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Boosting electrochemical reduction of CO₂ at a low overpotential by amorphous Ag-Bi-S-O decorated Bi⁰ nanocrystals

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Abstract: Bimetal-S-O composites have been rarely researched in electrochemical reduction of CO₂ field. In this work, an amorphous Ag-Bi-S-O decorated Bi⁰ catalyst derived from Ag_{0.95}BiS_{0.75}O_{3.1} nanorods by electrochemical pre-treatment was used for catalyzing eCO₂RR, which exhibited a formate FE of 94.3% with a formate partial current density of 12.52 mA cm⁻² at an overpotential of only 450 mV. This superior performance was attributed to the attached amorphous Ag-Bi-S-O substance. S could be remained in the amorphous region after electrochemical pre-treatment only in samples derived from metal-S-O composites, and it would greatly enhance the formate selectivity by accelerating the dissociation of H₂O. The existence of Ag would increase the current density, resulting in a higher local pH, which made the role of S in activating H₂O more significantly and suppressed H₂ evolution more effectively, thus endowing the catalyst with a higher formate FE at low overpotentials.

Since the last decades, for making life of human beings more convenient and comfortable, fossil fuels have been consumed without restraint and excess carbon dioxide CO_2 has been emitted into the atmosphere, which causes a series of problems such as energy crisis, global climate change and ocean acidification.^[11] As a result, exploring renewable energy sources for replacement of fossil fuels and developing effective methods for fixing the atmospheric CO_2 become urgent.^[2] Electrochemical reduction of CO_2 (eCO_2RR), which could utilize the electricity generated from renewable energy sources and convert waste CO_2 into valuable products such as CO, formate, C_2H_4 etc., has drawn more and more attention in recent years.^[3]

Owing to the inert CO₂ molecule, although various materials have been developed for eCO₂RR, it is still a great challenge to catalyze this reaction with satisfactory activity and selectivity at a low overpotential.^[4] Among the reported catalysts, metal oxides, metal sulfides and their derivants exhibit quite attractive eCO₂RR performance.^[5] It's commonly accepted that during the eCO₂RR process, metal oxides and sulfides would be reduced partially or entirely, endowing the catalyst with unique surface structures and local environments, such as defects and oxygen/sulfur modifiers, which would facilitate the reduction of CO₂.^[6] However, most of the research only focused on the simplex metal oxides or metal sulfides, and only a little work has

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investigated the catalytic performance of metal-S-O composites in eCO₂RR.^[7] There is every reason to believe that metal-S-O composites would exhibit some unique quality for catalyzing eCO₂RR.

Except single metal sulfides, there exists a large class of ternary metal sulfides, and they have exhibited some unique characteristics in H₂ evolution, O₂ evolution and O₂ reduction evolution reactions (such as NiCo₂S₄, FeNiS₂, etc.),^[8] or in bioimaging and photochemistry (such as AgInS₂, CuInS₂, etc.).^[9] By annealing ternary metal sulfides in air at high temperature, we could get a series of bimetal-S-O composites. Considering that bimetallic catalysts often exhibit more superior catalytic performance compared to the corresponding single metal catalysts due to the synergistic geometric and electronic effects between hetero metallic components,^[10] we could infer reasonably that bimetal-S-O composites may show attractive activity and selectivity in eCO2RR field. However, almost none of research has examined the eCO₂RR catalytic performance of bimetal-S-O composites. Therefore, it is of great significance for introducing bimetal-S-O composites into the eCO₂RR field. which may help us finding a large class of novel electrocatalysts with satisfactory performance for eCO₂RR.

Herein, we synthesized the bimetal-S-O composite Ag_{0.95}BiS_{0.75}O_{3.1} nanorods by annealing the AgBiS₂ nanorods in air at 500 °C. After electrochemical pre-treatment, this Ag_{0.95}BiS_{0.75}O_{3.1} nanorod was converted into Bi⁰ nanocrystals attached by amorphous substance composed of Ag, Bi, S and O (the whole synthesis procedure is shown in Fig.1a). The Ag-Bi-S-O decorated Bi⁰ catalyst exhibited a formate FE of 94.3% with a formate partial current density of 12.52 mA cm⁻² at an overpotential of only 450 mV, while a long-time measurement illustrates that this catalyst also showed a quite satisfactory stability.

