Arul Anandar Journal of Science & Arts

Volume 1, Februray 2026

SOLVENT FREE SYNTHESIS AND CHARACTERIZATION OF COBALT OXIDE / CARBON NANOCOMPOSITES FOR HYDROGEN GENERATION FROM SODIUM BOROHYDRIDE HYDROLYSIS

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ABSTRACT

Hydrogen production is one of the major research fields in the renewable energy area, and hydrogen is used as fuel in hydrogen fuel cells. Hydrogen can be produced from chemical hydrides via various production methods, with thermolysis and hydrolysis the most used. Although hydrolysis provides slower kinetics, it is possible to obtain high hydrogen generation rates with the acid of catalysts. In the present study, solvent free synthesis method was adopted for the preparation of Co/C nanocomposites as electrocatalysts for the electrochemical Hydrogen generation reactions. In this method, glucose, urea, and Cobalt chloride precursor was mixed in a mortar and pestle, grind well, and heated at air oven at 180 ˚C. Then obtained paste was dissolved in minimum quantity of water and reduced using $NaBH_4$. The formed catalyst was characterized using UV-visible spectroscopy, FT-IR spectroscopy, XRD and Raman spectroscopy. The spectral results confirmed the formation Co/C nanocomposites. The formed nanocomposites are drop casted on glassy carbon electrode and used as electrocatalyst for

hydrogen production reaction in NaOH medium. The electrocatalyst decreased the overpotential for the hydrogen production reactions.

Keywords: Solvent free synthesis; Spectral Characterization; $NaBH_4$ Hydrolysis; Hydrogen production Monitoring; Overpotential.

INTRODUCTION

The global demand of energy continues to grow rapidly due to industrial development, urbanization, and technological advancements. However, at the same time, the environmental impacts of fossil fuel burning such as greenhouse gas emissions, global warming, and air pollution became increasingly much worse. Therefore, these have stimulated an urgent search for clean, sustainable, and renewable energy which would gradually replace conventional fossil-fuels based energy sources [1-3]. Among those alternatives, hydrogen has become one of the most promising energy carriers of the future for various reasons. It has a high gravimetric energy density (120-142 MJ kg^{-1}), nearly three times that of traditional hydrocarbons, combusts to yield only water as by-product, and hence is classified as a zero-emission fuel [4,5]. These incredible properties have turned hydrogen into a prioritized contender as a futuristic clean fuel for applications like fuel cells, electric vehicles, and portable energy devices.

Despite the various advantages of hydrogen, storage of hydrogen fuel remains a major challenge toward its widespread application. Techniques of conventional hydrogen production, namely steam methane reforming, partial oxidation of hydrocarbons, and gasification of coal, are all existent methods yet solely depending upon fossil resources, with a large volume of carbon dioxide emission [6]. Cleaner has been water electrolysis, but it takes high electrical input, which mostly comes again from nonrenewable sources, thus limiting its sustainability overall. To solve these problems, researchers started to devote their efforts to chemical hydrogen storage materials, and the principle is hydrogen release from more harmless storage media through controlled chemical reactions.

Among the hydrogen storage materials available, sodium borohydride, $NaBH_4$, is being pursued on account of its high hydrogen content (10.8 wt%), non-toxicity, high stability in

alkaline solution, and controllable release of hydrogen through hydrolysis [7-9]. The hydrolysis reaction of sodium borohydride proceeds according to the following equation:

$$NaBH_4 + 2H_2O \text{ ------> } NaBO_2 + 4H_2$$

The resulting four moles of hydrogen theoretically produced per mole of $NaBH_4$ make it an effective and viable source for hydrogen. However, hydrolysis of $NaBH_4$ is kinetically slow at room temperature in neutral or basic media. Hence, catalyst selection was essential to fasten the process and result in efficient hydrogen release. Several noble metals (Pt, Pd, Ru, Rh) and some non-noble transition metals (Co, Ni, Fe, Cu) and their oxides have been examined for the purpose [10-13]. While showing maximum catalytic activity, noble metals are costly and therefore unsuitable for large-scale applications. Co, nevertheless, as noted earlier, has attracted increased interest since it is abundant, inexpensive, and quite active towards hydrolysis of $NaBH_4$ [14,15].

