Short communication

Catalytic activity of cobalt deposited on nanostructured poly(p-xylylene) films

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ABSTRACT

Nanostructured and planar films of poly(p-xylylene) (PPX) are fabricated by an oblique angle polymerization method and coated with cobalt using electroless deposition. The catalytic activity of cobalt coated on the nanostructured and planar PPX films is studied by measuring the rate of hydrogen evolution by the hydrolysis of alkaline-stabilized sodium borohydride ($NaBH_4$) solution. The hydrogen release rate data show an asymptotic increase for the structured PPX film as a function of the electroless bath time, but the planar PPX films show a lower catalytic activity due to the inefficiency of cobalt deposition. The hydrogen release rate of the cobalt-coated nanostructured PPX film shows a rate between 2000 and $4250 \, mL(g \, min)^{-1}$ (i.e., rate of hydrogen gas per cobalt mass at room temperature and pressure), which is comparable to the values obtained on platinum, and ruthenium systems.

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1. Introduction

Hydrogen is envisioned as the next-generation fuel to provide a clean alternative to the current hydrocarbon-based fuels in the field of transportation and even personal electronics. Hydrogen storage is thus a topic of great interest to the research community. Currently, techniques such as adsorption on activated carbon [1], carbon nanotubes [2], hydrogen bearing alloys [3], metal hydrides [4], and zeolites [5] have been proposed as better alternatives than compressed hydrogen tanks. It has been shown [6–9] that metals (i.e., platinum, ruthenium, cobalt, and nickel) act as a catalyst and produce hydrogen (H_2) gas when in contact with a $NaBH_4$ electrolyte. The reaction rate is controlled largely with the pH and temperature of the electrolyte.

$NaBH_4$ is a light yellowish-gray powder with a soapy appearance when dissolved in water. $NaBH_4$ can be stored as a solution in plastic containers under ambient temperature and atmospheric pressure. It is less toxic and less flammable than other regularly used fuels, such as methanol or gasoline. Alkaline solutions of $NaBH_4$ in contact with select metal catalysts can be hydrolyzed to release H_2 gas and

water-soluble sodium metaborate, $NaBO_2$ [10].

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} NaBO_2 + 4H_2$$
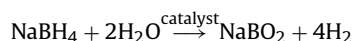
The reaction produces (in theory) up to eight hydrogen atoms (four molecules), with four atoms of hydrogen being present in the $NaBH_4$ and the rest coming from water molecules.

Hydrogen evolution occurs only on select catalysts and can be controlled carefully using a combination of parameters such as temperature, pH, and concentration. It should be noted that $NaBH_4$ easily hydrolyzes at conditions of pH < 9 even without the catalyst [6], but the hydrogen evolution rate decreases as the reaction proceeds due to the formation of basic sodium metaborate. Thus, to control the H_2 release, the solution is made alkaline with pH > 9, and the reaction is carried out in presence of a metal catalyst such as Pt, Ru, Co-B, and others. The hydrogen generation rate is directly proportional to the active surface area of the catalyst as well as the ability of the catalyst to adsorb the reactants and desorb the products. The selective hydrogen release from the alkaline-stabilized $NaBH_4$ solution in the presence of a catalyst can be used as a 'switch', where the hydrogen is released when the catalyst is in contact with the solution and ceased when the catalyst is removed.

We recently demonstrated that nanostructured polymers of poly(p-xylylene) (PPX) and its derivatives can be fabricated by oblique angle vapor deposition polymerization [11–13]. These structures are composed of approximately 40,000,000 aligned columns (approximately 100–150 nm in diameter) per square mil-

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limeter. The growth of nanostructured PPX films using this oblique angle technique is governed by three mechanisms: (i) geometrical self-shadowing [14], (ii) surface diffusion along the substrate [14], and (iii) surface roughening and nucleation (common in thin films [15–17]). The metallization of the nanostructured PPX film has a potential impact on the development of new materials for coatings, catalyst supports, medical implants, and sensor platforms. Recently, we showed that the pyridine can non-covalently bind to the poly(chloro-p-xylylene) (PPX-Cl) film and subsequently covalently bind a Pd colloid to initiate the electroless deposition of nickel at the surface [18].

