

Materials science communication

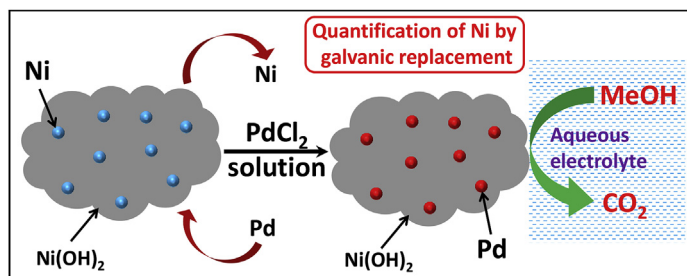
Controlled galvanic replacement of Ni in Ni(OH)₂ by Pd: A method to quantify metallic Ni and to synthesize bimetallic catalysts for methanol oxidation

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HIGHLIGHTS

- A new method to estimate the amount of metallic Ni quantitatively in Ni(OH)₂/Ni.
- Bimetallic NiPd was synthesized on Ni(OH)₂ by galvanic replacement of Ni by Pd.
- Catalysts show better activity towards methanol oxidation than commercial Pd/C.

GRAPHICAL ABSTRACT



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ABSTRACT

We have demonstrated a new and simple methodology to quantify the amount of metallic Ni present in the mixed nickel hydroxide/nickel surface using galvanic replacement reaction. This method was also used to manipulate the formation of nanocomposite, NiPd on Ni(OH)₂ support by controlling the extent of galvanic replacement of Ni by Pd. The bimetallic NiPd nanoparticles supported on Ni(OH)₂ prepared by galvanic reaction showed better electrocatalytic activity for methanol oxidation than commercial Pd/C. This approach can be extended to synthesize various nickel containing bimetallic nanoparticles essential for different catalysis.

1. Introduction

Bimetallic NiPd catalysts gained a lot of attention in recent years owing to their improved performance than the Pd catalysts in many industrially significant reactions such as hydrogen evolution reaction [1,2], oxygen reduction reaction [3,4], formic acid oxidation [1,5–7], methanol oxidation [8–12] and direct synthesis of hydrogen peroxide [13]. One of the methods often used to obtain NiPd nanostructure is the borohydride reduction of Ni and Pd salt precursors [9,13–17]. In

borohydride reduction, although Pd salt is fully reduced to Pd nanostructure, Ni salt mostly gets converted to Ni(OH)₂ and Ni due to higher pH associated with the addition of borohydride [9,13]. As a corollary, the obtained nanostructures mostly composed of Ni(OH)₂ and Ni nanoparticles in addition to NiPd bimetallic nanoparticles. Quantification of metallic Ni present in the Ni(OH)₂ is one of the challenging tasks, although metallic Ni (in zero oxidation state) can be analyzed using magnetic measurement due to its ferromagnetic behaviour [13]. The Ni nanoparticles in Ni(OH)₂ can be further estimated by converting it into

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Pd nanoparticles through galvanic replacement reaction [1,12]. This method not only allows us to estimate the total amount of Ni present in zero oxidation state in Ni(OH)₂, but also allows us to have a good control on the formation of NiPd bimetallic nanoparticles on Ni(OH)₂ support by controlling the time of galvanic replacement reaction.

In this work, we attempted to utilize high surface area porous Ni(OH)₂/Ni nanostructure prepared by borohydride reduction method developed by our group [13,18] as a substrate for galvanic replacement reaction with Pd. The as-synthesized nanostructure, Ni(OH)₂/Ni was used as a template for the galvanic replacement of Ni present in Ni(OH)₂/Ni by Pd. The resulting NiPd loaded on Ni(OH)₂ nanostructure was tested for the electrocatalytic activity for methanol oxidation as the test reaction.

2. Experimental section

2.1. Materials and characterization techniques

NiCl₂·6H₂O, NaBH₄, NaOH and Methanol (AR grade) were purchased from S D Fine Chemicals; PdCl₂ and Nafion were purchased from Sigma Aldrich; and Pd/C (5 wt%) was purchased from Alfa Aesar. All the chemicals were used as such without any further purification.

