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Enhanced catalysis of the electrochemical hydrogen evolution reaction using composites of molybdenum-based compounds, gold nanoparticles and carbon

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Molybdenum nitride has been recently reported to interact synergistically with gold to show an enhanced activity for the electrochemical hydrogen evolution reaction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, HER). In this work, we elucidated the roles of nitrogen, carbon, molybdenum and gold on this observed phenomenon. Composites of Mo-based compounds, carbon black (black pearl 2000) and/or Au nanoparticles (Au_{NP}) were prepared, and their activities for the HER in a 0.5 M H_2SO_4 electrolyte were measured using linear sweep voltammetry. We show and discuss here for the first time that, while the presence of carbon is necessary for the synergy phenomenon, the nitrogen atoms present in the compounds play no apparent role in this synergy. In fact, all the compounds containing Mo, namely Mo_2N , MoB and metallic Mo^0 , exhibited extensive synergy with Au for the HER. A hypothesis for the enhanced catalysis of H_2 evolution by the mixed metal composites is proposed and discussed.

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1. Introduction

The electrochemical hydrogen evolution reaction (HER) is one of the crucial means for converting electrical energy generated from solar and wind based power sources into clean H_2 fuel.¹ The efficiency of this reaction depends largely on the electrocatalytic properties of the cathode. To date, high performance electrocatalysts for HER have been based mostly on Pt.^{2–4} However, being intrinsically scarce in the earth's crust, Pt is not an appropriate candidate for large-scale water electrolysis. Hence, an extensive search for replacements has been ongoing.^{3,5–10} Among these alternatives, the chalcogenides, nitrides and carbides of Group 6B elements, especially that of molybdenum, have shown great promise due to their low cost, earth-abundance and resistance to corrosion.^{5,6} Activity-wise though, these catalysts are still inferior to Pt.

It has been recently demonstrated by Jaouen and co-workers that the electrochemical deposition of Au atoms onto a molybdenum

nitride (Mo_2N) + carbon catalyst can give a composite that has 100 times higher HER activity over that of Au or Mo_2N .¹¹ It was postulated that proton discharge could have occurred first on the Mo_2N , followed by rapid H diffusion across to the Au catalyst, where the H atoms combine with themselves or with H^+/e^- to give H_2 gas. However, neither the roles of nitrogen, molybdenum, gold and carbon atoms towards HER have been investigated, nor the mechanistic picture behind the synergy was experimentally shown. From an economic viewpoint, gold may not be a very apt candidate as an electrocatalyst. Nonetheless, it is important to better understand the factors responsible for this synergistic effect, since this knowledge can direct us to the design of better HER catalysts.

In this work, we elucidated the roles of nitrogen, molybdenum, gold and carbon in the above-mentioned synergistic phenomenon. All electrochemical experiments were performed in 0.5 M H_2SO_4 electrolytes, and the HER activities were characterized by linear sweep voltammetry (LSV). Experimental results using a variety of catalysts including Mo_2N , MoB, Mo^0 , VN, CrN, TiN and Au nanoparticles (Au_{NP}) are presented and discussed in order to give a better representation of the effect.

2. Experimental

We prepared our composite catalysts by physically mixing the metal-based compounds, gold and/or carbon. This experimental protocol gave us great flexibility in formulating the type of catalysts

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needed for our investigations. Mo_2N , CrN, VN and TiN were synthesized using the 'urea glass route'.^{12,13} Commercial MoB (~ 325 mesh, 99.5%, Sigma Aldrich), Mo^0 (1 μm , 99.99%, Acros), Au nanoparticles (Au amount: $63.2 \mu\text{g mL}^{-1}$, 5 nm, BBI Solution, UK), Black Pearl-2000 (BP₂₀₀₀, $1500 \text{ m}^2 \text{ g}^{-1}$, Cabot) and Vulcan XC72 (XC₇₂, $240 \text{ m}^2 \text{ g}^{-1}$, Cabot) were used as received. The synthesized catalysts were characterized using powder X-ray diffraction (Bruker Siemens D5005, Cu $K_{\alpha 1}$, $\lambda = 1.5406 \text{ \AA}$, scan range: 20° – 90° , scan rate: $0.1^\circ \text{ min}^{-1}$) and transmission electron microscopy (TEM, JEOL JEM-3010, 200 kV and JEOL JEM-2100, 200 kV). For TEM, the as-prepared catalyst powder was dispersed in isopropanol and a drop of this suspension was placed on a carbon-coated nickel grid, and allowed to dry. The Au_{NP} solution was similarly dropped onto a grid and allowed to dry. 10 μL of methanol was further dropped to ensure the dispersion of the Au nanoparticles.