In this paper, a nanoporous cobalt film is prepared by an oblique angle polymerization method using the nanostructured PPX-Cl film as a substrate. Here, we report the catalytic activity of a nanoporous cobalt film in $NaBH_4$ solution. Cobalt is an inexpensive material compared to platinum, and has a relatively high catalytic activity compared to nickel for hydrogen release from $NaBH_4$. The nanostructured PPX film is selected as a substrate for electroless cobalt deposition because PPX film offers the possibility of fabricating surfaces exhibiting tunable roughness [11–13]. The results show that the hydrogen release rate increases as a function of cobalt bath time. In contrast, the catalytic activity of cobalt deposited on planar PPX-Cl films shows one order magnitude lower hydrogen release rate than that of the cobalt-coated nanostructured films.

2. Experimental

2.1. Materials

All chemicals were A.C.S reagent grade and were used as received. Deionized water of 18.1 MΩ cm was used for all experiments using a Barnstead Nanopure Diamond™ dispenser. Dichloro-[2,2]paracyclophane (DCPC) was purchased from Parylene Distribution Services and deposited on p-type Si (1 0 0) wafers (Wafernet Inc., San Jose, CA).

2.2. Nanostructured PPX-Cl film preparation

Silicon wafers were first sonicated in acetone. Afterwards, the wafers were washed in water and dried under nitrogen gas flow. The wafers were then transferred to a 1/1 (v/v) solution of HCl (36.5–38%, w/w) and methanol (98.5%, w/w). After 30 min, the wafers were removed, washed with water, and dried with nitrogen gas. The wafers were then kept in concentrated H_2SO_4 (95–98%, w/w) for another 30 min, after which they were washed and sonicated in water for 10 min. The wafers were thoroughly dried under nitrogen gas. The self-assembled monolayer (SAM) solution was prepared by adding 1% (v/v) allyltrimethoxysilane (Gelest, PA) in toluene containing 0.1% (v/v) acetic acid. The cleaned wafers were transferred to this solution and left for SAM formation for 60 min at 25 °C. The wafers were removed after 60 min and sonicated in anhydrous toluene for 10 min. The wafers were then dried on a hot plate at 140 °C for 5 min. Nanostructured films of poly(chloro-p-xylylene) were deposited on these allyl functionalized silicon wafers using oblique angle vapor deposition at low-vacuum conditions (~10 Torr). The details of the procedure for preparing the nanostructured film have been explained previously [12,19]. Briefly, PPX-Cl films were deposited using 0.3 g of DCPC at a vaporizing temperature of 175 °C, while the pyrolysis chamber was maintained at 690 °C. The substrate was maintained at ambient temperatures. The columnar PPX-Cl films were deposited on these substrates using a deposition angle of $\alpha = 10°$, and the columns were grown up to a 50-μm thickness with diameters of approximately 150 nm.

2.3. Metallization of PPX-Cl films

The metallization was performed using a three-step process. First, the films were soaked in 1 M pyridine solution for 48 h. The films were then washed in water and dried by blowing N_2 gas. Second, the films were transferred to a Pd(II)-based solution [20]. The Pd(II)-based colloidal solution was prepared by hydrolysis of Na_2PdCl_4 at pH 5 in a 0.01-M NaCl solution. The solution was aged for approximately 20 h before use. The films were kept in the aged Pd(II) solution for 45 min at 25 ± 0.5 °C, after which they were washed in water and dried under N_2 gas. The final step is the metallization of the palladium seeded PPX-Cl film. The cobalt metallization bath was prepared by dissolving 0.9 g of EDTA, 1 g of ammonium chloride and 0.6 g of cobalt chloride in 15 mL of water. The pH of this bath was adjusted to 8.2 by the drop-wise addition of 0.1 M NaOH solution. Boranedimethylamine (0.4 g) was then dissolved in 5 mL of water and added to the bath. The bath temperature was stabilized at 25 ± 0.5 °C. Subsequently, the films were then placed in the bath for cobalt to deposit. By varying the bath time, cobalt films of different thicknesses were prepared. The films were then washed in deionized water and dried under N_2 gas. Dried samples were stored in Fluroware® containers until needed for characterization.

2.4. Film characterization

The surface topography of nanostructured PPX-Cl films was characterized using a Nanoscope-E atomic force microscope (Veeco Metrology, CA). All images were collected in ambient air at room temperature using triangular cantilever silicon nitride (SiN) contact mode tips. The cobalt films were characterized using a Philips XL-30 scanning electron microscope (SEM) to study the morphology of the prepared catalyst. The composition of the catalyst layer on the nanostructured PPX-Cl was characterized using EDAX.

