Ag-Cd-B-P ternary alloy with efficient electrocatalytic activity towards hydrogen evolution reaction (HER)

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Abstract. Recently, a stable and effective Pt-free electrocatalyst is hugely required for hydrogen generation through water splitting. In this article, we present an easy synthesis of very small particle sized electrocatalysts Ag-Cd-B-P and Cd-Ag-B-P with good catalytic activity and stability for electrochemical hydrogen evolution reaction in acidic medium. Ag-Cd-B-P catalyst exhibits better performance than Cd-Ag-B-P with lower onset potential of -0.25 V, higher electrochemical surface area of 0.50 cm², excellent current density of 1.18 A/cm² at -1.29 V, low tafel slop of 118 mV/dec and small overpotential of 50 mV to achieve 10 mA/cm² current density. The reported Ag-Cd-B-P electrocatalyst shows good storage stability of 2 months in normal condition with only ~2 % change in onset potential and current density.

Keywords: Water splitting, Hydrogen evolution reaction (HER), Onset potential, Tafel slope, Overpotential.

1. Introduction
The continuous rising of environmental pollution, economic development and energy shortage, stimulates a search for clean and sustainable energy. As a green and sustainable energy source, hydrogen has become one of the most assuring alternatives of fossil fuels [1]. Electrocatalytic water splitting is a green and sustainable process to generate hydrogen without harmful by-products [2]. Hydrogen evolution reaction (HER) is the cathodic part of water splitting reaction and requires a highly effective electrocatalyst to obtain lower overpotential [3]. The noble metals including Pt- group metals show ideal electrocatalytic activity towards HER, but the high price and insufficiency make them limit their wide industrial application [4]. Transition metal based materials including oxides, borides, phosphides, nitrides, sulphides, selenides, tellurides, carbides [3, 5-7] and also metal free materials [8] give satisfactory results as electrocatalyst to replace the Pt based materials. Among them transition metal borides and phosphides are widely studied as efficient electrocatalyst. Patel et al. first synthesized Co-P-B powder catalyst with B/P molar ratio 2.5 and applied in hydrogen production [9]. In comparison with Co-P and Co-B, enhanced catalytic efficiency was shown by Co-P-B due to presence of synergetic effect of P and B atoms and higher active surface area. Ternary boride phosphide was also studied as catalyst for hydrogen generation which also more efficient than only boride or phosphide [10, 11]. Recently, Ag and Cd based nanomaterials which are comparatively inexpensive electrocatalysts were widely studied and an excellent activity was shown in the field of HER [12, 13]. To the best of our information, this nanomaterial is the first ternary boride phosphide which is used as
electrocatalyst for hydrogen evolution reaction and gives a good performance comparing with other electrocatalysts available.

In this work, we have synthesized very small particle sized Ag-Cd-B-P and Cd-Ag-B-P nanomaterials by an easy and facile chemical reduction process at room temperature. The electrocatalytic activity of the nanomaterials towards HER was studied in acidic condition. Prepared Ag-Cd-B-P powder catalyst shows lower onset potential of ~0.25 V and small overpotential of 50 mV to achieve 10 mA/cm² current density. A very impressive storage stability of this electrocatalyst was observed with only ~2% change in current density and onset potential after two months of storage at normal condition.

2. Experimental Section

2.1. Chemical reagents and apparatus

All the chemical reagents were of analytical grade and used without any additional purification. Silver nitrate (AgNO₃) and cadmium chloride (CdCl₂.2.5H₂O) were purchased from SRL and Laboratory Rasayana Chemicals. Sodium borohydride (NaBH₄) and di-sodium hydrogen orthophosphate (Na₂HPO₄) were purchased from TCI chemicals (India) and CDH chemicals. Solvents including ethanol and dimethylsulfoxide (DMSO) were acquired from TCI chemicals (India) and Merck (India). The whole analysis was carried out in room temperature and stock solutions were prepared using distilled water.