Cobalt and its oxides (Co, CoO, Co_3O_4) exhibit specific redox behavior while facilitating adsorption and dissociation of hydride ions, which enhances the kinetics of hydrogen generation. The assembly of the above-cited metals with conductive carbon materials as activated carbon, graphene, or carbon nanotube may offer cobalt/carbon nanocomposites with advanced performance. The carbon matrix not only gives support with high surfaces, but also attaches cobalt nanoparticles dispersion, preventing their aggregation and thereby improving electron pathways during catalytic reactions [16-18]. The reactive entity generated between cobalt and carbon enhances their effectiveness toward catalysis, stability, and the reusability of the nanocomposite catalyst.

Preparation of cobalt-based catalysts and their carbon composites is mostly via wet-chemical synthesis methods like co-precipitation, sol-gel, hydrothermal, or solvothermal techniques [19]. Although they give a controlled morphology and composition for the resultant nanomaterials, these techniques often make use of toxic solvents and require prolonged reaction times with several purification steps. Additionally, these methods consume a lot of energy. In addition to all these, solvent-based synthesis generates large volumes of chemical waste,

resulting in environmental and economic problems [20]. Hence, efforts to surpass these limitations have seen researchers switch to solvent-free or solid-state techniques, the latest development in this backlash against the drawbacks by instituting greener and more sustainable preparation of nanomaterials.

In solvent-free synthesis, reactants are mixed and ground in the solid state and subjected to controlled thermal treatment, usually under air or inert atmosphere. This method is free of organic solvents or surfactants, reduces synthesis time, and minimizes environmental hazards [21-22]. Moreover, it improves uniform mixing to the molecular level, hence leading to better-dispersed nanocomposites optimum physicochemical properties. In the case of transition-metal catalysts, this solvent-free synthesis provides the cost-effective route to large-scale manufacture of such green and environment-friendly nanomaterials, which can be used for energy and environmental applications.

The present study explores a solvent-free synthesis technique in the preparation of cobalt oxide/carbon (Co/C) nanocomposites using glucose and urea as carbon and nitrogen sources, respectively, and cobalt chloride as the cobalt precursor. Glucose is a green carbon source that undergoes dehydration and polymerization under heat, producing a carbonaceous matrix that embeds cobalt species. In addition, urea serves a dual role: its decomposition releases ammonia and carbon dioxide, creating a mildly basic environment that facilitates the conversion of Co^{2+} ions into cobalt oxide and enhances carbonization of glucose. Collectively, these processes yield Co/C nanocomposites simply and environmentally benignly without using any solvents or surfactants and scalable.

EXPERIMENTAL SECTION

Chemicals

Glucose (99.5%), urea (98%), cobalt chloride (97%) and sodium borohydride ($NaBH_4$) were purchased from Merck. Sodium hydroxide, water and all other common chemicals were purchased from CDH. All reagents were used as received. Double distilled water was used throughout the experiments.

Instrumentation

The FT-IR spectra of the samples were measured in the form of KBr powder-pressed pellets in JASCO FT-IR 460 plus model under ambient conditions. The crystalline nature of the samples was studied by X-ray diffraction (XRD), Siemens D5000 using Cu-Kα radiation (λ = 1.5406 Å) and Ni filter.