2.5. Hydrogen release rate

Aqueous solutions of 2.5% $NaBH_4$ (0.677 M) and 1% NaOH (0.261 M) were used for all the experiments at room temperature. The pH (13) was kept constant, while the solution temperature was maintained at 25 ± 0.5 °C. The solution was contained in the 125 mL beaker, and the hydrogen gas generated was collected in the water column, which was immersed into a beaker. The amount of hydrogen release was recorded with respect to time. From these data, the release rate was obtained by differentiating the hydrogen release volume with respect to time. The hydrogen release rate was measured in mL of H_2 per square centimeter of the cobalt film per minute $(mL(cm^2 min)^{-1})$. The rate was also measured in mass units as mL of H_2 per gram of cobalt per minute $(mL(g min)^{-1})$ by calculating the mass of cobalt deposited on the PPX-Cl film.

3. Results

Poly(chloro-p-xylylene) films were grown by vapor deposition polymerization using di-chloro-[2,2]paracyclophane as the starting material [21]. For this study, both planar (conventionally deposited) and columnar PPX-Cl films were grown. Fig. 1 shows the cross-sectional SEM images of columnar and planar PPX-Cl films. We note that planar PPX-Cl films do not possess a nanostructured morphology. Both nanostructured and planar PPX-Cl films were then coated with cobalt by an electroless deposition method.

The metallization process relies on the non-covalent adsorption of the metal-binding ligand (i.e., pyridine) to the structured
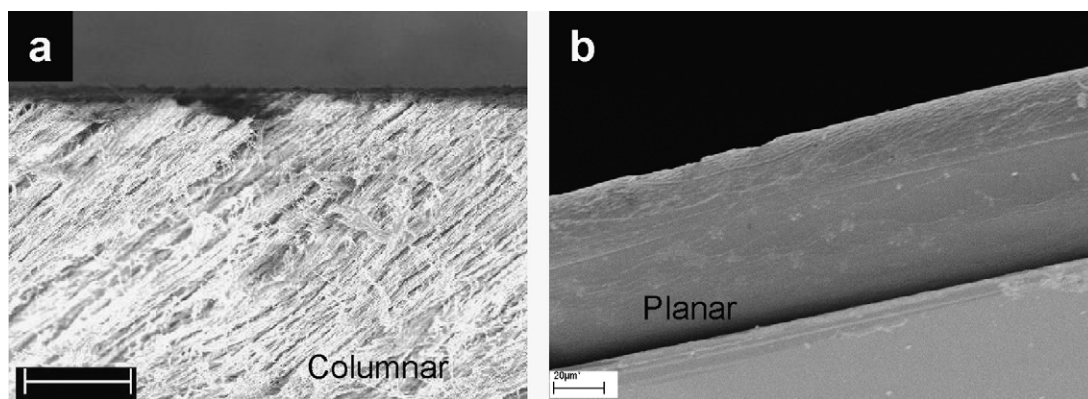
Fig. 1. Cross-sectional SEM images of PPX films deposited under (a) oblique angle (columnar morphology) and (b) conventional (bulk) methods (scale bar: 20 μm).