The working electrode consisted of a polished glassy carbon disk (CHI 104, diameter 3 mm) on which the catalyst ink was drop-cast. The ink was prepared by mixing 2 mg of the metal-based catalyst, 1.2 mg of BP₂₀₀₀ or XC₇₂, and 1 mL of a solution consisting of 89.5 vol% ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$, Barnstead), 10 vol% propanol, and 0.5 vol% Nafion (5% sol., Sigma-Aldrich). The mixture was ultrasonicated for 45 minutes to break up any visible agglomerates of particles. 5 μL of the resultant catalyst ink was then drop-cast onto the working electrode and dried under a halogen lamp (50 W, Philips) for 15–20 min. The distance between the electrode and the lamp was $\sim 5 \text{ cm}$, and the temperature of the electrode rose to about 30 – 35°C during drying. For samples containing gold, 20 μL of Au_{NP} solution was mixed with 5 μL of the catalyst ink, and then drop-cast and dried. In all the experiments, the loadings of the catalyst, the carbon and the gold on the working electrode were 141, 85 and $18 \mu\text{g cm}^{-2}$ respectively.

All electrochemical experiments were done in a glass cell, with a Hg/HgSO₄ (sat. K₂SO₄) reference electrode (CHI 151) and a graphite rod as the counter electrode. The platinum counter electrode was avoided, because it could dissolve during electrolysis. The Pt ions could then be gradually deposited onto the cathode, which would lead to an increase in the HER activity.¹⁴ Freshly prepared 0.5 M H₂SO₄ (96.9%, Sigma Aldrich) solution was used as the electrolyte. Linear sweep voltammetry at 2 mV s^{-1} scan rate was used to investigate the activity of hydrogen evolution reaction. Each stated figure-of-merit (Tafel slopes, current densities at fixed overpotentials, η) was an average of measurements from five independently prepared samples. All potentials indicated in this work were referenced against the reversible hydrogen electrode (RHE). All LSV curves were corrected for the iR_u drop (measured uncompensated resistance $R_u = 12 \Omega$). All reported current densities were normalized to the geometric surface area of the working electrode. Both Autolab PGSTAT30 and PINE potentiostats were used for the electrochemical measurements.

3. Results and discussion

3.1. HER activity of $\text{Mo}_2\text{N} + \text{Au}_{\text{NP}}$: with and without carbon

The identity of the as-synthesized molybdenum nitride was confirmed by X-ray diffraction (PDF-00-025-1366) to be $\gamma\text{-Mo}_2\text{N}$ (Fig. 1a).

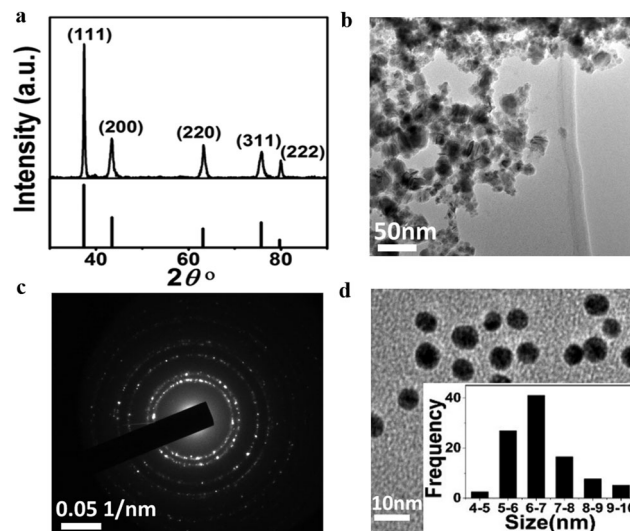


Fig. 1 (a) X-ray diffractogram of $\gamma\text{-Mo}_2\text{N}$. The expected XRD pattern, which is represented by the vertical lines, is included for comparison. (b) TEM image and (c) corresponding SAED pattern of the $\gamma\text{-Mo}_2\text{N}$ nanoparticles. (d) TEM image of Au_{NP} ; the inset indicates the particle size distribution of the Au_{NP} .

