



## Short communication

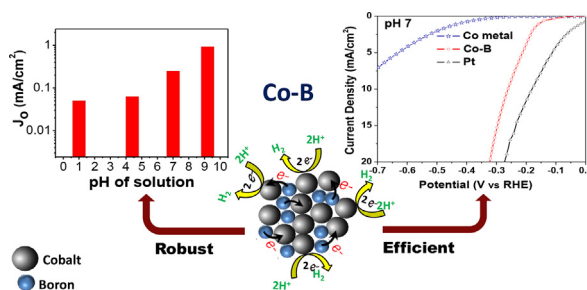
## Cobalt-Boride: An efficient and robust electrocatalyst for Hydrogen Evolution Reaction

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## HIGHLIGHTS

- Amorphous cobalt-boride nanoparticle: an efficient electrocatalyst for HER.
- Co–B NPs generate 10 mA/cm<sup>2</sup> at low overpotential (250 mV) in wide range of pH.
- Highly active Co surface sites are created by electron transfer from B to Co.
- Stability and reusability tests demonstrate the robust nature of the catalyst.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This work presents Cobalt-Boride (Co–B) as a non-noble, efficient and robust electrocatalyst for Hydrogen Evolution Reaction (HER) active in aqueous solution of wide pH values. In neutral solution, amorphous Co–B nanoparticles (30–50 nm size) generate high current density (10 mA/cm<sup>2</sup>) at low overpotential (250 mV) with Tafel slope of 75 mV/dec following Volmer–Heyrovsky reaction mechanism. Highly active Co surface sites created by electronic transfer from B to Co (as inferred from XPS analysis and supported by theoretical calculations) are responsible for this significant HER activity in wide range of pH (4–9) values. Stability and reusability tests also demonstrate the robust nature of the catalyst.

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## 1. Introduction

The hydrogen based economy seems viable only when environmental and energy issues related to hydrogen production are solved by utilizing water as a source of hydrogen and solar energy to split water. Although water splitting by photocatalysis seems to be a promising process, it has not yet become viable because of low

efficiency towards hydrogen production. Among the indirect routes, the electrochemical water splitting powered by photovoltaics is very attractive and feasible if cheaper and efficient electrocatalysts are available. Materials based on Pt metal show remarkable efficiency and stability, but are expensive and contribute in increasing the cost of an electrolyzer. Therefore, extensive research is oriented towards replacing Pt with earth-abundant materials exhibiting comparable performance for Hydrogen Evolution Reaction (HER).

In the past decade, most of the advances [1–19] were focused on Mo-based and Ni-based alloys as possible replacement of noble

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metals for HER where the former systems were restricted to acidic media and latter to basic media. Recently, there have been numerous reports on Co-based catalyst [20–27] where Co–P has turned out to be an excellent electrocatalyst under acidic conditions [20–23]. Cobalt-chalcogenides [24,25] have also been reported for their superior electrocatalytic activity in acidic medium. However, these catalysts are not tested in neutral water conditions. Following the work reported by Cobo et al. [26] on Janus cobalt-based catalyst for H<sub>2</sub> production from neutral water electrolysis, the current interest is now deviated towards alloying d-block transition elements with metalloids (P, S, and B). Among the low cost alternatives [26–34], Co–S film [27] and Co–P/CC [28] have exhibited the best HER activity with lowest overpotential and highest exchange current density (only one order of magnitude lower than Pt) in neutral water. These advances prompted us to test other metalloids such as B. Very recently, molybdenum boride [4] was found to be active in both acidic and basic conditions.

Motivated by these reports and also on our past experience in replacing noble metal catalyst for H<sub>2</sub> production by hydrolysis of chemical-hydrides [35,36], we undertook the experiments on using Cobalt-Boride (Co–B) as electrocatalyst for HER and, to the best of our knowledge, the study is reported for the first time. Outstanding activity was recorded with Co–B catalyst in wide range of pH values. Electronic transfer between Co and B possibly favors charge conduction during water reduction along with high resistance against deactivation and provides robustness to the catalyst.

## 2. Experimental methods

Co–B nanoparticles were synthesized by chemical reduction method. Aqueous sodium borohydride (0.3 M), used as a reducing agent, was added to an aqueous solution of cobalt chloride (0.05 M) under continuous stirring. As bubble generation ceased, the black precipitate in the solution was filtered and extensively washed with double distilled water and ethanol to remove any traces of unreacted and unwanted ions. The black powder obtained after cleaning was dried in vacuum at room temperature. Co metal sheet specimen (2 cm × 2 cm, 1 mm thick) was also used for the sake of comparison. Prior to their use, Co sheet and Pt rod electrode was cleaned with double distilled water followed by ultra-sonication in acetone bath for 10 min. Co–B powder catalyst was pressed in a conventional hydraulic press at 7 tons of pressure to obtain disc-shaped pellets of diameter 18 mm and thickness 1 mm.