PPX-Cl to covalently anchor the Pd(II) catalyst required for electroless metal deposition [18]. This is a facile method for conformal electroless cobalt deposition that permits the control of the cobalt morphology and topology via the use of tailored, nanostructured PPX-Cl film templates. In addition, the high surface energy of the nanostructured film surface also promotes pyridine adsorption that
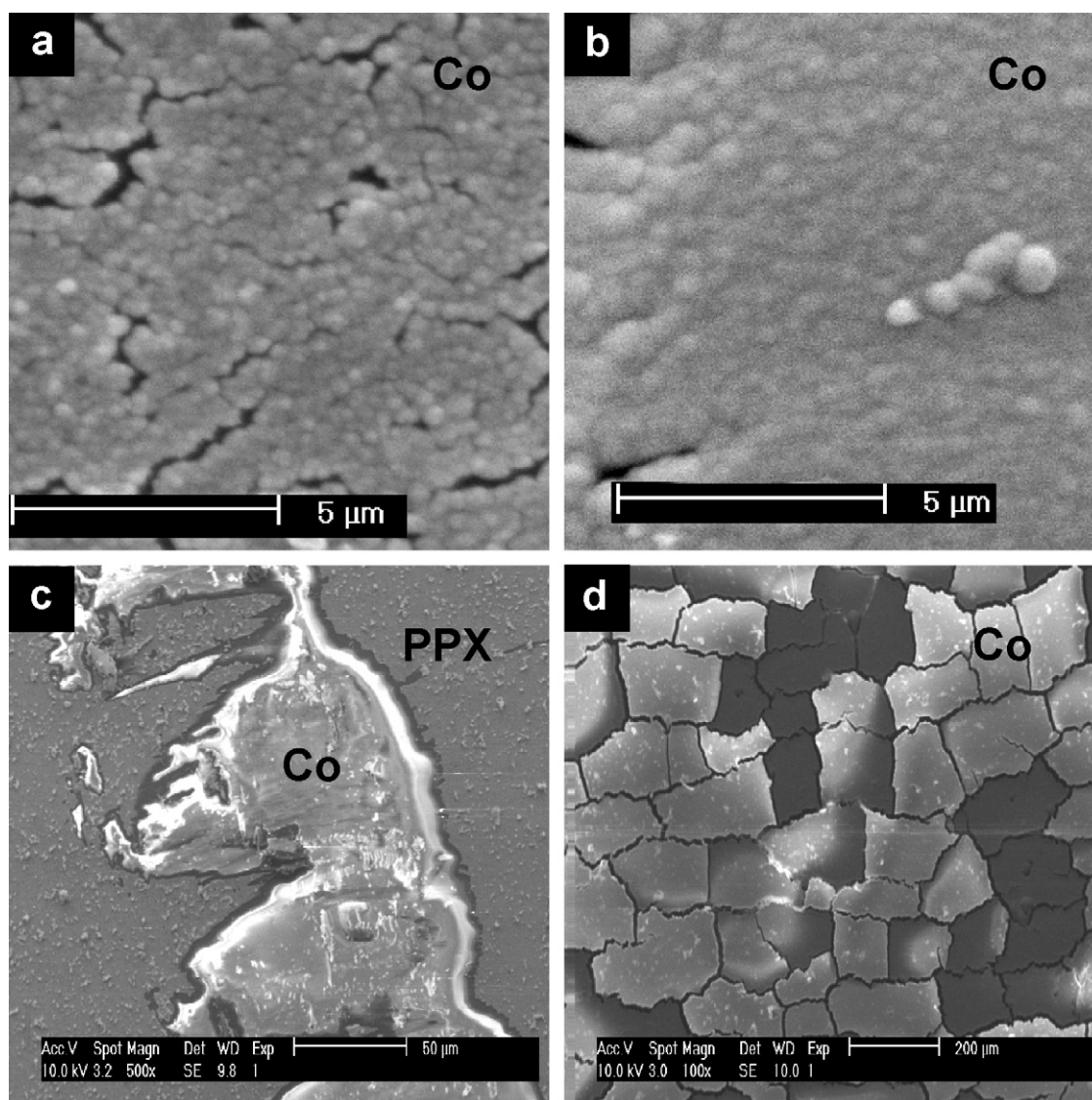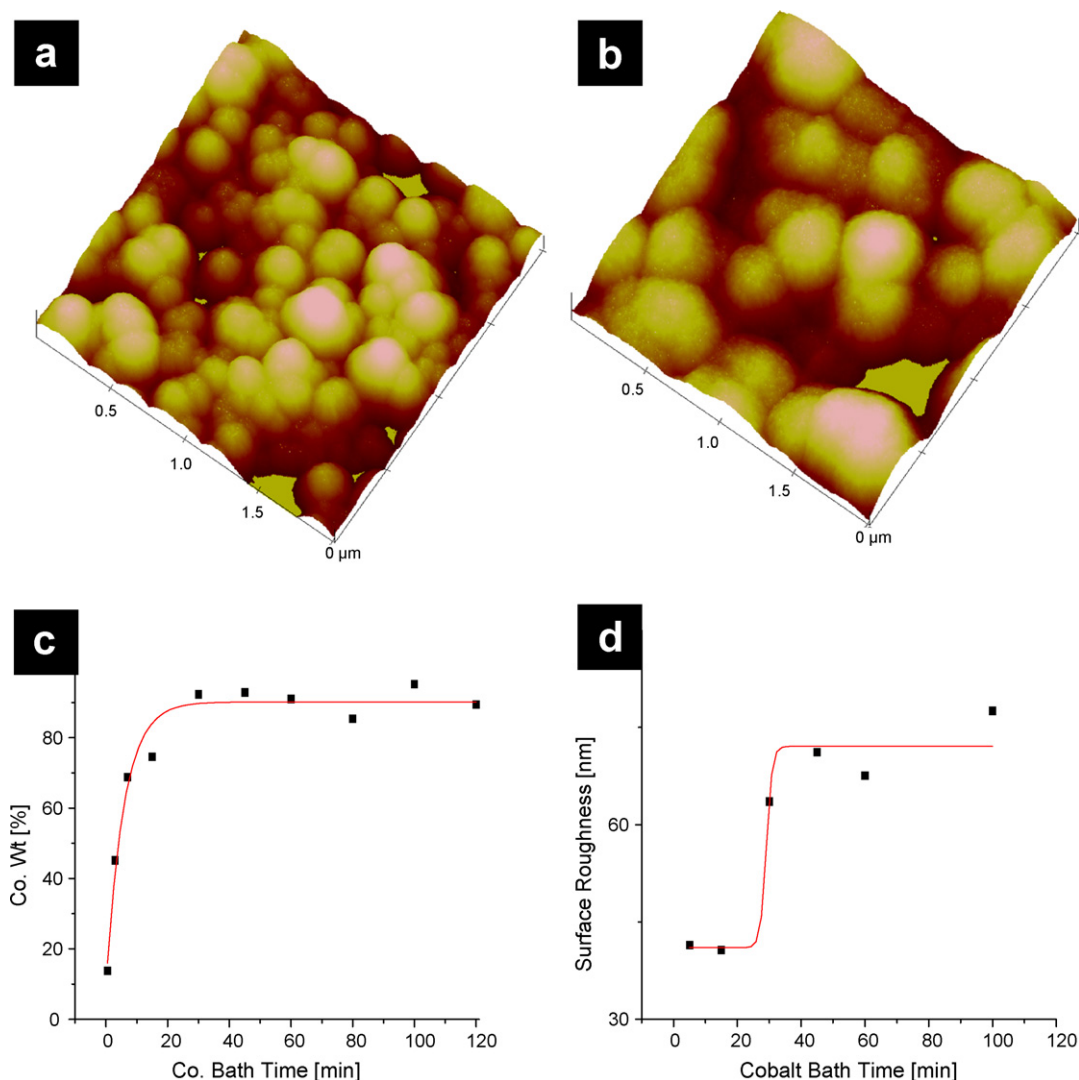