Synthesis of Cobalt/Carbon particles

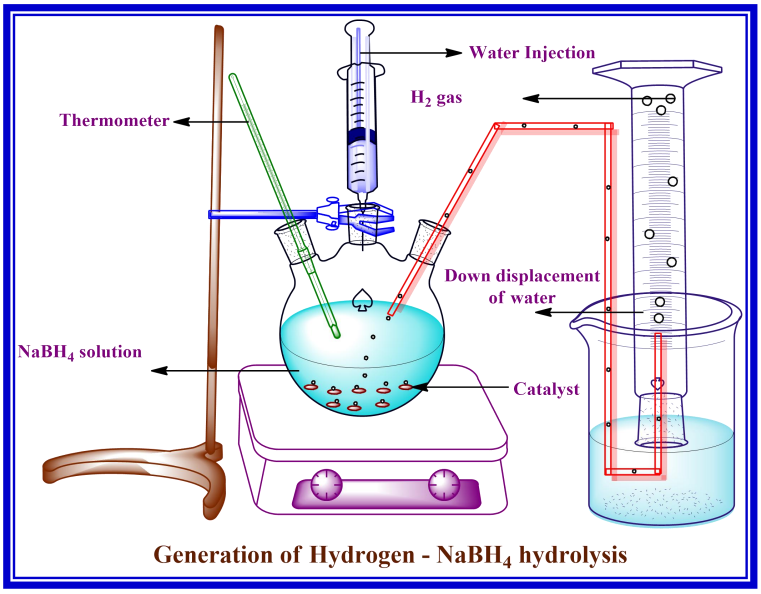
Cobalt chloride and glucose was used for the precursor of Co/C. In the present study, Co/C particles were prepared using solvent free synthesis (Scheme 1). In a typical procedure, 0.5 g of cobalt chloride, 1.5 g of glucose and 1 g of urea were mixed in a beaker and heated for 180 ˚C in a microwave oven. Then, 4 mL of deionized water was added to the above mixture and washed the sample. The block powder was collected and grind via centrifuging the mixture and the precipitate is washed with distilled water. Further, the particles are dried in a hot air oven at 110 ˚C. The as prepared Cobalt/Carbon was abbreviated as Co/C.

Scheme 1 shows the schematic illustration of synthesis of Cobalt/Carbon Nanoparticle

Catalytic Activity of Co/C catalyst towards hydrolysis of $NaBH_4$

The catalytic activity of various catalysts towards the hydrolysis of $NaBH_4$ for hydrogen generation was examined in neutral medium with and without catalysts using down displacement of water. Scheme 2 illustrates the experimental set-up for the hydrolysis of sodium borohydride by down displacement method. In a typical experiment, 0.1g $NaBH_4$ and the catalyst was taken a three-neck flask equipped with thermometer and syringe and the opening was connected to water filled inverted burette kept in water filled beaker. The water was introduced into the reaction via the syringe. The total volume was 100 cm^3 in each experiment. The amount of hydrogen generated due to the hydrolysis of sodium borohydride was measured by down displacement of water. The following equation is used for the calculation of rate of hydrogen generation from the slope of linear region of the plot obtained by plotting volume of displaced hydrogen versus time [23, 24]

$$Rate\ of\ hydrogen\ generation\ (k) = \frac{Amount\ of\ water\ displaced\ by\ Hydrogen}{time\ (min) * weight\ of\ the\ catalyst\ (g)} \qquad (1)$$



Scheme 2. Schematic illustration of reaction set-up of hydrogen production from sodium borohydride hydrolysis.

RESULTS AND DISCUSSION

Mechanism of formation of Cobalt/carbon particles

In a typical procedure, 0.5 g of cobalt chloride, 1.5 g of glucose and 1.0 g of urea were mixed in a beaker and heated for 180 ˚C in a hot air oven. Then, 4 mL of deionized water was added to the above mixture and washed the sample. The block powder was collected and grind via centrifuging the mixture and the precipitate is washed with distilled water. Further, the particles are dried in a hot air oven at 180 ˚C. The as prepared Cobalt/Carbon was abbreviated as Co/C.

In the present method, glucose acts as the carbon source and cobalt chloride acts as the source of Co metal. While heating the precursors at 180 degrees, the glucose molecules started losing the water molecules. In the meantime, the urea started to decompose to form NH_3 vapours which combine to form ammonium hydroxide and thus basic medium was generated. Under basic medium, Co^{2+} ions get converted into Cobalt oxide which gets reduced by glucose molecules present in the reaction medium. The formed black precipitate was washed thoroughly to remove the soluble urea and unreacted glucose molecules. Further, the dried black powder was characterized by FT-IR spectroscopy, UV-vis spectroscopy, XRD and Raman spectroscopy.