The powder X-ray diffraction (XRD) spectra of the nanomaterials were conducted using a Rigaku Smartlab X-Ray diffractometer. Zeiss-SUPRA 55 was used for field emission scanning electron microscopy (FE-SEM) study. The electrochemical analysis was carried out using CH instrument (USA, model number 440D).

2.2. Synthesis of Ag-Cd-B-P and Cd-Ag-B-P

Ag-Cd-B-P electrocatalyst was synthesized according to the previously reported procedure with some modifications [9]. Briefly, 1 mmol AgNO₃ (0.169 g) and 0.1 mmol CdCl₂ (0.0228 g) were taken in a round bottom flask with 20 ml deionised water. The mixture solution was stirred to get a homogeneous solution. After 30 minutes, 0.4 mmol Na₂HPO₄ (0.056 g) and 1 mmol NaBH₄ (0.037 g) were added to the previous solution and stirred for 10 h. The solution was cooled down to room temperature naturally. The black precipitation of final product was centrifuged at 10,000 rpm by washing several times with water and ethanol. The obtained product was dried in vacuum at 65°C for 12 h. The synthesized product was further calcinated at 300°C for 3 h.

Cd-Ag-B-P nanoparticles were prepared by similar method as described above only by changing the amount of silver and cadmium salt. In this case, 1 mmol CdCl₂ (0.228 g) and 0.1 mmol AgNO₃ (0.0169 g) were taken with previously described materials.

2.3. Electrochemical study

All the electrochemical studies were carried out using a nanomaterial-modified pencil graphite electrode (PGE). The pencil graphite leads with diameter 0.5 mm were purchased from Hi Par Camlin Ltd. (India) and micropipette tips were acquired from Tarsons Products Pvt. Ltd. The PGE which was the working electrode was fashioned in our laboratory using the pencil graphite lead. Pre-treatment of pencil graphite lead was carried out before the electrode fabrication using 6.0 M nitric acid and subsequently 2 times washing with water. After that, the surface of the lead was cleaned with cotton and dried at room temperature. The dried lead was then accommodated in a micropipette tip keeping 4.0 mm of pencil lead outside through the narrow end of micropipette tip to modify in future. A metallic wire was tied with the lead at the wider end of the micropipette tip to generate electrical contact. To modify the pencil lead, 2.0 mg nanomaterial was dispersed in 0.5 ml DMSO by ultrasonication for 1 h to get a homogeneous ink. The prepared ink (6 µL) was drop-casted onto the clean surface of PGE and dried. This method was replicated three times to get a good coating. Typically, in a three electrode electrochemical cell, a Pt wire and Ag/AgCl electrode were used as
counter and reference electrode, respectively and the prepared modified PGE was used as working electrode for the electrochemical analysis.

To analyse the electrochemical activities of four nanomaterials towards HER, 1.0 M H₂SO₄ (pH = 0) solution was taken as supporting electrolyte with scan rate of 50 mV/s throughout the measurement. Prior to the electrochemical analysis nitrogen gas was purged into the electrolyte solution for 30 min to remove the dissolved oxygen completely and sealed the electrochemical cell. After performing 10 cycles, stable polarisation curves were recorded. All the potentials were calculated keeping reversible hydrogen electrode (RHE) as reference using the equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E_{\text{Ag/AgCl}}$$ (1)

$E_{\text{Ag/AgCl}}$ (0.201 V) is the standard Ag/AgCl electrode potential at 25 °C and $E_{\text{Ag/AgCl}}$ is the potential measured during the experiment against Ag/AgCl electrode. The geometrical surface area of PGE was remained constant at 0.089 cm².

For HER, 1.0 M (pH = 0) H₂SO₄ was used, therefore, $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.210$. The equation used to calculate overpotential ($\eta$) which was $\eta = E_{\text{RHE}} - 1.23$. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were used to investigate the electrochemical activity of prepared electrocatalysts.