Powder X-ray diffraction (PXRD) patterns were recorded using Bruker-D8 diffractometer using Cu K α radiation, ($\lambda = 1.54 \text{ \AA}$, 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 200 kV. Samples were prepared by putting a drop of very dilute dispersion in ethanol on a TEM grid (carbon polymer, 300 mesh). Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) was carried out using a Perkin – Elmer Optima 7000 DV machine. Gas adsorption-desorption measurements were performed on Autosorb-iQ2 (Quantachrome corp.) at 77 K. The samples were degassed before starting the nitrogen gas sorption analysis under a high vacuum for 12 h at 373 K.

2.2. Synthesis of Ni(OH)₂/Ni nanostructure

The Ni(OH)₂/Ni nanostructure was synthesized via one step process by the reduction of aqueous NiCl₂ solution in presence of NaBH₄ at room temperature [1,2]. In a typical procedure, 20 mL 0.1 M aqueous solution of NiCl₂ was rapidly added to a 100 mL 0.1 M aqueous solution of freshly prepared NaBH₄ with vigorous stirring. The mixture was allowed to stir for 30 min. The solid product obtained after stirring was separated out and washed with water for several times and finally dried at 50 °C for overnight.

2.3. Galvanic replacement of Ni by Pd in Ni(OH)₂/Ni nanostructure

In a typical procedure, 50 mg of as-synthesized Ni(OH)₂/Ni nanostructure was soaked in 10 mL aqueous solution of 10 mM PdCl₂ solution with stirring for different time periods (5, 10, 30, 60 and 720 min). The solid product thus obtained was centrifuged and washed thoroughly with distilled water to make sure the complete removal of PdCl₂. Finally, the sample was dried at 50 °C for overnight. The Pd loading in all the galvanic replacement samples were analyzed by ICP-AES. The blank experiment was also carried out with Ni(OH)₂/Ni in absence of PdCl₂ and no leaching of Ni from the sample was observed in the similar conditions.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out using electrochemical work station obtained from CH instruments (660C, USA) using a three-electrode set-up. The measurements were carried out

using long Pt-wire having large area as a counter electrode, mercury-mercuric oxide (MMO) electrode as a reference electrode in strong alkaline medium (1 M NaOH) and glassy carbon (GC) electrode having 3 mm diameter (geometric area 0.07068 cm²) as working electrode. All the electrochemical experiments were carried out in deaerated solution by bubbling Ar gas for 30 min with a scan rate of 20 mV s⁻¹. The mass-current densities for all the samples are given with respect to the electrochemically active-mass calculated from Faraday's law.

2.5. Electrode preparation and methanol oxidation

2 mg of the sample was dispersed in a mixture of milli Q water (0.9 mL) and 5 wt % nafion (0.1 mL) solution and ultrasonicated to obtain a homogeneous catalyst ink. Then, 3 μ L of the catalyst ink was drop casted on a cleaned glassy carbon (GC) electrode (3 mm diameter) with a catalyst loading of $\sim 0.085 \text{ mg cm}^{-2}$. The GC electrode was dried in ambient conditions and used as working electrode in the electrochemical studies. The methanol oxidation was carried out using 0.5 M methanol in 1 M aqueous solution of NaOH.

3. Results and discussion

The Ni(OH)₂/Ni nanostructure was synthesized by reduction of NiCl₂ in presence of NaBH₄ (as discussed in the experimental section). This method produces mostly Ni(OH)₂ along with Ni nanoparticles as nickel is prone to hydrolyze to its hydroxide at higher pH produced by the presence of NaBH₄ [13]. The Ni nanoparticles dispersed in the Ni(OH)₂ nanostructure are difficult to detect using powder X-ray diffraction (PXRD) study and can't be quantified by inductively coupled plasma – atomic emission spectroscopic (ICP-AES) analysis [13]. The Ni(OH)₂/Ni nanostructure shows a broad X-ray diffraction peak (Fig. 1a) which confirms the amorphous nature of the sample. The field emission scanning electron microscopy (FESEM) image of Ni(OH)₂/Ni shows sponge like morphology (Fig. 1b).

