

New route for synthesis of electrocatalytic Ni(OH)₂ modified electrodes—electrooxidation of borohydride as probe reaction

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Abstract. Immobilization of redox species like Ni(OH)₂ onto the electrode surface is important in the application areas such as super capacitor, electrochromic displays and electrocatalysis. Nickel hexacyanoferrate (NiHCF) modified glassy carbon could be further derivatized with Ni(OH)₂ by electrochemical cycling in alkali. The electrodeposition of Ni(OH)₂ was usually carried out onto the electrode surface from nickel salt at high interfacial pH. This paper reports the preparation of Ni(OH)₂ from insoluble nickel tetracyanonickelate supported on carbon (NTN/C). This insoluble precursor complex was decomposed by two methods. (1) By potential cycling of modified electrode with the above complex in alkali. (2) By thermal decomposition of the precursor complex (NTN/C) to form metallic nickel followed by cycling in alkali. Ni(OH)₂ modified electrodes formed using both methods were characterized by cyclic voltammetry and also by Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscopy. Further, electrocatalytic properties of Ni(OH)₂/C modified electrodes formed by the above two methods were studied and compared using borohydride oxidation as probe reaction.

Keywords. Chemically modified electrodes; nickel hydroxide; borohydride oxidation; electrocatalysis.

1. Introduction

Electrodes chemically modified with Ni(OH)₂ have numerous technological importance and is being pursued by several research group due to their application in alkaline batteries, supercapacitors, electrocatalysis, electrochromic displays, etc. (Vidts *et al* 1998; Garcia-Miquel *et al* 2003; You *et al* 2003). Modification of electrodes with Ni(OH)₂ is generally carried out by electrodeposition from alkaline nickel-salt solution. We are first to report the conversion of electrochemically grown nickel hexacyanoferrate film on carbon surface to Ni(OH)₂ by alkali treatment (James Joseph *et al* 1991). Ni(OH)₂ films prepared by this method was found to electrocatalyse the oxidation of alcohols (Ganesh *et al* 2011). Bocarsly proposed the synthesis of ‘cyanogel precursors’ by mixing of chloro complex and cyano complex of transition metals (Brain *et al* 1993). This insoluble gels can thermally decomposed to form bimetallic alloy or mixed oxide by heating the gel in an argon or oxygen, respectively (Marija *et al* 1996; Christine *et al* 2008). Though magnetic properties of these materials have been investigated, there are no attempts so far to explore the electrocatalytic properties of the thermally decomposed cyanogels. The preparation of electrocatalyst

needs dispersion of catalyst in a high surface area matrix which is electronically conducting. In this work, a gelatinous Ni[Ni(CN)₄] complex was prepared in the presence of carbon powder. The precursor-carbon hybrid was converted to Ni(OH)₂/C distinctly by two different routes as mentioned in scheme 1 below.

First method involves the formation of an insoluble precursor ‘Nickel tetracyanonickelate’ supported on carbon (NTN/C) and its subsequent decomposition by electrochemical cycling in alkali to form Ni(OH)₂/C. The second method involves thermal decomposition of carbon supported ‘Nickel tetracyanonickelate’ under inert atmosphere (NTN-H/C) followed by its treatment in alkali. Both the methods described in this paper are new to the best of our knowledge. The electrocatalytic properties the Ni(OH)₂/C films prepared by the above methods were studied towards electrooxidation of borohydride in alkaline medium by cyclic voltammetry. The details of our investigation are described as follows.

2. Experimental

NTN/C is prepared by stirring 10 mL of 20 mM NiCl₂ (Merck) with equal volume of 20 mM solution of K₂[Ni(CN)₄] (Aldrich) along with Vulcan carbon XC-72 (cabot) powder. After the complete addition of K₂[Ni(CN)₄], mixture was vigorously stirred for 30 min.

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Later the mixture was allowed to stand for 20 min. All the experiments were carried out at room temperature of 25 °C. The mixture was centrifuged, washed with water, acetone (E-Merck) and dried in vacuum oven at 50 °C for 2 days. As formed NTN/C xerogels are heated at 700 °C under continuous flow of argon gas in a tubular furnace to form NTN-H/C. Cyanogen which is likely to evolve during decomposition was trapped in NaOH solution.