Fig. 2. SEM images for (a) 15 min cobalt bath time on nanostructured PPX-Cl (both microscopic and macroscopic porosity are observed), (b) 100 min cobalt bath time on nanostructured PPX-Cl (less porous compared to (c)) are shown. (c) Metalized planar PPX-Cl film which shows isolated patches of cobalt (scale bar: 50 μm), and (d) metalized nanostructured PPX-Cl at a 120-min bath time, which shows delaminating of the cobalt film (scale bar: 200 μm).

Fig. 3. AFM images for (a) 15 min and (b) 60 min cobalt bath times are shown. The scale bars for the AFM scans: X, 0.5 μm div^{-1}; Y, 0.5 μm div^{-1}; Z, 100 nm div^{-1}. (c) Cobalt weight percentage on nanostructured PPX film obtained from the EDAX data with respect to the cobalt bath time. (d) Roughness of nanoporous cobalt film on nanostructured PPX-Cl with varying bath times.

enhances the electroless metal deposition. SEM images of porous cobalt films are shown in Fig. 2. The images show the formation of the cobalt film that takes place conformally onto the structured PPX-Cl surface. Comparison of the SEM images in Fig. 2a (15 min bath time) and Fig. 2b (100 min bath time) show that the porosity decreases at higher bath time as expected. The electroless Co films deposited here on columnar PPXs exhibit good adhesion (<5% Co delamination in Scotch Tape® tests). In contrast, for a planar film, the level of pyridine adsorption is poor and thus does not promote enough Pd binding for metallization. The metallization in planar films takes places in patches (Fig. 2c), which have low adhesion compared to the metalized nanostructured films. The nanostructured film starts to delaminate at a bath time of 2 h due to large stress accumulation (Fig. 2d).