Galvanic replacement (details in the experimental section in supplementary information) was carried out by soaking of Ni(OH)₂/Ni in PdCl₂ salt solution (10 mM) at different periods of time (5, 10, 30, 60 and 720 min). During the galvanic replacement, Ni metal nanoparticles dispersed in Ni(OH)₂ nanostructure were replaced by Pd metal as the reduction potential of Pd²⁺/Pd ($E^\circ = +0.915 \text{ V}$) is higher than Ni²⁺/Ni ($E^\circ = -0.25 \text{ V}$). Since the galvanic replacement reactions occur with non-noble metal of zero oxidation state [19], the amount of metallic Ni present in the mixed metal hydroxide/metal surface can be directly correlated with amount of Pd (Table 1). The amount of Pd loading with time by galvanic replacement was quantitatively estimated by ICP-AES and the results are given in Table 1. From the table, it is observed that all the metallic Ni was replaced by Pd within 60 min which mostly corresponds to around 0.05 mol% of Ni present in Ni(OH)₂. Beyond 60 min time of galvanic replacement, no increase in the Pd loading confirmed from ICP-AES, suggesting that all the nickel (zero valent state) present in the as-prepared sample are replaced by Pd (Table 1).

The galvanic replacement reaction carried out for different time periods (10, 30, 60 and 720 min) shows diffraction patterns similar to that of Pd in Pd/C (Fig. S1 in supplementary information). FESEM analysis shows similar morphology as that of Ni(OH)₂/Ni nanostructure for all the synthesized samples. Ni(OH)₂/Ni_{0.25}Pd_{0.75} (after 30 min galvanic replacement) was chosen for further studies as it shows better electrocatalytic performance towards methanol oxidation among all the samples. The Ni(OH)₂/Ni_{0.25}Pd_{0.75} (abbreviated later as Ni(OH)₂/NiPd) sample shows bright spots in FESEM (Fig. 2a) associated with Pd (lighter element Ni is replaced by heavier Pd). Further, the energy dispersive X-ray spectroscopic (EDS) analysis shows the presence of Pd distributed over the Ni(OH)₂/NiPd nanostructure (Fig. 2a). The transmission electron microscopy (TEM) analysis of Ni(OH)₂/NiPd (Fig. 2b) further confirms the Pd dispersion over Ni(OH)₂ nanostructure. The Pd particles are polydispersed in nature and the particles size are in the

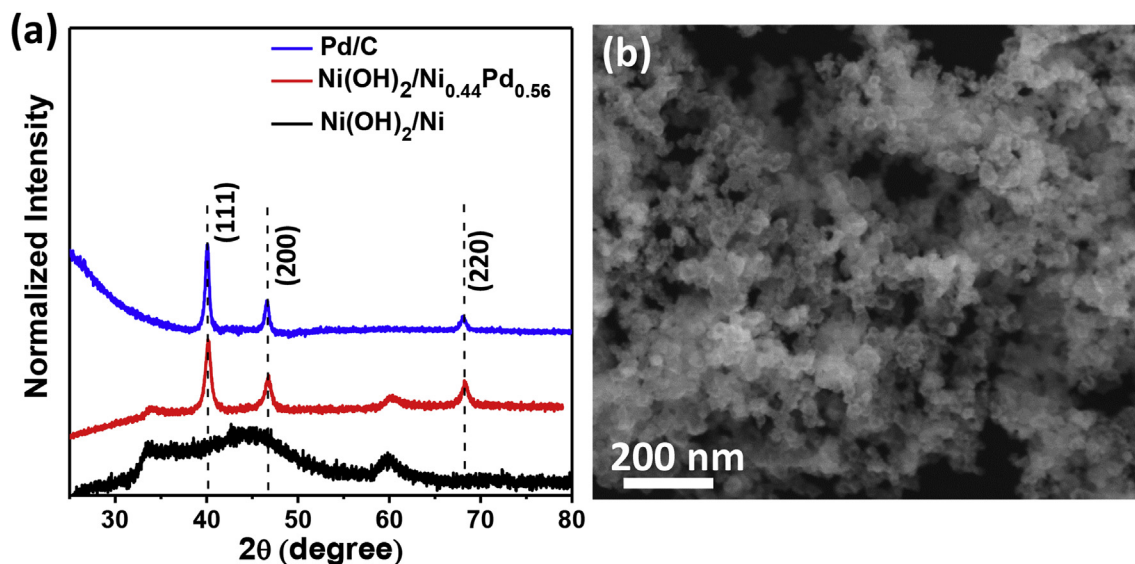


Fig. 1. (a) Powder X-ray diffraction (PXRD) patterns of Ni(OH)₂/Ni, Ni(OH)₂/Ni_{0.44}Pd_{0.56} (after 5 min galvanic replacement) and compared with commercial Pd/C. (b) Field emission scanning electron microscopy (FESEM) image of Ni(OH)₂/Ni.