NTN/C powders were formed on GC by the procedure given below. The carbon in the composition was optimized by performing cyclic voltammetric experiments of NTN/C coated on GC in NaOH with different weight of carbon. The carbon content in NTN/C was fixed from the voltammetric response of redox couple which gives maximum peak current.

The electrochemical experiments were performed in a three-electrode cell using a potentiostat, PGSTAT 30 Autolab Model, Netherlands. Impedance spectroscopy was carried out using IVIUM compact state between the frequency range of 10 kHz and 10 MHz at mid-peak potential of the redox couple and amplitude was fixed as 10 mV, number of frequency per decade: 11. The working electrode was a glassy carbon (GC) disc electrode (Bio Analytical System, USA, area 0.07 cm²). The working electrode was polished with 4/0 grade alumina coated emery paper. The polished electrode was cleaned by ultrasonication in Millipore water for 2–3 min to remove the alumina particles sticking on the surface. A large area (2 × 2 cm²) platinum foil fused to a glass tube served as the counter electrode. All the potentials were measured with respect to (0.1 M NaOH) mercuric oxide electrode

(Hg/HgO). All the solutions were prepared freshly using Millipore water of resistivity 18.2 MΩ cm. NTN/C, NTN-H/C modified electrodes were prepared by weighing 2.5 mg of respective compound and adding 20% nafion (tetrafluoroethylene-perfluoro-3,6-dioxo-4-methyl-7-octenesulphonic acid copolymer dissolved in ethanol), 80% water (volume percent) and sonicated for 20 min to get a uniform dispersion. Finally, about 3 μL of the prepared dispersion was dropped onto a polished GC electrode kept in the upright position. Electrochemical measurements were carried out after 30 min drying. Similar methodology was used for evaluating NTN-H/C electrodes.

Infrared spectroscopy (IR) measurement are performed to the catalyst using Nexus 670 model, (Thermo-Electron Corp., USA) spectrometer and surface characterization of NTN/C, NTN-H/C was studied by scanning electron microscope Hitachi Model S-3000H with acceleration voltage 10 kV. XRD analysis were performed for the catalyst in a PAN analytical diffractometer Model PW3040/60 X'pert PRO operating with X-ray source CuKα radiation (λ = 0.15406 nm) generated at 40 kV and 20 mA. Scans were done at 3° min⁻¹ for 2θ values between 20 and 90°.