AgBiS₂ nanorods (Fig. S1) were firstly synthesized and then annealed in air at 200 °C or 500 °C, and the obtained samples were named as AgBi-200b and AgBi-500b ('b' means before electrochemical pre-treatment), respectively (seeing Supporting Information for more details). The results of transmission electron microscopy (TEM), X-ray diffraction (XRD), Highresolution TEM (HRTEM), high angle annular dark field scanning TEM (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) (Fig.S2 to Fig.S4) demonstrate that AgBi-200b could still maintain the composition of AgBiS2 while AgBi-500b was composed of AgBiS₂, Ag₂O and $Bi_{28}O_{32}(SO_4)_{10}$. For comparison, Bi-200b and Bi-500b were also prepared through a similar procedure, and the relative characterization (Fig.S5 to Fig.S8) illustrates that Bi-200b could maintain the composition of Bi_2S_3 while Bi-500b was composed of Bi_2S_3 , Bi_2O_3 and $Bi_{28}O_{32}(SO_4)_{10}$. The shifting of Ag 3d, Bi 4f, S 2p and S 2s peaks to higher binding energies in X-ray photoelectron spectroscopy (XPS) spectra (Fig.S9 and Fig.S10) suggests the formation of Ag-O, Bi-O and S-O bonds in AgBi-500b and Bi-500b. Finally, XPS analysis illustrates the composition of AgBi-500b and Bi-500b to be Ag_{0.95}BiS_{0.75}O_{3.1} and BiS_{0.68}O_{2.7} (Table S1).



Figure 1. a) Schematic of the synthesis process of AgBi-500; b) to d) HRTEM images of AgBi-500, while c) and d) is a magnification of the orange squares in b) and c) respectively; e) to h) EDS elemental mappings of AgBi-500.

To simplify the problem that Bi species would be reduced in eCO₂RR process (the reduction degree depends on the testing potential) and the valence of Bi would greatly influence the catalytic performance.^[11] we conducted electrochemical reduction pre-treatment on the four samples and the obtained catalysts were denoted as AgBi-200, AgBi-500, Bi-200 and Bi-500, respectively. Fig.S11 to Fig. S14 show that all four nanorods decomposed into irregular nanoparticles after electrochemical pre-treatment. Only lattice spacing and peaks corresponding to Bi⁰ could be observed in HRTEM images and XRD patterns of these samples, suggesting the formation of Bi⁰ nanocrystals and that no Ag-Bi alloy was formed (Fig.1b to 1d, Fig.S11 to Fig.S15). In some part of the nanoparticles, no obvious lattice fringe could be observed (Fig.1c, Fig.S12b, Fig.S13b), suggesting the existence of amorphous substance. EDS elemental mappings (Fig.1e to 1h, Fig.S12, Fig. S13) demonstrate the uniform distribution of Ag, Bi, S, O in AgBi-500, Ag, Bi, O in AgBi-200 and Bi, S, O in Bi-500. Peaks corresponding to S 2s and S 2p (sulfate, +6) could be observed in XPS spectra of AgBi-500 and Bi-500, which did not appear in XPS spectra of AgBi-200 and Bi-200 (Fig.S16 to Fig.S19). Therefore, we could point out that after electrochemical pretreatment: 1) A large proportion of Bi would be reduced to Bi⁰ with fine crystallization; 2) Ag, S, O and the rest of Bi would attach to Bi⁰ in an amorphous form of metal-O-sulfate in AgBi-500, while in Bi-200 and AgBi-200, the amorphous species were composed of Bi, S, O metal-O-sulfate, and Ag, Bi, O metal oxide, respectively (seeing Table S2 for more information); 3) S would be totally removed out from the surface of AgBi-200 and Bi-200 while remained in the form of sulfates in the amorphous part of AgBi-500 and Bi-500, which could be explained by the different valence of S. In AgBi-200b and Bi-200b, all S presented a valence of -2, and S²⁻ would react with H⁺ in the electrolyte to form H₂S when the metal ions were reduced and leave out from the electrodes; in AgBi-500b and Bi-500b, part of S was oxidized to a positive valence of +6, and this part of S would not become H₂S and could remain in the samples.