Table 1

Estimation of Pd and Ni in Ni(OH)₂ sample at different time intervals of galvanic replacement reaction (analyzed from ICP-AES).

Time for galvanic replacement (min)	Pd loading in Ni(OH) ₂ /Ni (wt. %)	Pd loading in Ni(OH) ₂ /Ni (mol %) ^a	Remaining Ni in Ni(OH) ₂ /Ni ^b (mol %)	Ni:Pd (mol ratio)	Sample name ^c
5	2.9	0.027	0.021	44:56	Ni(OH) ₂ /Ni _{0.44} Pd _{0.56}
10	3	0.028	0.020	42:58	Ni(OH) ₂ /Ni _{0.42} Pd _{0.58}
30	3.8	0.036	0.012	25:75	Ni(OH) ₂ /Ni _{0.25} Pd _{0.75}
60	5.1	0.048	0	0:100	Ni(OH) ₂ /Pd
720	5.1	0.048	0	0:100	Ni(OH) ₂ /Pd

^a Pd loading (mol %) with respect to wt. of the catalyst.

^b Remaining Ni in metallic state (mol %) calculated by subtraction from complete galvanic replacement of Ni by Pd beyond 60 min.

^c Ni and Pd mol % is given in the sample name as calculated in the table.

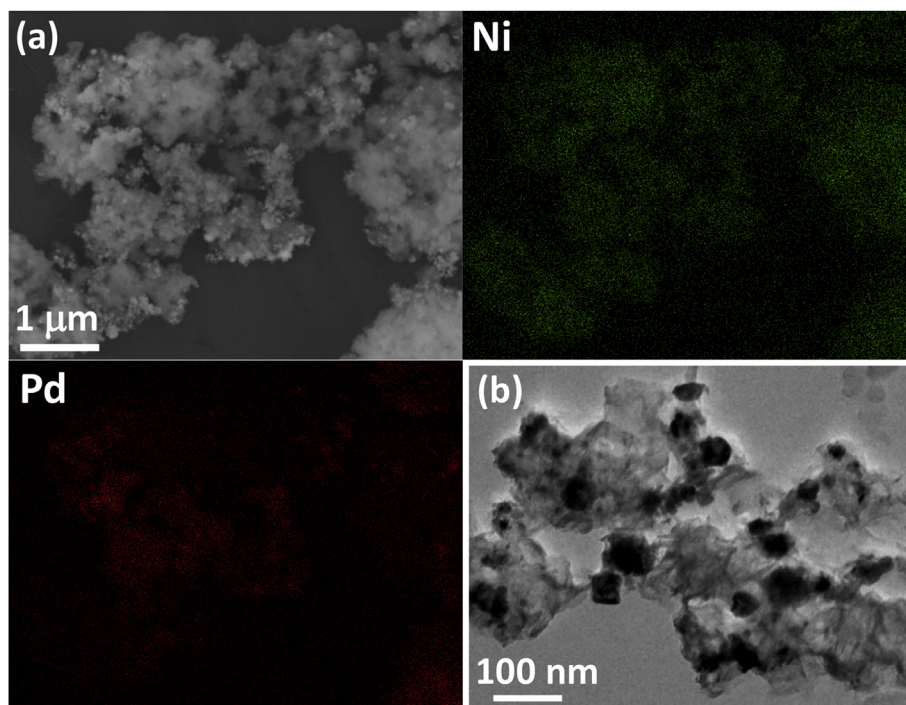


Fig. 2. Characterization of Ni(OH)₂/NiPd sample after 30 min of galvanic replacement. (a) Field emission scanning electron microscopy (FESEM) image of Ni(OH)₂/NiPd and the corresponding electron mapping of Ni and Pd respectively. (b) Transmission electron microscopy (TEM) image of Ni(OH)₂/NiPd.