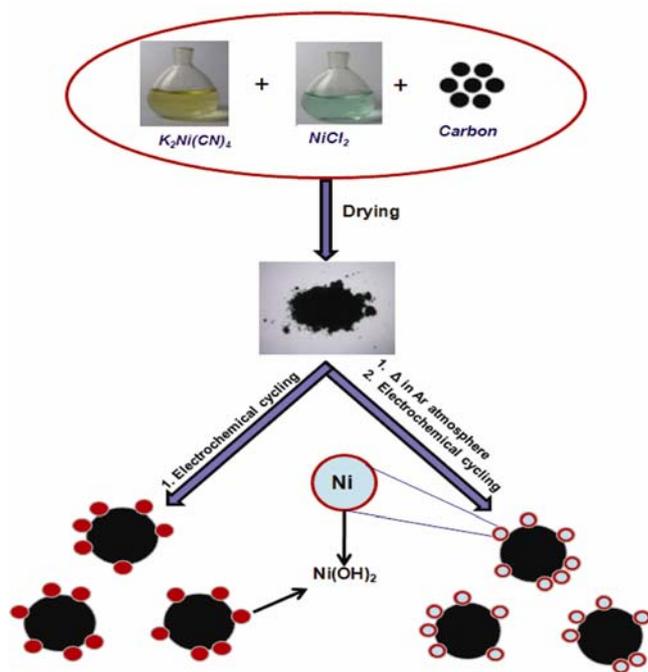
3. Results and discussion

3.1 Decomposition of NTN/C and NTN-H/C to Ni(OH)₂

Figures 1(a) and (b) show voltammetric response of NTN/C and NTN-H/C coated GC electrodes in 0.5 M NaOH. Both the electrodes show the presence of set of well-reversible redox couple typical of Ni(OH)₂. The redox process of (obtained by cycling) NTN/C coated electrode in alkali takes place at slightly less anodic potential (450 mV) compared to the redox process for NTN-H/C (480 mV). The anodic peak show higher peak current in the first and subsequent cycles for both the cases. The difference between the peak currents in the first and subsequent cycles in the forward direction can be ascribed to the oxidation of adsorbed -OH ions on porous Ni(OH)₂/C films. Stabilized voltammetric response was obtained from second onwards. Figure 1(c) shows that redox processes obey linear relationship between peak current and scan rate which is a characteristic of an ideal surface reaction (Murray 1984). On comparing the redox potentials, the redox couple is assigned to following reaction (1).



Conversion of electrochemically formed nickel hexacyanoferrate modified electrode to Ni(OH)₂ on electrochemically cycling in alkali was reported for the first time from the author's laboratory (James Joseph *et al* 1991). NTN/C electrode on treating with alkali show the removal of characteristic -CN stretching band observed at 2177 cm⁻¹ in FT-IR spectra (figures 2a and b). The



Scheme 1.

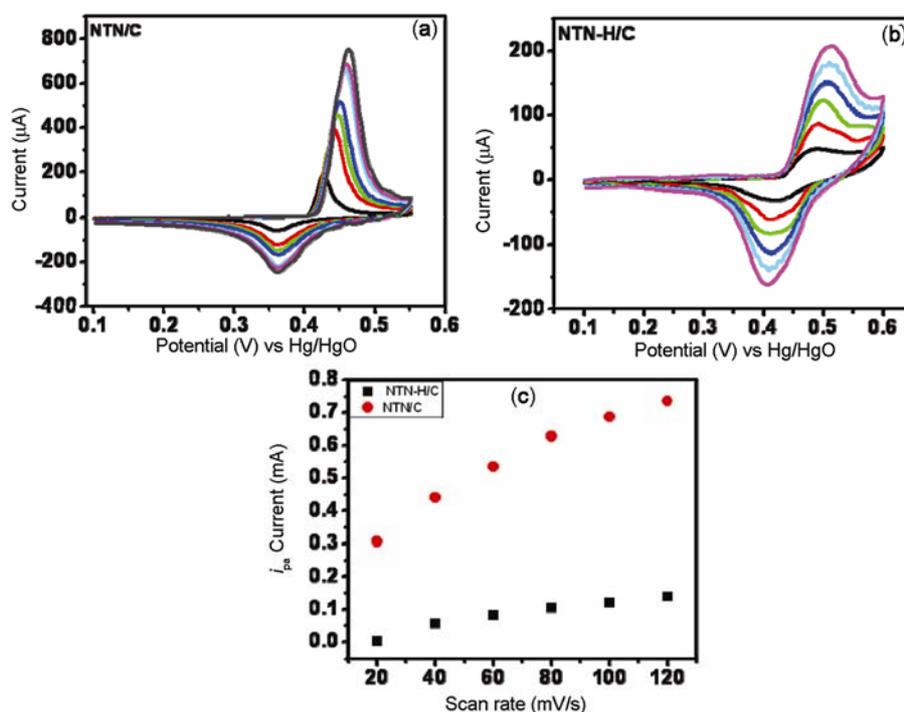


Figure 1. (a), (b) show voltammetric response of NTN/C and NTN-H/C in 0.5 M NaOH at different scan rates and (c) peak current (i_{pa}) vs scan rate graph for both NTN/C and NTN-H/C.