Figure 2. a) formate FE and b) formate partial current density for four samples in CO₂-saturated 0.1M KHCO₃ solution; c) stability test for AgBi-500 at -0.7 V vs. RHE; d) LSV curves of AgBi-500 in CO₂ and N₂ saturated electrolyte.

Linear sweep voltammetry (LSV) were first conducted for investigation of the electrochemical activity of the four samples. In Fig.S20, we could find that at potentials more negative than -0.45 V vs. reverse hydrogen electrode (RHE) (all potentials hereafter are provided with respect to RHE unless otherwise stated), current densities of these four catalysts followed the order of AgBi-500 > AgBi-200 > Bi-500 > Bi-200, meaning the introduction of Ag and the derivation from metal-S-O composites would ensure a large current density. The four samples were then examined as electrocatalysts for eCO₂RR by the controlled potential electrolysis method. Fig.2a and Fig.S21 provide the Faradaic efficiency of all products for these four samples. At all applied potentials, formate and H₂ were the main products, while trace CO could be detected at some potentials for AgBi-500 and Bi-500. AgBi-500 exhibited the most extraordinary formate selectivity among the four catalysts. It could reach the maximum formate FE of 94.3% at -0.7 V (only a 450 mV overpotential) with a formate partial current density of 12.52 mA cm⁻² (Fig.2b), and the formate FE could maintain over 90% in a wide potential range from -0.7 V to -1.0 V. Compared to other reported Bibased electrocatalysts, this AgBi-500 catalyst showed the highest formate FE at the lowest overpotential (Fig.S22). As for Bi-500, although it could reach a formate FE over 90% with a large overpotential (-0.9 V), it performed unimpressively at more positive potentials. At -0.7 V, its formate FE is ~70% and its formate partial current density was much lower than that of AgBi-500. The counterparts AgBi-200 and Bi-200 showed very poor performance at all applied potential, while AgBi-200 performed a little better than Bi-200. Thus, we could conclude that the existence of Ag and the derivation from metal-S-O composites would facilitate the eCO2RR process, which brought AgBi-500 with the most superior catalytic performance. A 12 h long-term electrolysis test (Fig.2c) demonstrates that whether the total current density or the formate FE of AgBi-500 were generally stable, suggesting a good stability of AgBi-500. Finally,

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to rule out the possibility that the formate could be produced by the decomposition of electrolyte, electrolysis on AgBi-500 in N₂saturated KHCO₃ was performed, and the much lower current density and no formate being detected in N₂-saturated electrolyte confirm the formate to be produced from the reduction of CO₂ (Fig. 2d and Fig. S23).