### 2.3.1. Tafel plots

The electrocatalytic activity of the nanomaterials towards HER was calculated using Tafel plots applying the equation [14]:

$$\eta = a + \frac{2.3 RT}{aF} \log(j)$$ (2)

This equation correlates with overpotential ($\eta$) and current density ($j$) with the slope $\frac{2.3 RT}{aF}$. Tafel slope gives the idea about HER reaction pathway. There are three types of reaction pathway including Tafel (slope 30 mV/dec), Heyrovsky (slope 40 mV/dec) and Volmer (slope 120 mV/dec) reaction. Lower tafel slope with rising current density, indicates a slower increment of overpotential which means a better reaction pathway for HER.

### 3. Results and Discussion

#### 3.1. Characterization of nanomaterials

The XRD spectra of the prepared electrocatalysts are shown in Fig. 1 (A) and (B). For Ag-Cd-B-P the peaks at the 20 values of 38.3° and 44.67° correspond with (111) and (200) planes of silver (JCPDS file no. 87-0720). The peak at 77.57° corresponds with the (104) plane of cadmium (JCPDS file no. 85-1328). The peaks at 33.48° and 64.69° associate with (009) and (214) planes of boron (JCPDS file no. 80-0322, 78-1571). The peak at 81.71° associates with (242) plane of phosphorus (JCPDS file no. 73-1358). For Cd-Ag-B-P the peaks at 38.55° and 77.80° correspond to (101) and (104) planes of cadmium (JCPDS file no. 85-1328). The peak at 44.84° corresponds with (200) plane of silver (JCPDS file no. 87-0720). The peaks at the 20 values of 16.63°, 29.43°, 54.03° and 64.86° associate with (110), (214), (511) and (214) planes of boron (JCPDS file no. 80-0322, 71-0157). The peaks at 50.97° and 81.87° associate with (112) and (242) planes of phosphorus (JCPDS file no. 73-1358). From these two XRD spectra we can conclude that Ag-Cd-B-P and Cd-Ag-B-P are successfully synthesized.
Figure 1: XRD spectra of the synthesized Ag-Cd-B-P (A) and Cd-Ag-B-P (B).

Morphological characterization of prepared nanomaterials was carried out by FE-SEM analysis. We can see in Fig. 2 both the powder electrocatalysts show particle like morphology and particles are arranged homogeneously. Ag-Cd-B-P contains (Fig. 2 (A and B)) smaller particles having size range between 20 to 30 nm. In Fig. 2 (C and D) Cd-Ag-B-P exhibits homogeneously distributed particles with size range 30 to 40 nm. The small particle size of the fabricated nanomaterials can be due to the use of strong reducing agent NaBH₄ during the synthesis process. A fast reduction of metal ions is caused because of NaBH₄ and the particles are not allowed to enlarge more than little nanometers. This type of morphological structure is advantageous in increasing the electroactive surface area.
3.2. Electrocatalytic activity and electrochemical surface area

Electrocatalytic activity and electrochemical surface area of the synthesized nanomaterials were studied with CV, taking potential range of -0.8 V to 1.2 V. The analysis was carried out at 100 mV/s scan rate using 0.2 M potassium ferrocyanide (K₄[Fe(CN)₆]) and 1.0 M KCl as electroactive probe molecule and supporting electrolyte respectively. The electrocatalytic activity of two nanomaterials and blank PGE is shown in the Fig. 3.

![Figure 3](image_url)

Figure 3: Comparative study of electrocatalytic activity of two nanomaterials and blank PGE.

Higher current was obtained from Ag-Cd-B-P (742 μA) modified PGE in comparison with Cd-Ag-B-P (546 μA) modified PGE. In Fig. 3, the extra peaks appeared in the CV plots of nanomaterial modified PGE, except the potassium ferrocyanide peaks are due to the presence of silver.