4.2. Characterization of Co/C by FT-IR spectroscopy

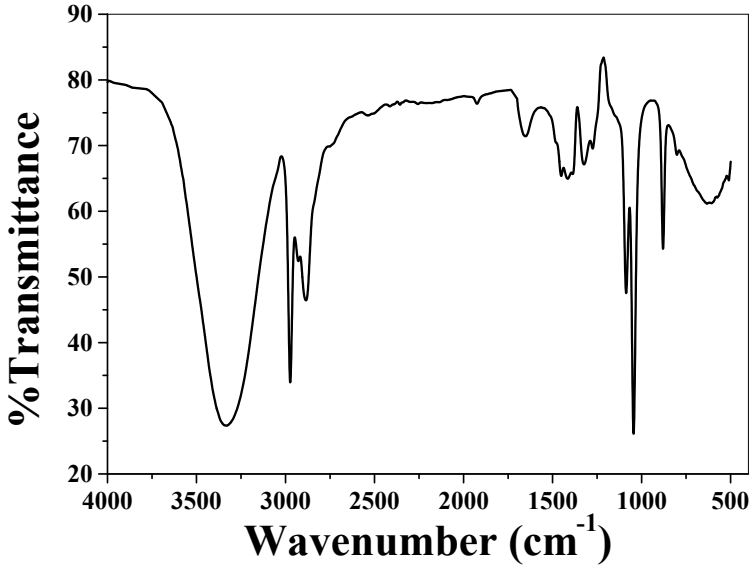


Fig. 1. FT-IR spectrum of Co/C nanocomposites.

The formed Co/C nanocomposites was characterized by FT-IR spectroscopy. Fig. 1 shows the FT-IR spectrum of Co/C nanocomposites. Generally, FT-IR spectroscopy is used to predict the functional groups present in the compound. FT-IR spectrum of Co/C exhibit many well defined peaks. A strong and broad peak at 3300 cm^{-1} was observed corresponding to -OH stretching frequency which confirms the formation of carbon (which contains oxygen functional groups like -OH) from glucose due to thermal decomposition. Further, the spectrum shows characteristic C-H asymmetric and symmetric stretching frequencies at 2926 cm^{-1} and 2853 cm^{-1}, respectively indicating the presence of C-H bond in carbon particles formed from dehydration of glucose. The strong intense peak at 1655 cm^{-1} indicated the C=C stretching frequency. Similarly, C-C stretching frequency was observed at 1427 cm^{-1}. The strong band at 1045 cm^{-1} indicated the bending vibrations of C-C bond presence in Co/C composite. The broad peak 623 cm^{-1} indicated the bonding between Co-O stretching band. The FT-IR spectral assignments for Co/C were summarized in table 1.

Table 1. FT-IR spectra data

Co/C (cm^{-1})	**Assignment**
3350	ν (O–H)
2926	ν (C–H) Asymmetric
2853	ν (C–H) Symmetric
1644	ν (C=C)
1427	ν (C-C)
1045	ν (C-C) Bending vibration
623	ν Co-C or Co-O

Characterization of Co/C by UV Visible spectroscopy

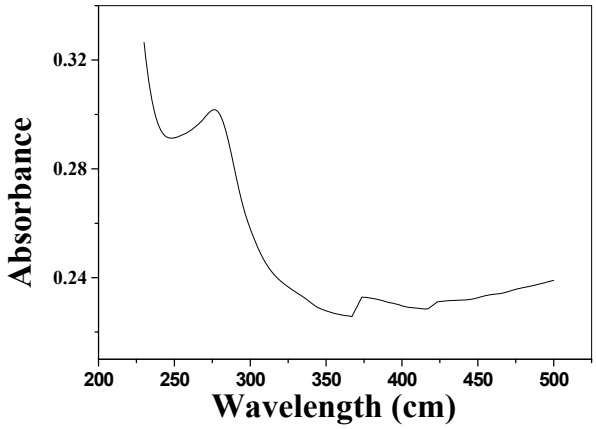


Fig. 2. UV-visible spectrum obtained for Co/C nanocomposites.