To figure out the origin of the superior performance of AgBi-500, Tafel plots (overpotentials versus logiHCOOH) were firstly used for investigating the reaction kinetics for CO₂ reduction to formate (Fig.3a). Compared to AgBi-200 and Bi-200, AgBi-500 and Bi-500 exhibited much lower Tafel slopes of 104 mV dec-1 and 137 mV dec⁻¹ respectively, which illustrates the great enhancement of kinetics activity for eCO2RR on samples derived from metal-S-O composites. Besides, Tafel slopes of AgBi-500 and Bi-500 were close to the theoretical value of 118 mV dec⁻¹, which means that the first electron transfer step (the adsorbed $CO_2 + e^- \rightarrow CO_2^-$) was the rate-determining step (RDS).^[12] For AgBi-200 and Bi-200, their Tafel slopes were much larger than 118 mV dec⁻¹, suggesting that the adsorbed CO₂ receiving an electron and combining with H⁺ from the electrolyte to form OCHO* (the adsorbed $CO^2 + [H^+ + e^-] \rightarrow OCHO^*$) became the RDS.^[13] This difference may reflect that H⁺ in the electrolyte was more difficult to be accessed when using AgBi-200 and Bi-200 for catalyzing eCO₂RR. Considering that no S species existed on the surface of AgBi-200 and Bi-200, while in the amorphous part of AgBi-500 and Bi-500, S would be remained, we could infer that it may be S species on the surface of AgBi-500 and Bi-500 that made H⁺ in the electrolyte more accessible and thus greatly enhanced the kinetics activity. Electrolysis in N2saturated 0.1 M KOH solution shows larger current density of AgBi-500 compared to that of AgBi-200 at the applied potentials, which means higher H₂ formation rate of AgBi-500, confirming that S on the surface could accelerate the dissociation of H₂O (Fig. S24). HCO3⁻ concentration dependence experiment (Fig.3b) points out that there was no correlativity between formate partial current density and HCO3⁻ concentration when adopting AgBi-500 or Bi-500 as the eCO2RR catalysts, evidencing that H⁺ anticipating the formation of OCHO^{*} was provided from the dissociation of H₂O.^[14] Thus, it was S on the surface of AgBi-500 and Bi-500 that accelerated the dissociation of H₂O to form H⁺, which could react with CO₂ to form OCHO^{*}, resulting in a faster eCO2RR kinetics and formate FE. Wang's group also discovered that S species in S-doped In₂O₃ would accelerate the activation of H₂O and thus enhance the formate selectivity.[7] That is why samples derived from metal-S-O composites (AgBi-500 and Bi-500) exhibited a much better eCO₂RR performance than their counterparts.

Then, we need to figure out why AgBi-500 exhibited higher current densities and formate FE at lower overpotentials compared to Bi-500. Firstly, the adsorption of OH⁻ as a surrogate of CO2⁻⁻ was examined for investigating the binding affinity of CO2⁻⁻ on AgBi-500 and Bi-500, and the reduction peak of AgBi-500 and Bi-500 appeared at nearly the same place (Fig.S25), demonstrating that their ability to stabilize CO2⁻⁻ intermediate differed very little.^[15] Thus, the stabilization of CO2⁻⁻ intermediate could not account for the different formate FE of AgBi-500 and Bi-500.

Secondly, electrochemical impedance spectroscopy (EIS) was conducted and the obtained Nyquist plots (Fig.3c) indicates that

AgBi-500 exceeded Bi-500 on the electrical conductivity, confirming that the existence of Ag in the catalyst would decrease the charge-transfer resistance and thus facilitate the charge-transfer process from electrode to the adsorbed CO2. Besides, the Tafel slope of AgBi-500 was a little smaller than that of Bi-500, also evidencing a faster charge-transfer process on AgBi-500. Both results could account for the enhancement in geometric current density of AgBi-500 at -0.7 V. It should be noted that this enhancement differed essentially from the increase of formate partial current density brought by the surface S spices because S activated the H₂O and made the adsorbed CO₂ react with H⁺ more easily, resulting in a faster eCO₂RR kinetics and thus larger formate partial current density. Moreover, we loaded 2 mol% Ag on Bi-500, and the new Ag/Bi-500 catalyst showed higher current density compared to Bi-500 at the applied potentials, confirming the role of Ag in enhancing the current density (Fig. S26 and S27a).



Figure 3. a) Tafel plots for four samples; b) HCO_3^- concentration dependence experiment on AgBi-500 and Bi-500; c) Nyquist plots for AgBi-500 and Bi-500; d) an illustration of local pH effect; e) pH dependence experiment on AgBi-500 and Bi-500 in 0.1 M K₂HPO₄, KHCO₃, K₂SO₄ solution at 7.11 mA cm⁻².