AFM images of porous cobalt films are shown in Fig. 3. The metallization process starts on the tip of columns and grows as the electroless cobalt deposition proceeds. Fig. 3a shows an average size of 250 nm for the metal particles (for a 15-min bath time), whereas the average size increases to approximately 1 μm in Fig. 3b (for a 60-min bath time). Fig. 3c shows the EDAX data obtained for the weight percentage of deposited cobalt as a function of increasing

bath time. This is an indication of how the cobalt deposition rate proceeds with respect to bath time. The cobalt weight percentage saturates at around 90%, which corresponds to a 40-min bath time. These data are in agreement with the morphology of the cobalt surface characterized in Fig. 2a and b. The roughness of the electroless deposited cobalt on the PPX-Cl film is plotted against bath time in Fig. 3d. The roughness of the cobalt on the nanostructured PPX-Cl substrate increases as a function of the bath time.

Fig. 4 shows the hydrogen release rate of a stabilized alkaline solution of NaBH$_4$ from the cobalt surface under different conditions. Fig. 4a shows an asymptotically increasing trend with respect to the amount of cobalt. Three films were tested for each bath time, and error bars show the standard deviation of hydrogen release rate between samples. Initially, the cobalt deposited on the nanostructured PPX-Cl films was insufficient to show any catalytic activity, but, as the cobalt deposition proceeds, the roughness of the surface increased and so did the hydrogen release rate. Fig. 4b and c shows the dependence of the hydrogen release rate for metal hydride concentration and pH dependence, respectively. The maximum rate of hydrogen release is obtained at 2.5% of NaBH$_4$ concentration and at pH 11.5.
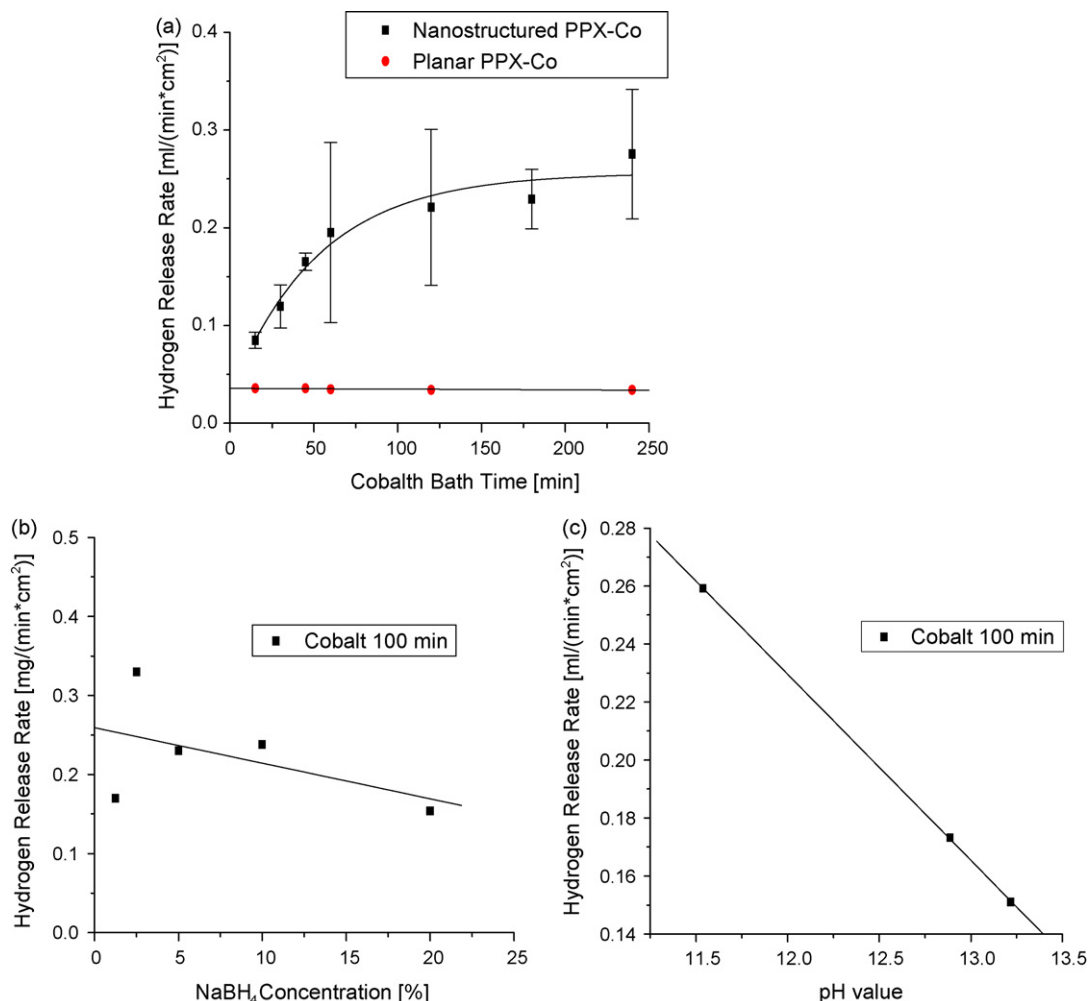
Fig. 4. (a) The hydrogen release rate ($mL(min\,cm^2)^{-1}$) from the nanoporous and planar cobalt surface measured in 2.5% $NaBH_4$ and 1% NaOH at 25 °C. (b) Hydrogen release rate dependence on $NaBH_4$ concentration measured for a 100-min bath time sample at a pH of 11.5 and at 25 °C. (c) Hydrogen release rate dependence on pH measured for a 100-min bath time sample with 2.5% $NaBH_4$ concentration at 25 °C.