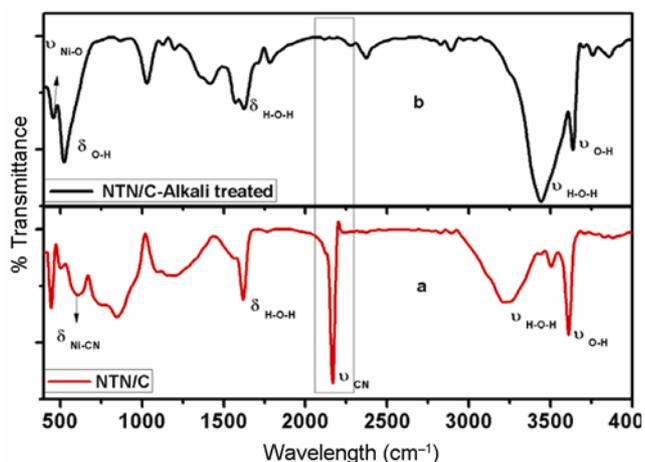
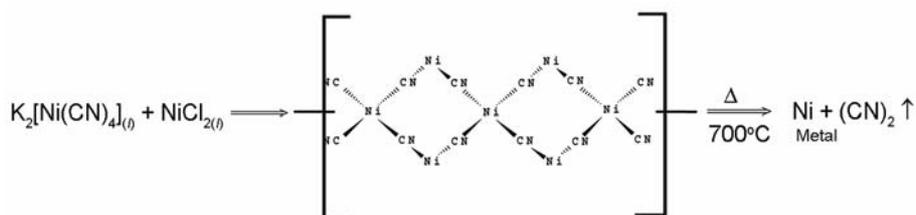


Figure 2. FT-IR spectrum of NTN/C before (a) and after treatment in alkali (b).

Ni(OH)₂/C modified electrode show anodic shift in the redox peak potential with the alkali concentration in a near Nernstian manner clearly indicating the involvement of -OH ions in the redox process. This observation confirms the conversion of NTN to Ni(OH)₂. Electrochemical precipitation of Ni(OH)₂ on gold substrate from alkaline bath containing K₂[Ni(CN)₄] for the selective electrooxidation of sugars is reported recently (Innocenzo and Maria 2001). The magnitude of redox peak currents

obtained for identically prepared NTN/C electrode is 4–5 times higher than that of NTN-H/C. This difference can be attributed to the highly porous nature of NTN/C derived Ni(OH)₂. It is interesting to see that, on thermal decomposition of NTN/C in argon results in the formation of metallic Ni supported on carbon. Bocarsly *et al* have extensively synthesized bimetallic alloys of Pd-Co, Pt-Fe, etc, by heating the cyanogel complex precursor in an inert atmosphere. They have reported the removal of -CN ligands as cyanogen gas from the decomposition of the cyanogel. However, they failed to observe the reduction of prussian blue to metallic iron during thermal decomposition under an inert atmosphere (Marija *et al* 1996). Here, we emphasize that our group attempted for the preparation of mono metal supported on carbon based on the decomposition of cyanogel, i.e., from nickel tetracyanonickelate/C to Ni. The decomposition of NTN/C can be represented by scheme 2.

The electrochemical response of NTN/C and NTN-H/C in 0.5 M NaOH is given in figures 1(a and b). The conversion of NTN/C or NTN-H/C to Ni(OH)₂ is marked by the redox peaks at around 0.450 and 0.485 V, respectively. However the magnitude of redox peak current for NTN/C is much more than that obtained for NTN-H/C. This result prompted us to believe that on treating NTN-H/C, all Ni may not be completely converted to Ni(OH)₂/C. This proposal is further confirmed by analysing XRD data. The average particle size of Ni deposits calculated



Scheme 2.

using Scherrer formula is 27 nm. It is possible that the conversion of Ni to Ni(OH)₂ takes place only at the surface of metal particles. Slight anodic shift in the redox potential of NTN–H/C compared to NTN/C in alkali is probably due to the additional metallic Ni interface between GC and Ni(OH)₂. The plot of the peak current to scan rate for NTN–H/C has lower slope than NTN/C in alkali. This is probably indicating slow electron transfer kinetics for NTN–H/C in alkali. This observation is further substantiated by a.c. impedance studies as described later.