As illustrated in Fig.3d, the consumption of H⁺ in H₂ evolution and eCO₂RR would increase the local pH near the cathode, and a higher current density would result in a larger local pH.^[16] A phenolphthalein color transition experiment was conducted on AgBi-500 and Bi-500,^[17] and the result showed that after 1 min electrolysis at -0.7 V, the electrolyte's color would change to pink

only in AgBi-500 system, confirming that the local pH around the cathode was truly higher in AgBi-500 system (Fig. S28). At a higher local pH value, as reported by Wang's work, the role of S in accelerating the dissociation of H₂O would be more significant, which would enhance the formate selectivity; besides, H₂ evolution would also be suppressed more effectively.^[7, 18]

To verify the local pH effect, we examined the formate FE of AgBi-500 and Bi-500 in three electrolytes with different buffer capacity at a constant current density. Fig.3e illustrates that with the local pH increasing, the formate FE of AgBi-500 and Bi-500 both increased, which confirms that a high local pH was preferred for eCO₂RR than H₂ evolution. Besides, in the same electrolyte, AgBi-500 and Bi-500 showed comparable formate FE, which may be attributed to their similar ability for stabilizing CO2" intermediate. Furthermore, Ag/Bi-500 exhibited a higher formate FE (81.5%) at -0.7 V compared to Bi-500 (70.3%), also confirming the higher local pH resulted from the larger current density facilitated the formation of formate (Fig. S27b). Now, we could conclude that at more positive potentials, the existence of Ag in AgBi-500 would greatly enhance the geometric current density, resulting in a higher local pH and thus S species on the surface would accelerate the dissociation of H₂O more dramatically. Besides, H₂ evolution would be suppressed more significantly. That's why AgBi-500 exhibited a superior formate FE at a low overpotential. At more negative potentials, the formate FE of Bi-500 increased, which may be attributed to the larger overpotential and higher geometric current density. As for AgBi-500, although the formate selectivity did not rise with the increasing current density and overpotential at potentials ranging from -0.7 V to -1.0 V, its formate FE could maintain over 90% and H₂ FE could maintain beneath 8%, also suggesting the important role of the local pH effect. Finally, Ag is commonly believed to convert CO2 to CO, and in AgBi-500 there existed a large proportion of Ag, but CO₂ was still reduced to formate with high selectivity. This could be ascribed to the stronger adsorption of acidic CO₂ molecule on alkaline main group metal Bi (Ag is a kind of more inert noble metal) and Bi would reduce CO₂ to formate due to the intrinsic property of Bi (seeing supplementary remark in supporting information).^[19]

In summary, we have developed an amorphous Ag-Bi-S-O decorated Bi⁰ nanocatalyst derived from Ag_{0.95}BiS_{0.75}O_{3.1} nanorods, which exhibited a formate FE of 94.3% with a formate partial current density of 12.52 mA cm⁻² at a low overpotential. Because it was derived from the metal-S-O composites, S could be remained in the amorphous region after electrochemical pretreatment, which could facilitate the eCO₂RR by accelerating the dissociation of H₂O. The existence of Ag could enhance the current density at lower overpotentials, resulting in a higher local pH, which boosted the formation of formate by making the role of S in activating H₂O more significantly and suppressing H₂ evolution more effectively. This work may guide us for developing more bimetal-S-O composites derived materials for catalyzing eCO₂RR with satisfactory performance.

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Larger

current density

Hydrogen
Carbon
Oxygen

ocal pH

Entry for the Table of Contents

Jun-Hao Zhou, Kun Yuan, Liang Zhou, Yu Guo, Ming-Yu Luo, Xiao-Yan Guo, Qing-

Yuan Meng and Ya-Wen Zhang*

Boosting electrochemical reduction of CO₂ at a low overpotential by amorphous Ag-Bi-S-O decorated Bi⁰ nanocrystals

Low overpotential selective eCO₂**RR:** A formate efficiency of 94.3% at a low overpotential of 450 mV was achieved by an amorphous Ag-Bi-S-O decorated Bi⁰ nanocatalyst derived from bimetal-S-O composite $Ag_{0.95}BiS_{0.75}O_{3.1}$ due to the role of S in accelerating the dissociation of H₂O and the higher local pH resulted from the existence of Ag.

Amorphous

Ag-Bi-S,0

Activating

Bi⁰ nanocrystals