Electrochemical surface area was calculated following Randles-Sevcik equation [15]:

\[
I_p = (2.687 \times 10^5)n^{1/2}D^{1/2}v^{1/2}C_0^{3/2}A
\]

Where \(I_p\) (μA), \(n\), \(D\), \(v\), \(C_0\), \(A\) are peak current, number of electron transfer during the reaction, diffusion coefficient, scan rate, concentration of potassium ferrocyanide and electrochemical surface area respectively. Normally, in this redox reaction Fe²⁺ converts to Fe³⁺ that means one electron transfer (\(n = 1\)) occurs. Diffusion coefficient (D) has the definite value of 0.76×10⁻⁵ cm²/s. The calculated electrochemical surface area, peak current and roughness factor are given in Table 1. We can see that modification of PGE with Ag-Cd-B-P has higher electroactive surface area (0.50 cm²) than that of Cd-Ag-B-P (0.37 cm²) due to increment of charge transfer. The roughness factor is higher in the case of Ag-Cd-B-P modified PGE (5.62) than Cd-Ag-B-P modified PGE (4.14).

Table 1: Comparative analysis of two different nanomaterial modified PGEs.

| Electrode fabricated | Peak current (μA) | Electrochemical surface area (cm²) | Roughness factor (Rᶠ) |
|----------------------|-------------------|-----------------------------------|-----------------------|
| Ag-Cd-B-P            | 742.25            | 0.50                              | 5.62                  |
| Cd-Ag-B-P            | 546.40            | 0.37                              | 4.14                  |

3.3. Electrochemical behaviour towards HER

The optimization processes of some important parameters including scan rate, supporting electrolyte concentration and mass loading amount of the catalysts were performed before studying HER activity.
of nanomaterials. We know that smaller onset potential and larger current density indicates a better electrocatalytic activity. The optimization study is shown in Fig. 4 with LSV polarization curve. At first scan rate was optimized (Fig. 4A) by recording LSV with different scan rates (100 mV/s, 50 mV/s, 10 mV/s, 5 mV/s and 2 mV/s). Electrolytes were optimized (Fig. 4B) by using H₂SO₄ with different concentrations (0.1 N, 0.5 N, 1 N, 2 N and 3 N). Mass of the electrocatalyst loaded onto the bare PGE was optimized (Fig. 4C) by coating different amount of nanomaterial (1 mg, 2 mg, 5 mg and 8 mg) on PGE. It was noticed that lower onset potential as well as higher current density is acquired at 50 mV/s scan rate with 1.0 M supporting electrolyte (H₂SO₄) concentration. For the case of loading amount of nanomaterials it was seen that with 2 mg catalyst coating the better result was obtained.

Figure 4: LSV plots for optimization study of Ag-Cd-B-P catalyst with (A) different scan rate, (B) different electrolyte concentration and (C) different mass loading.

After optimisation, onset potentials (highest cathodic potential at which the product of a reaction is obtained) of two nanomaterials were compared with optimized parameters using CV and LSV (shown in Fig. 5). In the LSV plot (Fig. 5 A) performed within the potential range 0 to - 1.3 V, it was observed that Ag-Cd-B-P showed best electrochemical activity with lowest onset potential (- 0.25 V) as well as high current density (1.18 A/cm² at - 1.29 V). The other nanomaterial Cd-Ag-B-P showed onset potential of - 0.34 V and current density 0.76 A/cm² at - 1.29 V. Lower the overpotential value better the electrocatalytic activity of the nanomaterials. In the case of Ag-Cd-B-P, the calculated overpotential value was 50 mV which was much smaller than that of Cd-Ag-B-P (108 mV). From the Fig. 5 (B) we can observe that CV curve was studied under same reaction condition with LSV and Ag-Cd-B-P modified electrode shows higher current density than Cd-Ag-B-P electrode.
Figure 5: Comparison of LSV (A) and CV (B) plots for two electrocatalysts in optimised condition.

Tafel slopes were obtained by plotting the linear portion of LSV curve with optimized parameters in non-stirred solution. For Ag-Cd-B-P the calculated tafel slope was 118 mV/dec and that for Cd-Ag-B-P was 192 mV/dec shown in Fig. 6. So it can be concluded that the two nanomaterial modified electrodes adopt Volmer reaction pathway and Ag-Cd-B-P modified electrode shows much lower tafel slope than Cd-Ag-B-P modified electrode.