3.2 FT-IR spectrum analysis

FT-IR analysis for both NTN/C and alkali treated NTN–H/C were done by ordinary pellet method in the transmittance mode. The spectrum obtained for NTN/C shows a characteristic stretching frequency (ν_{CN}) for bridged –CN ligand at 2177 cm⁻¹, which is a characteristic stretching vibration frequency for bridged cyanocomplexes like prussian blue and its analogue (Kulesza 1996; Shou and Hong 2002). It is conspicuous from FT-IR spectrum for alkali treated NTN/C (figure 2(b)), the stretching vibration of CN at 2177 cm⁻¹ disappeared and confirms the deformation of cyanogel network to form Ni(OH)₂ in 0.5 M NaOH. The sharp peak that appears at 1629 cm⁻¹ for both NTN/C and alkali treated NTN/C in figures 2(a and b) is attributed to the bending mode of water molecule ($\delta_{\text{H-O-H}}$) trapped in cyanogel network. In addition to that a broad and sharp peak that appears at frequencies 3300 and 3601 cm⁻¹ in both samples (figures 2a and b) corresponds to the stretching vibration of H–O–H and O–H, respectively. An additional peak that is observed in the frequency range 1000–1500 cm⁻¹ in figure 2(b) is due to intense deformation vibration bands of various hydroxyl groups in β -Ni(OH)₂.

3.3 Impedance spectroscopy analysis

Figures 3(a and b) shows a.c. impedance spectra of NTN/C and NTN–H/C coated electrodes in 0.5 M NaOH, respectively. The modified electrodes are activated by cycling the electrode by cyclic voltammetry prior to taking impedance spectra. NTN/C electrode shows semicircle

followed by a Warburg line. The charge transfer resistance calculated for NTN/C is 28 ohm.cm². NTN–H/C did not show the initial semicircular arc and exhibit a capacitive behaviour. The deviation of Warburg line with phase angle of 45° denotes the change in charge transport mechanism at higher frequency. A positive deviation from the phase angle denotes the capacitive behaviour of the electrode. Ni(OH)₂ modified interfaces were studied for their electrochromic and super capacitor applications (Hao *et al* 2011). Chrono-potentiometric studies clearly shows faster charge-discharge behaviour for NTN/C than NTN–H/C (figure not shown). The slow charge transport in NTN–H/C film is evident from the studies on the electrooxidation of borohydride by cyclic voltammetry as described in detail.

3.4 X-ray diffraction analysis

Figure 4(a) shows XRD pattern of NTN–H/C peaks at 2θ values of 44.4 (111), 51.7 (200), 76.5 (222) unequivocally indicate the presence of metallic Ni and the particle size was calculated from reflections in the (111) plane using Sherrer formula given in (2) was 27 nm (Dong and Chih 2002) (2).

$$d = k\lambda/(\beta\cos\theta). \quad (2)$$

Here d is the particle size and k is the constant of 0.9 and λ is the wavelength of X-ray. β is FWHM of (111) plane and θ the Bragg's angle. Alkali treated NTN–H/C (figure 4b) does not show any change in XRD reflections of NTN–H/C before alkali treatment as shown in figure 4(c). XRD values of alkaline treated NTN/C has exactly matched with β -Ni(OH)₂ (Freitas 2001). This observation prompted us to believe that Ni particle is converted to Ni(OH)₂ only at the surface in NTN–H/C on NaOH treatment. This may be the reason for the observed lower magnitude of current for the redox peaks obtained on cycling on 0.5 M NaOH for NTN–H/C electrode compared to that of NTN/C (figures 1a and b).

3.5 Surface analysis through SEM

Figures 5(a and b) shows scanning electron micrographs of NTN/C before and after alkali treatment. NTN/C

powders show big particles of NTN supported on carbon. There is no distinct region representing carbon indicating that NTN uniformly surrounds carbon particle during precipitation. On comparing SEM micrographs of figures 5(b and d), it is clear that Ni(OH)₂ was formed through derivatization of NTN/C and NTN-H/C in alkali. We observed that the conversion of Ni(OH)₂ is complete and uniform in the case of NTN/C, whereas Ni(OH)₂ formed on NTN-H/C show only a slight difference in morphology of NTN-H/C as seen from figure 5(c). This observation prompted to think that the conversion of NTN/C to Ni(OH)₂ was complete on alkali treatment whereas in the case of NTN-H/C, the conversion is limited to the surface of metallic Ni. The micrograph of NTN-H/C figure 5(c) was uniformly brighter indicating good electronic

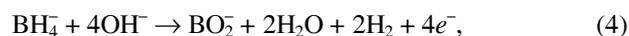
conductivity of NTN-H/C samples. This result is consistent with the proposed conversion of NTN/C to metallic Ni/C on heating under an Ar atmosphere.