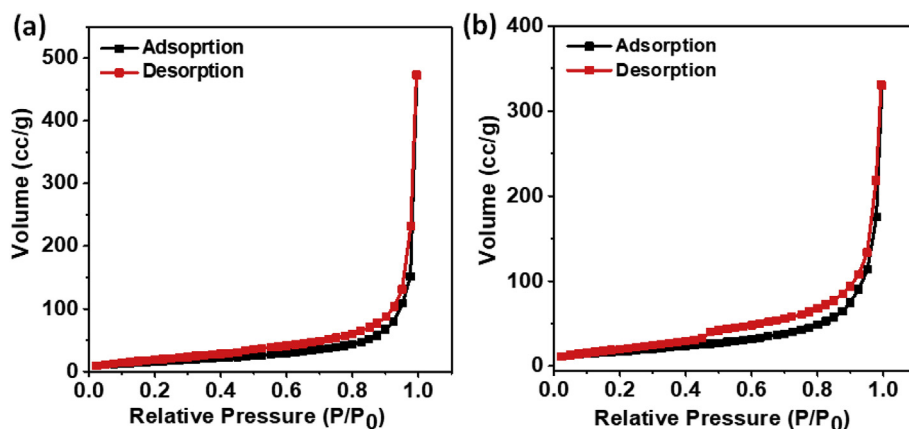


Fig. 3. N_2 adsorption-desorption isotherms of (a) $Ni(OH)_2@Ni$ and (b) $Ni(OH)_2@Ni_{0.25}Pd_{0.75}$ (after 30 min galvanic replacement) nanostructure measured at 77 K.

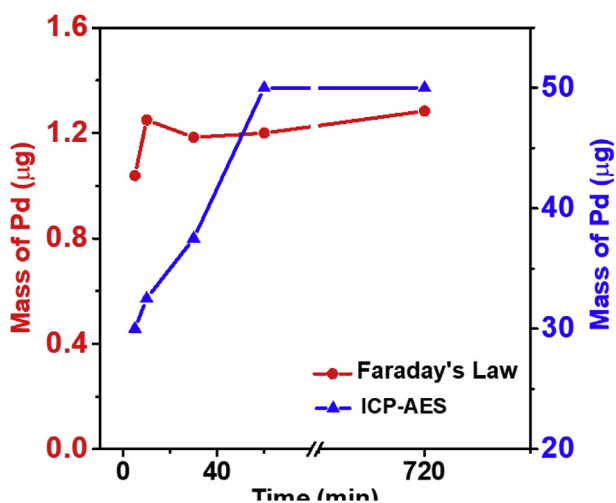


Fig. 4. The time (for galvanic replacement) versus amount of Pd (per mg of catalyst) analyzed from Faraday's law and inductively coupled plasma - atomic emission spectroscopy (ICP-AES) analyses.

range of 30–50 nm. The Brunauer-Emmett-Teller (BET) surface area calculated from N_2 adsorption-desorption isotherm for $Ni(OH)_2/Ni$ (Fig. 3) at 77 K is around $64 \text{ m}^2/\text{g}$ which did not change significantly for $Ni(OH)_2/NiPd$ sample. This suggests that in galvanic replacement reaction the morphology and surface area of the template, $Ni(OH)_2$ is retained [12].

The electrochemical response of $Ni(OH)_2/Ni$ nanostructure was studied in deaerated 1 M NaOH solution (purged with Ar gas for

30 min) using long Pt-wire having large area as a counter electrode, mercury-mercuric oxide (MMO) electrode as a reference electrode. The cyclic voltammogram (CV) of $Ni(OH)_2/Ni$ nanostructure shows a couple of redox peaks at 1.4 V and 1.73 V (vs. RHE, reversible hydrogen electrode) (Fig. S2) associated with the formation of $NiOOH$ from $Ni(OH)_2$ as reported in the literature [20]. The characteristic response of Pd in CV was observed (like hydrogen adsorption-desorption behaviour) in the potential regime -0.06 V to 0.35 V (vs. RHE) and PdO reduction peak at 0.68 V (vs. RHE) (Fig. 5a and S3). The amount of active Pd present in each sample was calculated from coulombic charge for the reduction of PdO using Faraday's law. The coulombic charge for mono layer desorption of oxygen from the Pd surface is $405 \mu\text{C cm}^{-2}$ [21]. These values were compared with ICP-AES analyses and it was observed that the amount of Pd calculated from Faraday's law is very less than the ICP-AES analysis (Fig. 4). This can be attributed to the fact that the Faraday's method takes into account only the electrochemically active Pd present in the sample whereas, the ICP-AES gives the total amount of Pd present in the sample. It is important to note that Pd loading due to galvanic reaction is very fast as complete replacement occurs in 60 min as estimated from ICP-AES (Table 1). The reaction time (galvanic replacement) versus the amount of Pd deposited on $Ni(OH)_2$ shows that all the nickel in zero valent state is replaced within 60 min as there is no significant difference in the amount of Pd loading beyond 60 min of galvanic reaction (Fig. 4).