The reusability of the cobalt catalyst deposited on the PPX films was tested under identical experimental conditions (2.5% $NaBH_4$ and 1% NaOH at room temperature and pressure). The cobalt film was washed with water and dried with N_2 after each 1 h cycle. The hydrogen release rate for 240 min sample showed 8% variation in the catalytic activity during four cycles.

4. Discussion

Hydrogen release results are presented in surface area units in this paper since our technique involves the deposition of cobalt on a surface. It is also possible to present the hydrogen release data in mass units. Performing a theoretical calculation of the rate in $mL(g\,min)^{-1}$, considering the thickness of the cobalt film of 50 nm [18] and a density of $8.9\,g\,cm^{-3}$ (i.e., theoretical density is considered), gives a value of approximately $10,100\,mL(g\,min)^{-1}$, which is the upper bound value for the rate. It should be noted that the actual density of the film is significantly lower than the theoretical density, which would give a higher rate value. We also measured the weight of the cobalt film and obtained the release rate in mass units by measuring the weight of the cobalt deposited on the PPX film. The hydrogen release rate varies in between 2000 and $4250\,mL(g\,min)^{-1}$. We note that the hydrogen release rate at a 240-min bath time shows the highest value ($4250\,mL(g\,min)^{-1}$ in mass units or $0.36\,mL(min\,cm^2)^{-1}$ in surface area units). This is due to the surface roughness of cobalt, which asymptotically increases

Table 1
Comparison of the hydrogen release rate from $NaBH_4$ for various catalysts.

Catalyst	$NaBH_4$ concentration (wt.%)	NaOH concentration (wt.%)	Temperature (°C)	Hydrogen release rate ($mL(g\,min)^{-1}$)	Reference
A-26 (Ru-based)	20	10	25	4,032	[23]
IRA-400 (Ru-based)	12.5	1	25	~9,600	[6]
Pt/C	10	5	No data	23,090	[24]
CoB	2	5	15	~3,500	[7]
Pt–LiCoO$_2$	5	5	25	~24,000	[8]
CoB	25	3	25	~7,500	[25]
Co/PPX-Cl	2.5	10	25	4,250	This work

as the cobalt is kept in the electroless bath for longer periods of time.

We should note that our hydrogen release rate is significantly higher compared to that of a metallic cobalt catalyst (i.e., 32 mL(g min)$^{-1}$ [22]). Some of the prominent data published in literature are presented in Table 1. Other metal-based catalysts, such as platinum and ruthenium, show higher release-rates than our results (Table 1). The facile preparation technique, with comparable release rate results, makes our method promising for future development in this area.

5. Conclusion

In conclusion, we studied the hydrogen release of a stabilized alkaline solution of NaBH$_4$ on the cobalt catalyst film. The cobalt film is deposited by electroless deposition on nanostructured PPX-Cl films that are grown using an oblique angle polymerization method. The hydrogen release rate data show an asymptotic increase as the film is incubated for longer times in the electroless bath. In contrast, the metalized planar PPX-Cl films show very little catalyst activity due to the patchy nature of the cobalt deposit. Our method of preparing the cobalt catalyst is attractive because the process can be easily scaled up. The nanostructured polymer film can be easily prepared without using any template or lithography. In addition, the cobalt films can be reused without any significant reduction in catalytic activity. In short, the cobalt-based catalyst promises to be a cost efficient way of releasing hydrogen from sodium borohydride, and it may replace the more expensive noble metal catalysts.

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