3.6 Cyclic voltammetry studies

The electrooxidation of borohydride was studied on Ni, Au, Pt and Ag substrates including bimetallic alloys (Bin *et al* 2003; Gyenge 2004; Chatenet *et al* 2006; Xiaoying *et al* 2008; Peiying *et al* 2011). Among these metal catalyst Au and Ag are widely used for BH₄⁻ oxidation, because of its less reactivity towards BH₄⁻ hydrolysis step (hydrogen generation). Eventhough the oxidation kinetics of BH₄⁻ on these metals is slow results in high open circuit potential by giving 7.5 electrons during oxidation process which is close to that of theoretical value of 8 electrons (3) (Jia *et al* 2010).



However, it is worth mentioning here that BH₄⁻ hydrolysis on Ni electrode (hydrogen evolution rate) depends on the concentration of [BH₄⁻]. Bin *et al* (2004) demonstrated that oxidation of BH₄⁻ in 4e⁻ pathway (4) at higher concentration [BH₄⁻] > 1.5 M and 6e⁻ pathway (5) at lower concentration of [BH₄⁻] < 1.5 M.



In this study the concentration of BH₄⁻ used was 0.005 M. We presume that at 0.005 M concentration range BH₄⁻ oxidation would takes place via 6e⁻ pathway (Bin *et al* 2004). Taking this in to account, we did a comparative study on the electrocatalytic activity of Ni(OH)₂/C prepared by two different routes using cyclic voltammetry. We have chosen electrochemically formed Ni(OH)₂ (by electrochemical potential cycling of NTN/C and NTN-H/C precursors) as a electrocatalyst for borohydride oxidation. Figures 6(A and B) depicts the electrocatalytic oxidation of borohydride in both NTN/C and NTN-H/C electrodes in alkali. It is evident from voltammetric signal that, electrocatalytic oxidation gave rise to irreversible oxidation of BH₄⁻. In figure 6(C), we have shown the linear relationship between anodic peak current (*i*_{pa}) vs concentration of borohydride for both NTN/C and NTN-H/C modified electrodes. Interestingly for NTN-H/C modified electrode the line has smaller slope value, indicating slow electron transfer for BH₄⁻ oxidation. On comparing the non-faradaic regions in cyclic voltammogram of both NTN/C and NTN-H/C modified electrodes, it is clear that NTN-H/C modified electrodes exhibits a gradual rise in double layer capacitance (*C*_{dl}). On further analysis of the voltammogram obtained at higher concentrations of borohydride for both NTN/C and NTN-H/C electrodes, a cross over loop is seen on the reverse scan. This effect is probably due to the adsorption of borohydride or other

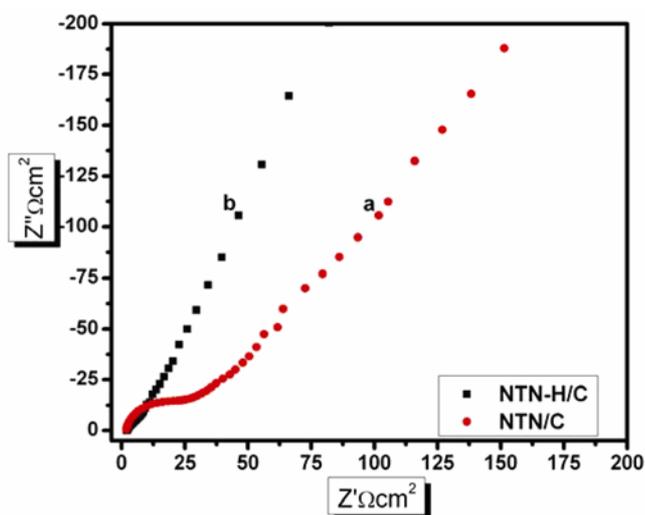


Figure 3. Shows Nyquist plots for (a) NTN/C and (b) NTN-H/C modified GC in 0.5 M NaOH.