Transmission electron microscopy and selected area electron diffraction confirmed that the catalyst was in the form of polycrystalline particles with a size of $\sim 30 \text{ nm}$ (Fig. 1b and c). Some smaller primary amorphous nanoparticles, from which the bigger particles obviously form, can be also observed in the TEM image. The Au nanoparticles (Au_{NP}) were 5 to 8 nm in size (Fig. 1d).

$\gamma\text{-Mo}_2\text{N}$, Au_{NP} and BP₂₀₀₀ were then physically mixed, and the HER catalytic activity of this composite ($\text{Mo}_2\text{N} + \text{Au}_{\text{NP}} + \text{BP}_{2000}$) was measured in 0.5 M H₂SO₄ electrolyte *via* linear sweep voltammetry. At $\eta = 250 \text{ mV}$, it gave a H₂ current of $2.43 \pm 0.25 \text{ mA cm}^{-2}$ (Fig. 2a). The individual Mo_2N and Au_{NP} (both dispersed in BP₂₀₀₀), in contrast, only gave respective currents of 0.28 ± 0.03 and $0.51 \pm 0.07 \text{ mA cm}^{-2}$ at the same overpotential. Thus, the composite catalyst exhibited a HER activity that was 3 times the sum of the activities of $\text{Mo}_2\text{N} + \text{BP}_{2000}$ and $\text{Au}_{\text{NP}} + \text{BP}_{2000}$. A reference glassy carbon electrode loaded with only BP₂₀₀₀ gave negligible currents.

When compared to the study by Jaouen and co-workers,¹¹ the Au nanoparticles in this work were not deposited electrochemically but physically mixed with Mo_2N . The Mo_2N particles were also larger in size by an order of magnitude, and the carbon matrix was not synthesized *in situ* but added externally. Because of the dissimilarity between the two composite systems, the figures-of-merit for the catalysis of HER are difficult to compare. Nonetheless, our key observations are consistent with each other, namely the $\text{Mo}_2\text{N} + \text{Au}_{\text{NP}} + \text{BP}_{2000}$ composite was more HER active than the simple sum of activities of $\text{Au}_{\text{NP}} + \text{BP}_{2000}$ and $\text{Mo}_2\text{N} + \text{BP}_{2000}$ catalysts.

Furthermore, the $\text{Mo}_2\text{N} + \text{Au}_{\text{NP}} + \text{BP}_{2000}$ composite had a unique Tafel slope of $63 \pm 3 \text{ mV dec}^{-1}$, which was 28 – 36 mV dec^{-1} lower than that of $\text{Mo}_2\text{N} + \text{BP}_{2000}$ ($91 \pm 1 \text{ mV dec}^{-1}$) and $\text{Au}_{\text{NP}} + \text{BP}_{2000}$ ($99 \pm 3 \text{ mV dec}^{-1}$) (Fig. 2b). This value ($63 \pm 3 \text{ mV dec}^{-1}$) did not match with any of the commonly predicted Tafel slopes

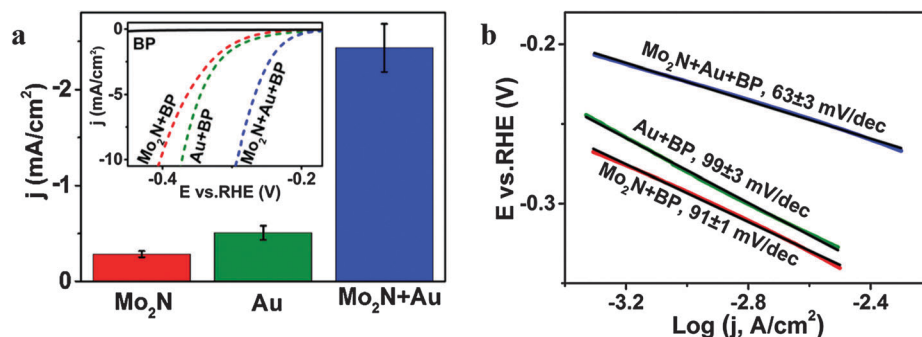


Fig. 2 (a) Bar chart for the HER activity measured at -250 mV for Mo₂N + BP₂₀₀₀, Au_{NP} + BP₂₀₀₀ and Mo₂N + Au_{NP} + BP₂₀₀₀. Inset: Linear sweep voltammograms of the catalysts and BP₂₀₀₀. (b) Respective Tafel plots of the catalysts studied in (a).

based on the following steps as the rate determining reaction, namely the Heyrovsky step ($H_{ad} + H^+ + e^- \rightarrow H_2$; 40 mV dec⁻¹), Volmer step ($H^+ + e^- \rightarrow H_{ad}$; 116 mV dec⁻¹) and Tafel step ($H_{ad} + H_{ad} \rightarrow H_2$; 30 mV dec⁻¹).^{6,15} These collective pieces of evidence suggest the existence of a synergistic effect between these materials which led to an enhancement in the HER activity.

To probe the role of carbon, HER experiments were first conducted on Mo₂N, Au_{NP} and Mo₂N + Au_{NP}, without the addition of BP₂₀₀₀ (Fig. 3a(i and ii)). Unexpectedly, we discovered that the activity of Mo₂N + Au_{NP} (no BP₂₀₀₀ added) was only 0.29 ± 0.12 mA cm⁻² at $\eta = 250$ mV. This is even lower than the sum of the activities of the individual components Au_{NP} (0.37 ± 0.06 mA cm⁻²) and Mo₂N (0.29 ± 0.11 mA cm⁻²). The Tafel slope of the carbon-free Mo₂N + Au_{NP} composite was also higher at 106 ± 4 mV dec⁻¹. HER experiments were also performed using Vulcan XC₇₂-based

composites (Fig. 3b(i and ii)). The Mo₂N + Au_{NP} + XC₇₂ composite showed slight increases in activities compared to the sum of individual activities of Mo₂N + XC₇₂ and Au_{NP} + XC₇₂. We thus conclude from these experiments that carbon played a crucial role in mediating the synergy phenomenon for enhanced HER.

3.2. HER activity using Mo⁰, MoB, VN, CrN and TiN catalysts

To probe whether the synergistic phenomenon is based on the interaction of Mo or N atoms (in Mo₂N) with Au_{NP}, the catalysis of HER using non-nitrogen containing Mo compounds, namely metallic Mo⁰ and MoB, were performed. At $\eta = 250$ mV, the activities of Mo⁰ + BP₂₀₀₀, Au_{NP} + BP₂₀₀₀ and Mo⁰ + Au_{NP} + BP₂₀₀₀ systems were respectively 0.10 ± 0.02 , 0.51 ± 0.07 and 4.79 ± 0.76 mA cm⁻² (Fig. 4a(i)). Thus, the Mo + Au_{NP} + BP₂₀₀₀ composite exhibited a HER activity 8 times the sum of the

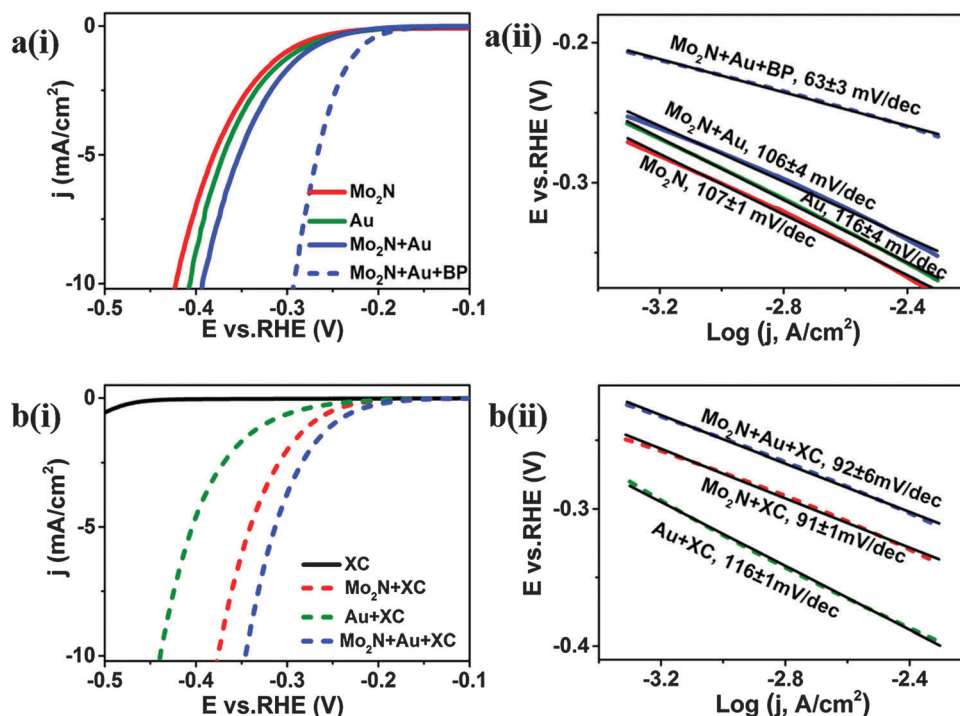


Fig. 3 (i) Linear sweep voltammograms and (ii) Tafel plots for (a) Mo₂N, Au_{NP}, Mo₂N + Au_{NP} and Mo₂N + Au_{NP} + BP₂₀₀₀; (b) XC₇₂, Mo₂N + XC₇₂, Au_{NP} + XC₇₂ and Mo₂N + Au_{NP} + XC₇₂.

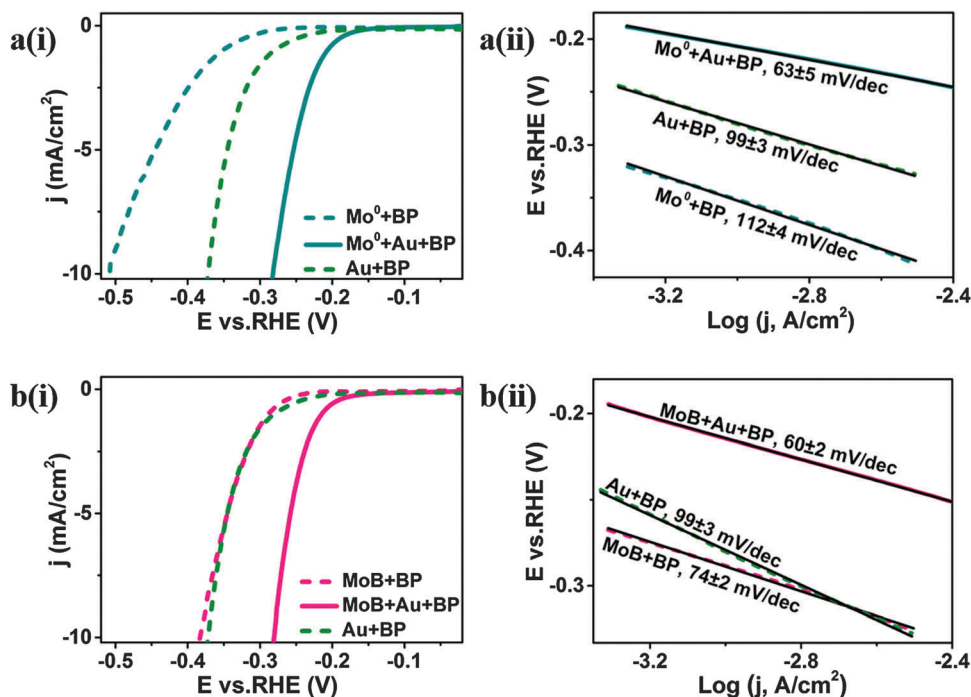


Fig. 4 (i) Linear sweep voltammograms and (ii) Tafel plots for (a) Mo⁰ and (b) MoB, with and without Au_{NP}. All catalysts contain BP₂₀₀₀.

individual activity of each added component and 2 times larger than that of the Mo₂N + Au_{NP} + BP₂₀₀₀ composite catalyst. The Tafel slope of the Mo⁰ + Au_{NP} + BP₂₀₀₀ composite, which was 63 ± 5 mV dec⁻¹, was also smaller than that of Au_{NP} + BP₂₀₀₀ and Mo⁰ + BP₂₀₀₀ (Fig. 4a(ii)). A similar synergistic phenomenon was observed for the MoB + Au_{NP} + BP₂₀₀₀ composite (Fig. 4b(i and ii)).

To further rule out any nitrogen atom induced enhancement of HER activity (which was previously proposed and shown for Cu and Si catalysts^{16,17}), experiments were performed using VN, CrN and TiN mixed with Au_{NP} and BP₂₀₀₀ (Fig. 5). No significant improvement (synergy) in the HER activities of the VN + Au_{NP} + BP₂₀₀₀, CrN + Au_{NP} + BP₂₀₀₀ and TiN + Au_{NP} + BP₂₀₀₀ catalysts were found. The Tafel slopes of all these metal nitride composites were also higher than 90 mV dec⁻¹. These results demonstrate that Mo atoms, rather than N, are involved in the synergy with the Au_{NP} for H₂ evolution.

3.3. Proposed model for hydrogen evolution reaction

Recapping the key findings of this work, we first discovered that carbon played a crucial role in mediating the synergistic phenomenon. Secondly, we found that the effect is between Mo (rather than N) and Au_{NP}. We note that composites of Au and Mo-based compounds such as MoS₂ have been previously shown to exhibit enhanced HER activities.¹⁸

The Brewer Engle theory¹⁹ has suggested a synergy based on d-d electronic interaction between Mo(d⁵) and Au(d¹⁰). However, if this had been the case for this work, we should observe the synergy even in the absence of BP₂₀₀₀. Hence, we believe that d-d interaction between Mo and Au is probably not the underlying cause of the synergy. In support of this, we note that an extended X-ray absorption fine structure spectroscopy study

by Jaouen *et al.* on similar catalyst composites also did not detect the presence of Mo-Au interactions or perturbations to the electronic structure of Au.¹¹ We thus postulate instead a two-site model for the synergy: proton discharge ($H^+ + e^- \rightarrow H_{ad}$) could have occurred preferentially on the Mo₂N site. The adsorbed H atoms then diffused on the Mo₂N particles and spilled over onto the carbon support.²⁰ Such a kind of hydrogen spillover phenomenon from catalytic active sites onto the carbon support has been previously reported.^{21–24} It is noteworthy that Tafel slopes of 60 to 65 mV dec⁻¹ were measured for the Mo-based compounds + Au_{NP} + BP₂₀₀₀ composites (Fig. 2b, 4a(ii) and b(ii)). This could be attributed to a rate determining step consisting of the diffusion of the H atoms on the carbon support (a non-electrochemical step).¹⁵ The adsorbed hydrogen on carbon can then diffuse onto the Au particles. Direct recombination of two adsorbed H atoms ($2H_{ad} \rightarrow H_2$), or combination of adsorbed H with the proton from the electrolyte *via* the ion-atom reaction ($H_{ad} + H^+_{(aq)} + e^- \rightarrow H_2$) could finally occur to give H₂ gas.

The spillover effect, where H⁺ discharge takes place on one metal and two adsorbed H recombines to give H₂ gas on the second metal has been previously reported in pure Pd/Au electrocatalysts (where Au serves as the site for the recombination of H atoms).^{25,26} The present work demonstrates a new class of carbon-supported bimetallic catalysts for HER, where carbon in the form of BP₂₀₀₀ serves as a mediator for the diffusing H atoms. Interestingly, the composite catalyst with Vulcan XC₇₂ (Mo₂N + Au_{NP} + XC₇₂) showed only a slight increase in the activity compared to the sum of individual activities from Au_{NP} + XC₇₂ and Mo₂N + XC₇₂. This could be due to the smaller surface area (per gram) or local surface chemistry of XC₇₂,

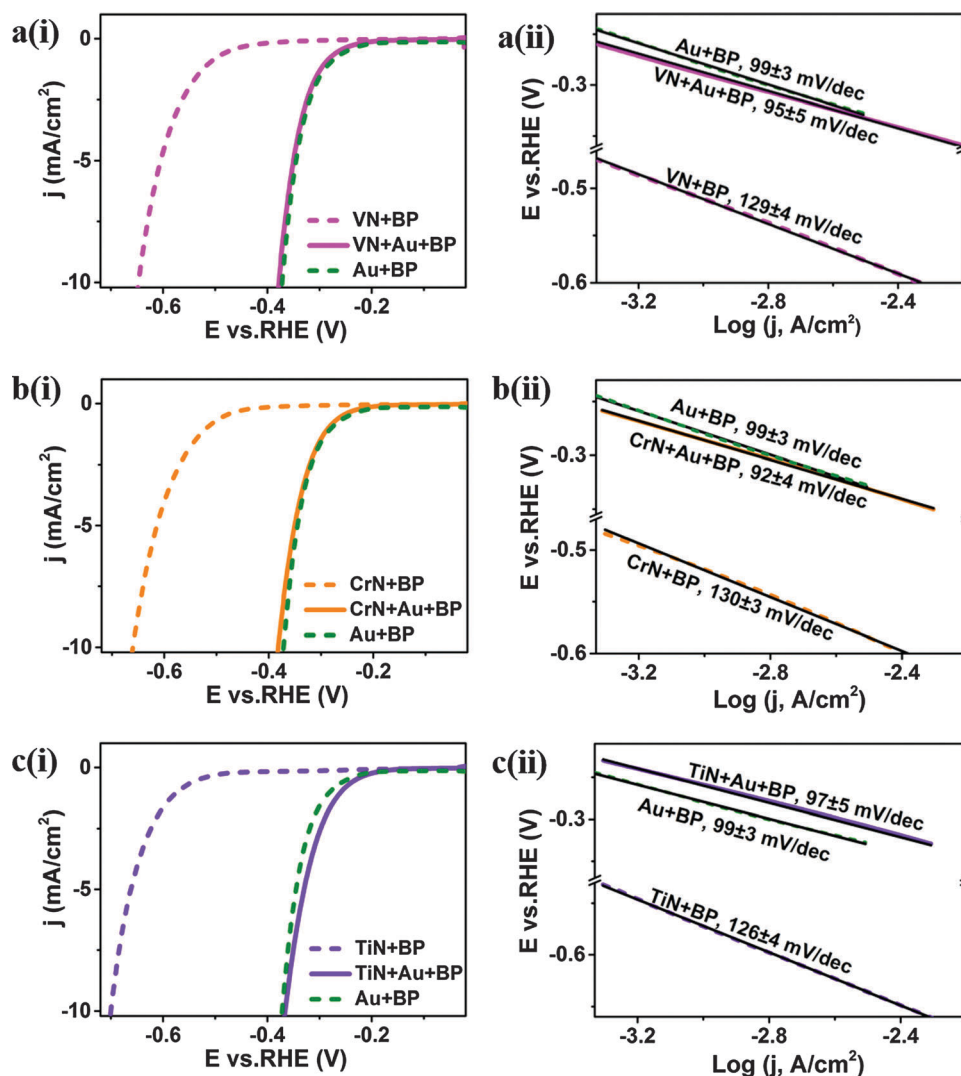


Fig. 5 (i) Linear sweep voltammograms and (ii) Tafel plots for (a) VN, (b) CrN and (c) TiN with and without AuNP. All catalysts contain BP₂₀₀₀.

which may have affected the spillover of H and/or dispersion of the Mo-based particles or Au_{NP}. Since the rate-determining step with the use of our carbon-based composite catalysts is believed to be hydrogen diffusion on carbon, a more extensive investigation to understand and modulate their HER activities will be made in the future using different types of carbon supports.

4. Conclusion

In this work, we first showed that Mo₂N interacted synergistically with Au_{NP} and BP₂₀₀₀ to give an enhanced activity for the electrochemical hydrogen evolution reaction in 0.5 M H₂SO₄ electrolyte. We further found that this phenomenon can be extended to MoB and Mo⁰, but not to VN, CrN, and TiN particles. We thus conclude that Mo atoms, rather than N atoms, are responsible for this synergistic effect. We also demonstrate that the presence of carbon is essential for the synergy. A two-site based mechanistic picture was proposed to rationalize the effect.

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References

- 1 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
- 2 B. Conway and B. Tilak, *Electrochim. Acta*, 2002, **47**, 3571–3594.
- 3 J. R. McKone, S. C. Marinescu, B. S. Brunschwig, J. R. Winkler and H. B. Gray, *Chem. Sci.*, 2014, **5**, 865–878.

- 4 J. K. Nørskov, T. Bligaard, A. Logadottir, J. Kitchin, J. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23–J26.
- 5 L. Ma, L. R. L. Ting, V. Molinari, C. Giordano and B. S. Yeo, *J. Mater. Chem. A*, 2015, **3**, 8361–8368.
- 6 W.-F. Chen, J. T. Muckerman and E. Fujita, *Chem. Commun.*, 2013, **49**, 8896–8909.
- 7 J. L. Dempsey, B. S. Brunschwig, J. R. Winkler and H. B. Gray, *Acc. Chem. Res.*, 2009, **42**, 1995–2004.
- 8 W.-F. Chen, S. Iyer, S. Iyer, K. Sasaki, C.-H. Wang, Y. Zhu, J. T. Muckerman and E. Fujita, *Energy Environ. Sci.*, 2013, **6**, 1818–1826.
- 9 S. Trasatti, *J. Electroanal. Chem. Interfacial Electrochem.*, 1972, **39**, 163–184.
- 10 L. R. L. Ting, Y. Deng, L. Ma, Y.-J. Zhang, A. A. Peterson and B. S. Yeo, *ACS Catal.*, 2016, **6**, 861–867.
- 11 A. Morozan, V. Goellner, A. Zitolo, E. Fonda, B. Donnadieu, D. Jones and F. Jaouen, *Phys. Chem. Chem. Phys.*, 2015, **17**, 4047–4053.
- 12 C. Giordano, C. Erpen, W. Yao and M. Antonietti, *Nano Lett.*, 2008, **8**, 4659–4663.
- 13 C. Giordano, C. Erpen, W. Yao, B. Milke and M. Antonietti, *Chem. Mater.*, 2009, **21**, 5136–5144.
- 14 G. Dong, M. Fang, H. Wang, S. Yip, H.-Y. Cheung, F. Wang, C.-Y. Wong, S. T. Chu and J. C. Ho, *J. Mater. Chem. A*, 2015, **3**, 13080–13086.
- 15 S. Fletcher, *J. Solid State Electrochem.*, 2009, **13**, 537–549.
- 16 C. C. Văduva, N. Vaszilcsin, A. Kellenberger and M. Medeleanu, *Int. J. Hydrogen Energy*, 2011, **36**, 6994–7001.
- 17 Q. Li, K. Schönleber, P. Zeller, I. Höhle, B. Rieger, J. Wintterlin and K. Krischer, *Surf. Sci.*, 2015, **631**, 185–189.
- 18 X. Ge, L. Chen, L. Zhang, Y. Wen, A. Hirata and M. Chen, *Adv. Mater.*, 2014, **26**, 3100–3104.
- 19 Č. M. Lačnjevac, N. M. Marković and M. M. Jakšić, *Surf. Technol.*, 1984, **22**, 51–59.
- 20 Y. Zhang, Y. Li, C. Li and Q. Xin, in *Stud. Surf. Sci. Catal.*, ed. L. Can and X. Qin, Elsevier, 1997, vol. 112, pp. 457–464.
- 21 E. Bittner and B. Bockrath, *J. Catal.*, 1997, **170**, 325–330.
- 22 P. Badenes, L. Daza, I. Rodriguez-Ramos and A. Guerrero-Ruiz, in *Stud. Surf. Sci. Catal.*, ed. L. Can and X. Qin, Elsevier, 1997, vol. 112, pp. 241–250.
- 23 W.-J. Liu, B.-L. Wu and C.-S. Cha, *J. Electroanal. Chem.*, 1999, **476**, 101–108.
- 24 P. C. H. Mitchell, A. J. Ramirez-Cuesta, S. F. Parker, J. Tomkinson and D. Thompsett, *J. Phys. Chem. B*, 2003, **107**, 6838–6845.
- 25 S. Pandelov and U. Stimming, *Electrochim. Acta*, 2007, **52**, 5548–5555.
- 26 L. Wang, U. Stimming and M. Eikerling, *Electrocatalysis*, 2010, **1**, 60–71.