Figure 6: Tafel plots of Ag-Cd-B-P and Cd-Ag-B-P.

3.4. Stability Study

Stability is very important for an efficient electrocatalyst used in water splitting. To prepare a cost effective and good catalyst for HER, stability also plays a vital role. At first the cyclic stability of Ag-Cd-B-P was studied with CV and LSV within the potential range of 0 – 1.3 V. It was observed in Fig. 7(A, B) that after 200 and 500 cycles no such significant change was occurred in onset potential and current density. CV and LSV runs were also compared before and after the whole electrochemical performance within the same potential range shown in Fig. 7(C, D). The recorded current densities in the LSV curve (Fig. 7 C) were 1.18 A/cm² and 1.13 A/cm² at -1.29 V for initial and after the whole electrochemical study respectively. There was almost no change in onset potential before and after the electrochemical performance.
Figure 7: LSV and CV analysis the nanomaterial showing cyclic (A, B) and electrochemical (C, D) stability.

The storage stability of Ag-Cd-B-P was also examined with LSV analysis after 1 month and 2 months of storage at normal conditions in room temperature. In Fig. 9 we can observe that a slight change (~2%) in onset potential and current density was occurred after 2 months of storage period.

Figure 9: LSV study of the electrocatalyst showing storage stability.

4. Conclusion
We have synthesized Ag-Cd-B-P and Cd-Ag-B-P by a facile chemical reduction process by changing the amount of silver and cadmium. Different characterization methods confirm the successful synthesis of the nanomaterials. Between the two, Ag-Cd-B-P showed better electrocatalytic property towards HER than Cd-Ag-B-P with small onset potential and higher current density. Tafel plot also
indicate that HER mechanism of Ag-Cd-B-P is superior. Also, Ag-Cd-B-P shows good storage stability for 2 months with almost unchanged electrocatalytic behaviour for HER. This storage stability is very crucial for an efficient electrocatalyst and also unchanged activity is resulted from our material after all the electrochemical study. In summary, our material is a promising HER catalyst which can be easily synthesized and have good storage stability.

5. References
[1] Liu T, Liu D, Qu F, Wang D, Zhang L and Ge R 2017 Adv. Energy Mater. 7 1700020
[2] Li TT, Niu K, Yang M, Shrestha NK, Gao ZD and Song YY 2017 J. Power Sources 15 89
[3] Eftekhari A 2017 Int. J. Hydrogen Energy 42 11053
[4] Kim H, Choe SH, Park H, Jang JH, Ahn SH and Kim S-K 2017 Nanoscale 9 19045
[5] Subbaraman R, Tripkovic D, Chang K-C, Strmcnik D, Paulikas AP and Hirunsit P 2012 Nat. Mater. 11 550
[6] Kong D, Cha JJ, Wang H, Lee HR and Cui Y 2013 Energy Environ. Sci. 6 3553
[7] Xiao P, Chen W and Wang X 2015 Adv. Energy Mater. 5 1500985
[8] Zheng Y, Jiao Y, Zhu Y, Li L, Han Y, Chen Y, Du A, Jaroniec M and Qiao S 2014 Nat. Commun. 5 3783
[9] Patel N, Fernandes R and Miotello A 2009 J. Power Sources 188 411
[10] Fernandes R, Patel N and Miotello A 2009 Int. J. Hydrogen Energy 34 2893
[11] Fernandes R, Patel N, Miotello A and Calliari L 2012 Topics in Catalysis 55 1032
[12] Campbell FW, Belding SR, Baron R, Xiao L and Compton RG 2009 J. Phys. Chem. C 113 14852
[13] Faber MS and Jin S 2014 Energy Environ. Sci. 7 3519
[14] Yin K, Cheng Y, Jiang B, Liao F and Shao M 2018 J. Colloid Interface Sci. 522 242
[15] Mukherjee R, Krishnan R, Lu T-M and Koratkar N 2012 Nano Energy 1 518

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