Methanol oxidation was carried out using 0.5 M methanol in 1 M NaOH solution for all the synthesized catalysts and compared with commercially purchased Pd/C. $Ni(OH)_2/Ni$ nanostructure shows methanol oxidation at the potential where $NiOOH/Ni(OH)_2$ transformation and oxygen evolution reaction occurs (Fig. S4) as observed in the literature [14,20]. By replacing of Ni by Pd using galvanic replacement

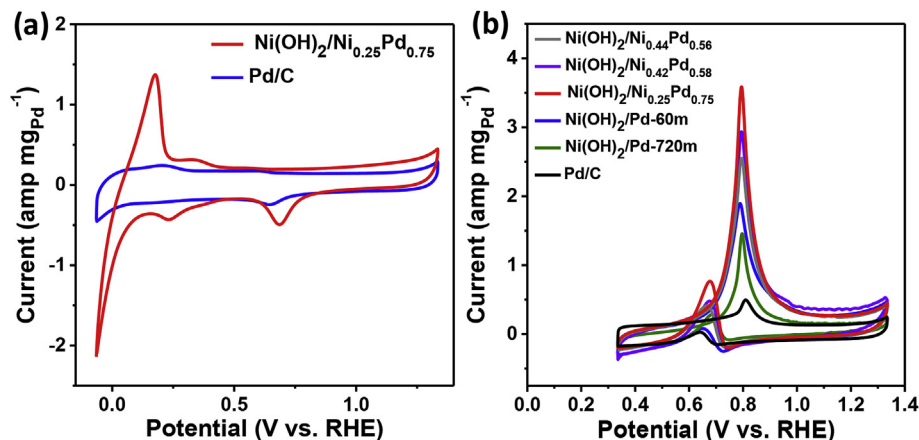


Fig. 5. Electrochemical characterization of $Ni(OH)_2@Ni_{0.25}Pd_{0.75}$ sample and Pd/C. (a) Cyclic voltammograms of $Ni(OH)_2@Ni_{0.25}Pd_{0.75}$ and Pd/C measured in 1 M NaOH with a scan rate of 20 mV s^{-1} . (b) Cyclic voltammograms of different galvanic replacement samples towards MeOH oxidation carried out using 0.5 M MeOH in 1 M aqueous solution of NaOH.

reaction, methanol oxidation was observed at very low potential of 0.79 V vs. RHE for Ni(OH)₂/NiPd (Fig. 5b). On comparison to Pd/C, it shows large potential shift, 18 mV towards lower potential signifying the role of synergistic effect of Ni with Pd for the oxidation of methanol (Fig. 5b). Ni(OH)₂/NiPd catalysts with different Ni and Pd compositions also show relatively better activity for methanol oxidation as compared to Pd/C (Fig. 5b). It is also interesting to note that there is almost no change in the onset potential of methanol oxidation for the catalysts prepared by 5, 10 and 30 min galvanic replacements, whereas the catalysts obtained beyond 60 min show similar onset potential as that of Pd/C (Fig. 5b). This indicates that the catalysts contain only Pd nanoparticles (no NiPd) is less active for methanol oxidation compared to other catalysts prepared at shorter time periods.

The catalyst stability towards methanol oxidation is studied using current-time study at fixed potential for 1 h period. The current-time study shows stability of Ni(OH)₂/NiPd catalyst similar to Pd/C (Fig. S5). In addition, the current observed is higher in Ni(OH)₂/NiPd than Pd/C which is also reflected in cyclic voltammetry studies.

4. Conclusion

In conclusion, galvanic replacement was successfully employed to quantitatively estimate the amount of Ni present in the Ni(OH)₂/Ni. This method was also used to synthesize bimetallic NiPd supported on Ni(OH)₂ which can be used as a “carbon-free” catalyst. NiPd nanoparticles (with different Ni:Pd ratio) supported on Ni(OH)₂ were prepared by controlling the galvanic replacement time. Bimetallic NiPd (Ni(OH)₂/NiPd) prepared by 30 min galvanic replacement reaction showed better performance towards oxidation of methanol as compared to commercial Pd/C catalyst. As this method of preparation is simple and doesn't require any additional additives, this can be extended to prepare other nickel containing noble metal nanostructures for various electrochemical applications.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2018.09.071>.

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