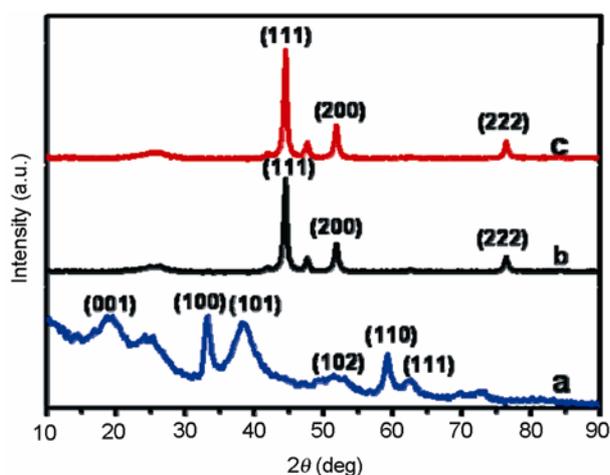


Figure 4. (a) XRD pattern for NTN/C treated in 0.5 M NaOH, (b) and (c) XRD patterns for NTN-H/C and NTN-H/C after and before treatment in 0.5 M NaOH.

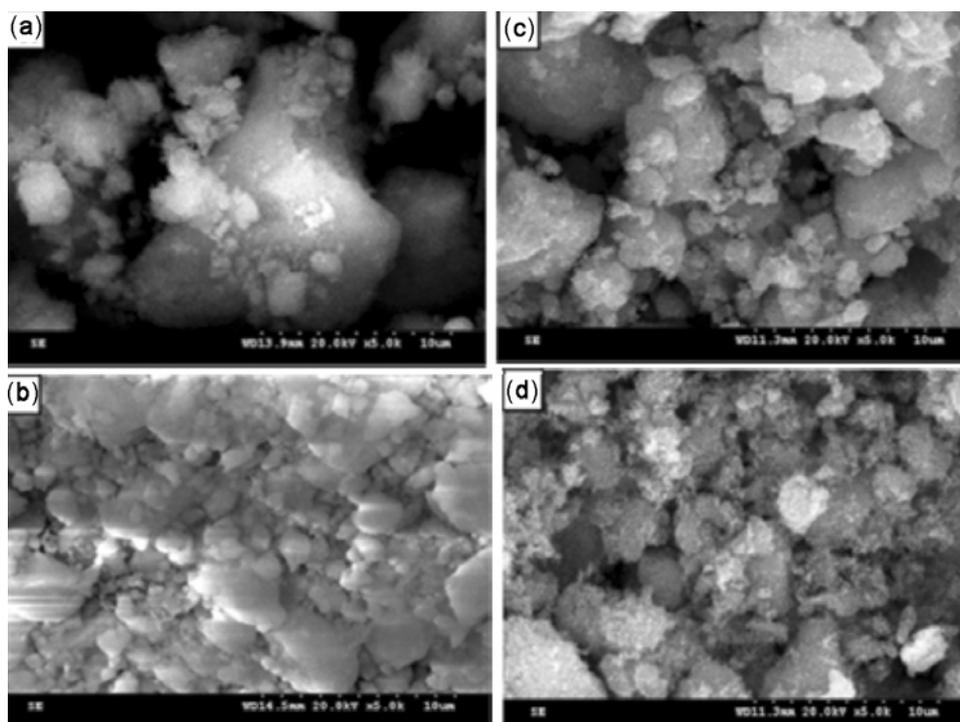


Figure 5. SEM images of (a) NTN/C and (c) NTN-H/C. SEM images of (b) NTN/C and (d) NTN-H/C after treatment in 0.5 M NaOH for 30 min.