The as-prepared Co/C nanocomposite was characterized using UV-visible spectroscopy. For UV-visible spectral studies, the Co/C nanocomposite was dispersed in a mixture of ethanol/water solvent and the clear supernatant solution was used for the UV-visible measurements. Fig. 2. shows the UV-visible spectrum obtained for Co/C nanocomposites. It showed well defined peak at 290 nm indicating the n-π* transition of carbon particles presents in Co/C nanocomposites. The peak correspond to Co was observed was clearly observed at 375 nm which confirmed the formation of Co/C nanocomposites.

Characterization of Co/C by XRD

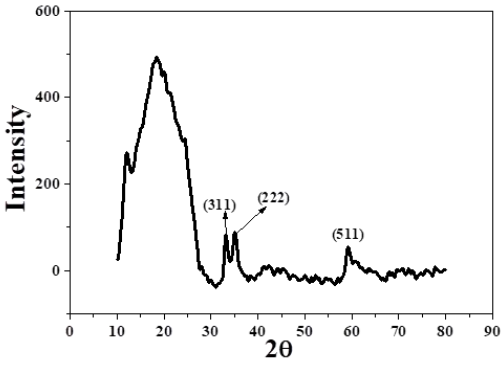


Fig. 3. XRD spectrum obtained for Co/C nanocomposites.

XRD is used to know the crystalline nature of the compound. Fig. 3. shows the XRD spectrum obtained for Co/C nanocomposites. It showed a broad peak around 22 degree which might be due to the amorphous carbon nanoparticles. In addition to that, the Co nanoparticles showed peaks at 33, 34.5 and 59 degrees corresponding to the crystalline planes of (311), (222) and (511), respectively. The results are in accordance with the JCPDS file No. 75-0605 [25]. It is obvious that the crystalline planes correspond to cobalt oxide nanoparticles. Further studies like XPS may be required in order to confirm the nature of Co and also C nanostructures.

Characterization of Co/C by Raman Spectroscopy

Raman spectroscopy is mainly used to characterize carbon-based materials. Fig. 4. shows the Raman spectrum obtained for Co/C nanocomposites. The Raman spectrum of Co/C shows peaks at 505.93 cm^{-1} and 669.84 cm^{-1}. The peak at 669.84 cm^{-1} (A_{1g}) corresponds to the vibration and the peak at 505.93 cm^{-1} corresponds E_g vibrations of cobalt oxide. These results confirmed the formation of cobalt oxide nanoparticles. In addition to the above-mentioned peaks, strong vibrational bands were observed at 1353.85 cm^{-1},1548.05 cm^{-1} and 2883 cm^{-1} attributed to the D, G and 2D bands of carbon which are assigned to the E_{2g} phonon of sp_2 carbon atom and the breathing mode of κ-point phonons of A_{1g} symmetry, respectively. From the intensity of D and G bands the average crystalline size can be calculated using the following formula [26].

$$L_a = (2.4 \times 10^{-10})\, \lambda_{laser}^4 \left(\frac{I_D}{I_G}\right)^{-1}$$

where La is the average crystalline size and λ is the laser wavelength in nm. The calculated crystalline size of Co/C nanocomposites will be 21.9 nm.

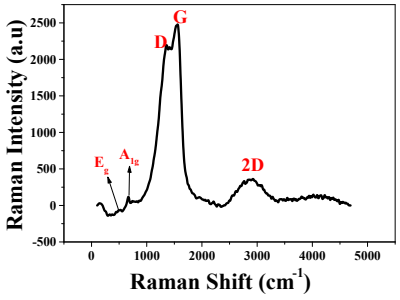


Fig. 4. Raman spectrum obtained for Co/C nanocomposite.

Catalytic activity of Co/C towards $NaBH_4$ hydrolysis

The primary aim of the present investigation is to prepare a heterogeneous catalyst for the generation of hydrogen from sodium borohydride hydrolysis. The hydrolysis of $NaBH_4$ in neutral and acidic solution is spontaneous and in basic solution the solution of $NaBH_4$ is highly stable. Hence, the catalyst which generates hydrogen in basic medium has more advantages. In the present investigation, Co/C nanocomposite was used as catalyst for the generation of hydrogen from sodium borohydride hydrolysis.

