd, Ni and O in Ni$_{0.4}$Pd$_{0.6}$ shows uniform distribution of Pd, Ni and O.
**Figure S13:** XPS spectra of Pd3d in Pd and Ni$_{0.1}$Pd$_{0.9}$-1h nanostructure. The shifts in binding energy of Pd3d$_{3/2}$ (0.35 eV) and Pd3d$_{5/2}$ (0.2 eV) towards lower value observed in Ni$_{0.1}$Pd$_{0.9}$-1h nanostructure indicates the formation of NiPd alloy after 1h dissolution time.
Figure S14: PXRD pattern of (i) Pd (for reference), (ii) sample obtained after soaking the mixture of Ni and Pd nanostructures (1:1 weight ratio) in the reaction condition, in presence of HCl, H$_2$O$_2$ and H$_2$ (H$_2$ flow rate was 20 mL min$^{-1}$) and (iii) sample obtained after soaking the mixture of Ni$_{0.4}$Pd$_{0.6}$ and Pd nanostructures (4:1 weight ratio) in the same reaction condition for 48h. The resulting composition of Ni:Pd for last one is 3:97 determined by ICP-AES.

References: