Enhanced Catalysis of the Electrochemical Hydrogen Evolution Reaction using Composites of Molybdenum-Based Compounds, Gold Nanoparticles and Carbon

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Abstract

Molybdenum nitride had been recently reported to interact synergistically with gold to give an enhanced activity for the electrochemical hydrogen evolution reaction ($2H^{+}+2e^{-}\rightarrow H_2$, 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 HER in 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 played 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.

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 fuels.[1] The efficiency of this reaction depends largely on the electrocatalytic property of the cathode. To date, high performance electrocatalysts for HER are based mostly on noble metals such as Pt and Pd.[2-4] However, being intrinsically scarce in the earth's crust, these noble metal based catalysts are not appropriate candidates for large-scale water electrolysis. Hence, an extensive search for replacements has been on going.[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 the above-mentioned noble metals.

It has been recently demonstrated by Jaouen and co-workers that the electrochemical deposition of Au atoms onto molybdenum nitride (Mo_2N)+carbon catalyst can give a composite that has 100 times larger 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 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 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 on the above-mentioned synergistic phenomenon. All electrochemical experiments were performed in 0.5 M H_2SO_4 electrolyte, 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 needed for our investigations. Mo$_2$N, CrN, VN, 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 μg/ml, 5nm, BBI Solution, UK), Black Pearl-2000 (BP$_{2000}$, 1500 m^2/g, Cabot) and Vulcan XC-72 (XC$_{72}$, 240 m^2/g, Cabot) were used as received. The synthesized catalysts were characterized using powder x-ray diffraction (Bruker Siemens D5005, Cu K$_{\alpha 1}$, λ = 1.5406 Å, scan range: 20°-90°, scan rate: 0.1°/min) 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 put 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-casted. The ink was prepared by mixing 2 mg of the metal-based catalyst, 1.2 mg of BP$_{2000}$ or XC$_{72}$, and 1 mL of a solution consisting of 89.5 vol % ultrapure water (18.2 MΩ.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-casted onto the working electrode and dried under a halogen lamp (50 W, Philips) for 15-20 min. The distance between the electrode and lamp was ~5cm, and the temperature of the electrode rose to about

30-35 ^{o}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-casted and dried. In all the experiments, the loading of the catalyst, the carbon and the gold on the working electrode were 141, 85 and 18 µg/cm^2 respectively.

All electrochemical experiments were done in a glass cell, with Hg/HgSO$_4$ (sat. K$_2$SO$_4$) reference electrode (CHI 151) and a graphite rod as a counter electrode. 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 H$_2$SO$_4$ (96.9 %, Sigma Aldrich) solution was used as the electrolyte. Linear sweep voltammetry at 2 mV/s 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) is 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 Ω). 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 Mo$_2$N+Au$_{NP}$: with and without carbon

The identity of the as-synthesized molybdenum nitride was confirmed by x-ray diffraction (PDF-00-025-1366) to be γ-Mo$_2$N (Figure 1a). Transmission electron microscopy and selected area electron diffraction confirmed that the catalyst was in the form of polycrystalline particles with sizes of ~30 nm (Figures 1b and c). Some smaller primary amorphous nanoparticles, from which the bigger particles obviously form from, can be also

observed in the TEM image. The Au nanoparticles (Au_{NP}) were 5 to 8 nm in size (Figure 1d).

γ-Mo_2N, Au_{NP} and BP_{2000} were then physically mixed, and the catalytic activity of this composite (Mo_2N+Au_{NP}+BP_{2000}) for HER was measured in 0.5 M H_2SO_4 electrolyte by linear sweep voltammetry. At η=250 mV, it gave a H_2 current of 2.43±0.25 mA/cm^2 (Figure 2a). The individual Mo_2N and Au_{NP} (both dispersed in BP_{2000}), in contrast, only gave respective currents of 0.28±0.03 and 0.51±0.07 mA/cm^2 at the same overpotential. Thus, the composite catalyst exhibited a HER activity that was 3 times the sum of the individual activity of Mo_2N+BP_{2000} and Au_{NP}+BP_{2000}. A reference glassy carbon electrode loaded with only BP_{2000} gave negligible currents.

As 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 Mo_2N+Au_{NP}+BP_{2000} composite was more HER active than the simple sum of activities of Au_{NP}+BP_{2000} and Mo_2N+BP_{2000} catalysts.

Furthermore, the Mo_2N+Au_{NP}+BP_{2000} composite had a unique Tafel slope of 63±3 mV/dec, which was 28-36 mV/dec lower than that of Mo_2N+BP_{2000} (91±1 mV/dec) and Au_{NP}+BP_{2000} (99±3 mV/dec) (Figure 2b). This value (63±3 mV/dec) did not match with any of the commonly predicted Tafel slopes based on the following steps as rate determining reaction, namely the Heyrovsky step (H_{ad}+H^++$e^- \rightarrow H_2$; 40 mV/dec), Volmer step (H^++$e^- \rightarrow H_{ad}$; 116 mv/dec) and Tafel step (H_{ad}+$H_{ad} \rightarrow H_2$; 30 mV/dec).[6, 15] These collective evidence suggest the existence of a synergistic effect between these materials which lead to an enhancement in the HER activity.

To probe the role of carbon, HER experiments were first conducted on Mo_2N, Au_{NP} and

Mo$_2$N+Au$_{NP}$, without the addition of BP$_{2000}$ (Figures 3a(i,ii)). Unexpectedly, we discovered that the activity of Mo$_2$N+Au$_{NP}$ (no BP$_{2000}$ added) was only 0.29±0.12 mA/cm^2 at η = 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 Mo$_2$N (0.29±0.11 mA/cm^2). The Tafel slope of the carbon-free Mo$_2$N+Au$_{NP}$ composite was also higher at 106±4 mV/dec. HER experiments were also performed using Vulcan XC$_{72}$-based composites (Figures 3b(i,ii)). The Mo$_2$N+Au$_{NP}$+XC$_{72}$ composite showed slight increases in activities compared to the sum of individual activities of Mo$_2$N+XC$_{72}$ and Au$_{NP}$+XC$_{72}$. 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 Mo^0, MoB, VN, CrN and TiN catalysts

To probe whether the synergistic phenomenon is based on the interaction of Mo or N atoms (in Mo$_2$N) with Au$_{NP}$, the catalysis of HER using non-nitrogen containing compounds, namely metallic Mo^0 and MoB, were performed. At η=250 mV, the activities of Mo^0+BP$_{2000}$, Au$_{NP}$+BP$_{2000}$ and Mo^0+Au$_{NP}$+BP$_{2000}$ systems were respectively 0.10±0.02, 0.51±0.07 and 4.79±0.76 mA/cm^2 (Figure 4a(i)). Thus, the Mo+Au$_{NP}$+BP$_{2000}$ composite exhibited a HER activity 8 times larger than the sum of the individual activity of each added component and 2 times larger than the Mo$_2$N+Au$_{NP}$+BP$_{2000}$ composite catalyst. The Tafel slope of the Mo^0+Au$_{NP}$+BP$_{2000}$ composite, which was 63±5 mV/dec, was also smaller than that of Au$_{NP}$+BP$_{2000}$ and Mo^0+BP$_{2000}$ (Figure 4a(ii)). A similar synergistic phenomenon was observed for the MoB+Au$_{NP}$+BP$_{2000}$ composite (Figures 4b(i,ii)).

To 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 with VN, CrN and TiN mixed with Au$_{NP}$ and BP$_{2000}$ (Figure 5). The VN+BP$_{2000}$, CrN+BP$_{2000}$ and TiN+BP$_{2000}$ catalysts did not show any significant enhancement in their HER activity after the

addition of Au$_{NP}$. The Tafel slopes of all these metal nitrides+Au$_{NP}$+BP$_{2000}$ composites were also higher than 90 mV/dec. These results demonstrate that Mo atoms, rather than N, are involved in the synergy with the Au$_{NP}$ for H$_2$ 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 MoS$_2$ have been previously shown to exhibit enhanced HER activities.[18]

The Brewer Engel theory[19] has suggested a synergy based on d-d electronic interaction between Mo(d^5) and Au(d^{10}). However, if this had been the case for this work, we should observe the synergy even in the absence of BP$_{2000}$. Hence, we believe that d-d interaction between Mo and Au is probably not the underlying cause of the synergy. An extended x-ray absorption fine structure spectroscopy study 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 a two sites model for the synergy: proton discharge (H$^+$ + e$^-$ → H$_{ad}$) could have occurred preferentially on the Mo$_2$N site. The adsorbed H atoms then migrated on the Mo$_2$N particles and spilled over onto the carbon support.[20] Such 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 were measured for the Mo-based compounds+Au$_{NP}$+BP$_{2000}$ composites (Figures 2b, 4a(ii) and 4b(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 diffused onto the Au particles. Direct recombination of two adsorbed H atoms (2H$_{ad}$ → H$_2$), or combination of adsorbed H with proton from electrolyte via ion-atom reaction (H$_{ad}$ + H$^+_{(aq)}$ + e$^-$ → H$_2$) could

then occur to give H_2 gas.

The spillover effect, where H^+ discharge takes place on one metal and two adsorbed H recombines to give H_2 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 catalyst for HER, where carbon serves as a mediator for the diffusing H atoms. Compared to the individual Au, BP_{2000} and Mo-based components in the catalyst, the composite catalyst was observed to exhibit higher HER activity. Interestingly, the composite catalyst with Vulcan XC_{72} showed only slight increase in activity compared to sum of individual activities from $Au_{NP}+XC_{72}$ and Mo_2N+XC_{72}. This could be due to local surface chemistry or smaller surface areas of XC_{72} which 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 this composite catalyst is believed to be hydrogen diffusion on carbon, further investigations to understand the actual HER mechanism and to modulate the H_2 evolution activity will be made using different types of carbon supports.

4. Conclusion

In this work, we first showed that Mo_2N interacted synergistically with Au_{NP} and BP_{2000} to give an enhanced activity for the electrochemical hydrogen evolution reaction in 0.5 M H_2SO_4 electrolyte. We further found that this phenomenon is extended to MoB and Mo^0, 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 sites based mechanistic picture was incorporated to rationalize the effect.

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