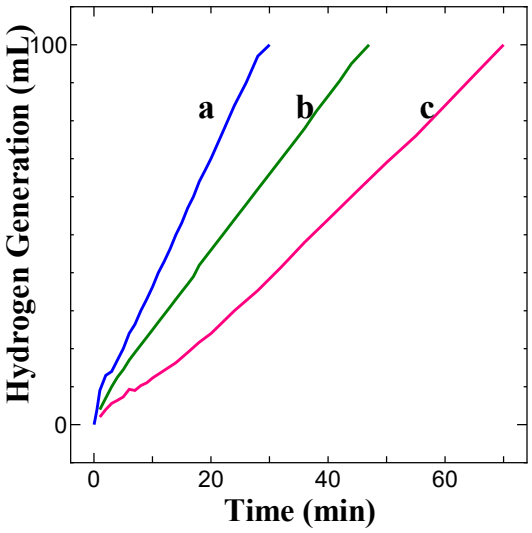


Fig. 5. Hydrogen generation from sodium borohydride (0.1 g) hydrolysis in 0.01 N NaOH solution using (a) 0.01 (b) 0.0075 and (c) 0.005 g Co/C nanocomposite.

Fig. 5 shows the effect of catalyst concentration on the evolution of hydrogen from $NaBH_4$ hydrolysis. In the absence any catalyst, the $NaBH_4$ hydrolysis at 0.01 N NaOH solution was completely inert. While adding 0.01 g catalyst, the hydrogen evolution was triggered, and 100 mL of water was down-displaced in 30 min with a rate of hydrogen generation of 333.3 mL min^{-1} g^{-1} of catalyst. The hydrogen generation rate was calculated by assuming the reaction kinetics as zero order reaction. The rate can be derived from the slope of linear portion of the curve.

Further, the effect of $NaBH_4$ hydrolysis with respect to the concentration of the catalyst is also studied. While using lesser amount of catalyst 0.0075 and 0.005 g, the hydrogen generation

rate was slightly decreased as 296.3- and 285.7-mL min^{-1} g^{-1} of catalyst. The decrease in hydrogen production rate might be due to the clogging of active sites of catalyst. Table 2. shows the effect of catalyst concentration on the hydrogen evolution rate from $NaBH_4$ hydrolysis.

Table 2. Effect of catalyst concentration on hydrogen evolution rate from $NaBH_4$ hydrolysis

S.No.	Amount of Catalyst (g)	Hydrogen evolution rate (mL min^{-1} g^{-1})
1	0.005	285.7
2	0.0075	296.3
3	0.01	333.3

CONCLUSION

Co/C catalysts prepared via solvent free synthesis was successfully employed for the hydrolysis of sodium borohydride for the generation of molecular hydrogen. For the preparation of Cobalt and Carbon, Cobalt chloride and glucose were used as the precursor. The Co/C nanocomposite was prepared via solvent free synthesis using a simple thermal decomposition. Further, the as-prepared catalysts were characterized using FT-IR spectroscopy, XRD, UV and Raman spectrum. FT-IR spectral results confirmed the presence of C-H stretching, OH stretching, C=C stretching and Co-O bond in Co/C nanocomposites. The appearance of A_{1g}, E_g peaks corresponding to the vibrations of Co-O and the appearance of D, G and 2D bands confirms the formation of Co/C nanocomposites. XRD results showed the crystalline nature of the as prepared nanocomposites. Further, the prepared nanocomposite acts as heterogeneous catalyst for the generation of hydrogen from sodium borohydride hydrolysis. The catalyst showed concentration dependent activity towards the $NaBH_4$ hydrolysis. While using 0.01 g of catalyst for 0.1 g of NaBH4, the hydrogen generation rate of 333.3 mL min^{-1} g^{-1} of catalyst was observed. The adsorption of hydride ion on Cobalt surface and the higher surface area provided by carbon nanomaterials are the cause for the improved catalytic activity of Co/C nanocomposites towards $NaBH_4$ hydrolysis.

Acknowledgement

The author sincerely thanks the management of Arul Anandar College for providing the Seed Money Research Grant (AAC/Dean-Res/Seed Money/097/2024 dated: 23.09.2024) and for extending the use of the instrument facilities at the DST-FIST Laboratory, Arul Anandar College.

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