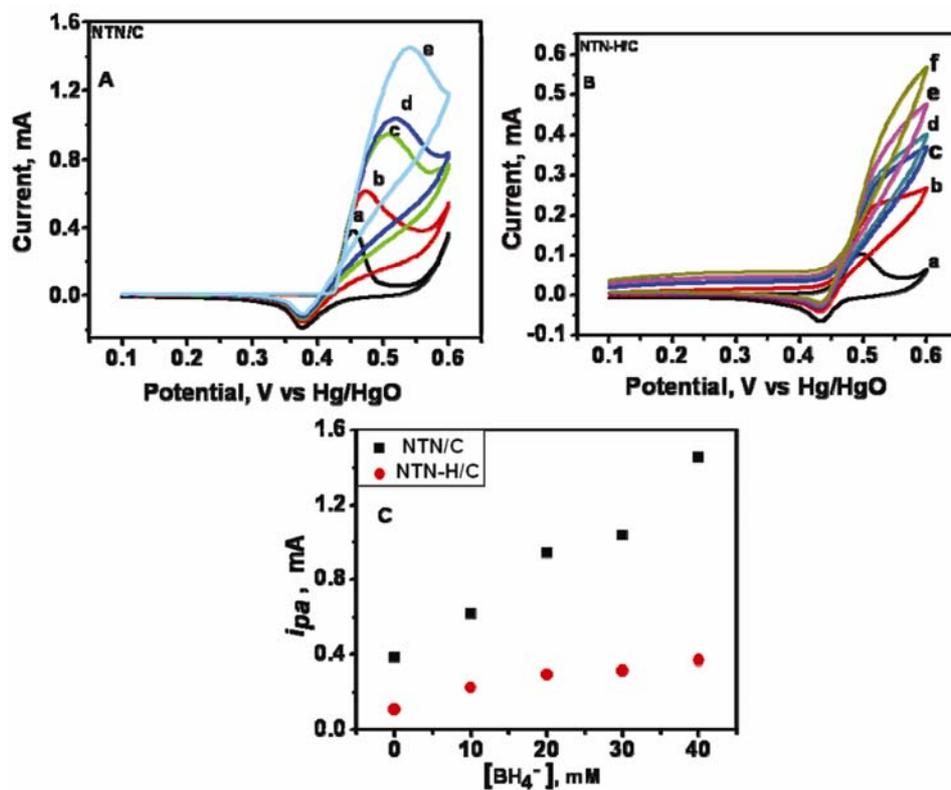


Figure 6. (A) and (B) show voltammetric response of NTN/C and NTN-H/C towards borohydride oxidation in 0.5 M NaOH. (a) 10 mM, (b) 20 mM, (c) 30 mM, (d) 40 mM and (e) 50 mM NaBH₄, (C) shows linear graph between anodic peak current (*i_{pa}*) of NTN/C and NTN-H/C modified electrodes vs concentration of borohydride.

reaction intermediates like H₂, BO₂⁻ formed during electrocatalysis of BH₄⁻ oxidation on Ni substrate (Maurice and Richard 1962) on both NTN/C and NTN-H/C electrodes. Such voltammetric behaviour confirms that BH₄⁻ at the electrode surface is not completely oxidized on both NTN/C and NTN-H/C substrates. This effect was much more pronounced, when we use Ni electrode for BH₄⁻ electrooxidation in alkali. Pseudo limiting current in the voltammograms observed for borohydride electrooxidation on NTN-H/C is also indicative of the slow electron transport in NTN-H/C films in alkali compared to that in NTN/C.

4. Conclusions

The work demonstrates a new route for the conversion of insoluble carbon supported nickel tetracyanonickellate precursors for the synthesis of Ni(OH)₂/C. This method is amenable for the preparation of Ni(OH)₂ films doped with many other transition metal ions such as Co²⁺, Pd²⁺, etc. Understanding the changes in electrocatalytic properties of Ni(OH)₂ on doping is interesting and currently being pursued in our laboratory. In the present study, Ni(OH)₂/C prepared from electrochemical cycling gave better electrocatalytic activity towards borohydride oxidation compare to preparation through thermal decomposition. However, here it is worth to mention that the decomposition of transition metal cyanocomplexes either in alkali or thermally is generic and expected to pave way for the synthesis of many new transition (mixed) metal oxide catalyst for electrocatalytic applications.

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