HClO<sub>4</sub> (0.1 M) was used as the electrolyte for all the electrochemical measurements at pH 1. For neutral pH (7), 0.5 M potassium phosphate buffer solution was prepared by mixing K<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> in appropriate concentrations. 0.5 M KH<sub>2</sub>PO<sub>4</sub> and 0.4 M K<sub>2</sub>HPO<sub>4</sub> solutions were used as electrolytes for the measurements at pH = 4.4 and pH = 9.2 respectively. All the electrochemical measurements were carried out in a 3 electrode based flat electrochemical cell (Princeton) equipped with a Pt mesh as the counter electrode. The cell was designed such that it exposes 1 cm<sup>2</sup> circular area of the catalyst to the electrolyte solution. Catalysts in the form of pellets were used as the working electrode. A saturated calomel electrode (SCE) (Equiptronics) with a standard potential of 0.241 V was used as the reference electrode. All the potentials measured with respect to SCE were later converted to reversible hydrogen electrode (RHE) potential by adding a value of 0.241 + (0.05916 × pH). All solutions were continuously stirred to avoid any bubble accumulation over the electrodes. The electrochemical measurements and analysis were performed using a potentiostat-galvanostat system from Autolab (PGSTAT 30) and their GPES software. Current-interrupt method was used to determine the ohmic resistance which was later compensated by subtracting iR from the obtained potential values for all the

measurements. Linear polarization curves were recorded in the cathodic potential range starting from 0 V (vs RHE) with a scan rate of 10 mV/s. Tafel slope and exchange current density values were obtained by linear fitting the plot of log (i) versus overpotential ( $\eta$ ) in the range of  $\eta = 100$ –300 mV. Turnover frequency (TOF) value was determined using the procedure and equation reported by Popczun et al. [11]. BET technique was used to establish the actual surface area of the pellets used for the electrochemical measurements. Long-term stability was examined in potentiostatic mode by maintaining the potential at certain value and measuring current density with respect to time in hours. Reusability behavior of the catalyst was tested by conducting cyclic voltametric sweep in a range between 0 V and –0.5 V (vs RHE) with a scan rate of 150 mV/s.

Structural characterization of all the catalyst powders was performed by conventional X-Ray Diffractometer (XRD) using the Cu K $\alpha$  radiation ( $\lambda = 1.5414$  Å) in Bragg-Brentano ( $\theta$ – $2\theta$ ) configuration. X-ray photoelectron spectroscopy (XPS) was used to determine the surface electronic states and the related atomic composition of the catalysts. XPS was acquired using a Kratos AXIS Ultra instrument equipped with a monochromatic Al K $\alpha$  (1486.6 eV) X-ray source and a hemispherical analyzer. Electrical charge compensation was required to perform the XPS analysis. The molar ratio of elements was estimated by considering the area under the peak of the corresponding XPS spectrum. A Shirley background was subtracted from each spectrum and peaks were fitted by Voigt functions. The BET surface area of the powder catalysts was determined by nitrogen adsorption at 77 K (Micromeritics ASAP 2010) after degassing at a temperature of 423 K for 2 h. The size of Co–B NPs was examined using a transmission electron microscope (TEM). HR-TEM image and selected area electron diffraction (SAED) pattern was recorded by JEOL-JEM 2100F TEM microscope operating at an accelerating voltage of 200 kV. The surface morphology of the catalyst samples was also analyzed by scanning electron microscope (SEM-FEG, JSM 7001F, JEOL) equipped with energy-dispersive spectroscopy (EDS, INCA PentaFET-x3) to determine the composition of the samples.

## 3. Results and discussion

SEM (Fig. 1a) and bright field TEM image (Fig. 1b) of Co–B catalyst shows particle-like morphology with spherical shape and size in the range of 30–50 nm. Elemental mapping with EDS (Fig. S1) did not display any phase separation of Co and B hence suggesting that both the elements in the catalyst are well mixed at macroscopic level. The amorphous nature of the powders with long range disorder and short range order was confirmed through XRD pattern (Fig. 1c) and HRTEM image (Fig. 1d), which was also verified from the SAED pattern (inset of Fig. 1d). The broad peak centered at 45° in XRD pattern (Fig. 1c) is assigned to the amorphous state of Co–B phase [37]. Investigation of chemical states of each element in the catalyst was carried out using XPS (Fig. 1e and f). It shows the presence of two peaks in Co 2p level with binding energy at 778.2 and 781.6 eV with a satellite peak at 785 eV indicating that Co metal exists in both elemental and oxidized state [Co(OH)<sub>2</sub>] (Fig. 1e). Similar states were also detected in B1s level with peaks at binding energies of 188.2 and 192.1 eV respectively (Fig. 1f). Most importantly, when compared to binding energy of pure B (187.1 eV), the elemental B in the catalyst is positively shifted by 1.1 eV suggesting an electron transfer from alloying B to vacant d-orbital of metallic Co making former electron deficient while later enriched with electron as indicated by small negative shift (0.2 eV) in the Co elemental peak. These results suggest that the surface of Co–B catalyst is composed of electron enriched Co sites bonded with B, and of cobalt hydroxide [Co(OH)<sub>2</sub>] in ratio of 1:1.38 as inferred from

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