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Influence of the Chemical Compositions of Bismuth Oxyiodides on the Electroreduction of Carbon Dioxide to Formate

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Abstract: Bismuth oxyiodides with varied chemical compositions were fabricated to effectively electrochemical reduce CO₂ to formate. Bi₅O₇I and Bi₇O₉I₃ nanosheets assemble irregularly, and BiOI nanosheets form a sphere-like structure. Compared with BiOI and Bi₇O₉I₃, Bi₅O₇I exhibits an excellent formate Faradaic efficiency of 89% with the partial current density of 13.2 mA/cm² at -0.89 V vs. RHE, owing to the elevated amounts of Bi metal sites reduced from Bi³⁺ during electrolysis. It is worth noting that the partial current densities of formate on BiOI were higher than those on Bi₇O₉I₃ which

is attributed to high contents of iodine. The synergistic effect of bismuth and iodine of bismuth oxyiodides is responsible for their electrocatalytic properties during CO₂ reduction in aqueous solutions.

Introduction

Electrochemical CO₂ reduction reaction (CO₂RR) has been receiving great attention, attributed to the promising proposal to reduce greenhouse gases and dependence on fossil fuels, especially with a combination of solar and wind energy to generate electricity.^[1] Due to a multi-electron and multi-step process, CO₂RR leads to the wide C₁-C₃ products, including CO, methane, formate, ethylene, ethanol, oxalic acid and n-propanol (total of about 16 products).^[2] Formate, as one of the main C₁ products, is an important raw material for synthetic drugs in the pharmaceutical industry, and also widely used in the chemical, pesticide and rubber fields.^[3] Considering that it is a simple twoelectron process, selective electroreduction CO₂ to formate has potential for application and theoretical significance.^[4]

Usually, metal electrocatalysts, including Bi, Sn, Pb, Cd, Hg, In and Tl can efficiently catalyze CO₂ to formate in aqueous solutions.^[5] Recently, some groups made great progresses on developing high-efficiency CO₂RR electrocatalysts for producing formate such as Bi nanosheets,^[6] Bi nanowires@Cu foam,^[4] Bi₂O₃ nanosheets/carbon supports,^[7] Bi₂O₃ nanotubes,^[8] Bi-Sn,^[9] Sn,^[10] SnO₂,^[11] Ag-Sn,^[12] Sn-Cu@SnO_x,^[13] and S-doped In.^[14] ChemPlusChem

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Research on Bi-based catalysts for CO₂RR has attracted a lot of attention, due to Bi metal with the advantages of less toxicity and low cost compared with heavy metals.^[4,6b,7b] Over Bi-based catalysts reported by Rosenthal et al., the main products in acetonitrile containing ionic liquids were CO with Faradaic efficiencies (FEs) of 74-95%.^[15] Interestingly, bismuth single-atom catalysts on N-doped carbon networks (Bi-N-C) reported by Li et al. were prepared by pyrolysis of a bismuth-based metal-organic framework and dicyandiamide, and the reduction products in 0.1 M NaHCO₃ solutions were not formate but CO with a high FE of 97% and high turnover frequency of 5535 h^{-1} at -0.50 V vs. hydrogen electrode (RHE).^[16] reversible However, **Bi-based** most electrocatalysts for CO₂RR in aqueous solutions favorably brought about the formation of formate. Bi nanoflakes fabricated by a pulse electrodeposition method achieved a highly selective production to formate with nearly 100% FE at -0.6 V vs. RHE.^[17] And Bi nanosheets prepared via electroreduction of bismuth oxide sulfates and bismuth sulfides could effectively reduce CO₂, where formate FE reached over 90% in the potential range of -0.9 to -1.2 V vs. RHE, because under-coordinated Bi sites can stabilize the intermediate species to form formates.^[18]

Significantly, Bi nanosheets could also be obtained via electrochemical reduction of BiOI,^[6b] showing the superior electrocatalytic performances for CO₂RR to formate. In addition, Bi-based electrocatalysts prepared by *in-situ* transformation from BiOI micro-flowers were composed of oxidized Bi₂O₂CO₃

and metallic Bi; due to shortened inter-layer Bi-Bi bonds, they exhibited over 90% FEs of formate in a broad region from -0.80 to -1.50 V vs. RHE.^[19]

Bismuth oxyiodides belong to a new type of catalysts, and possess unique layered structures, excellent electrical and optical properties.^[20] They are composed of $[Bi_xO_y]$ layers interleaved with iodide $[I_z]$ layers via van der Waals forces.^[21] Up to now, all bismuth oxyiodides with varied chemical compositions include BiOI,^[22] Bi₇O₉I₃,^[23] α -Bi₅O₇I,^[23-24] β -Bi₅O₇I,^[25] Bi₄O₅I₂^[26] and Bi₃O₅I₂.^[27] So far, the literature on bismuth oxyiodides electrocatalysts for CO₂RR especially is still scarce, and the detailed influence of chemical compositions on the electrocatalytic performances is obscure.

Herein, bismuth oxyiodides nanosheets electrocatalysts for CO₂RR with three chemical compositions, Bi₅O₇I, Bi₇O₉I₃ and BiOI, were fabricated via a solvothermal method with ethylene glycol as the solvent. The electrocatalytic properties on three bismuth oxyiodides at different applied potentials in CO₂saturated 0.5 M KHCO₃ solutions were investigated. The influence of the contents of bismuth and iodine on the FEs and partial current densities of formate was studied.

Results and discussion

Textural properties

The Powder X-ray diffraction (XRD) patterns of all bismuth oxyiodides are shown in Fig. 1. For three catalysts, α -Bi₅O₇I, BiOI and Bi₇O₉I₃ are identified according to the standard PDF cards (α -Bi₅O₇I PDF#: 97-041-1666, Orthorhombic, Ibca; BiOI PDF#: 97-039-1354, tetragonal, P₄/nmm) and the literature.^[23,28] Distinct differences are observed between the patterns of BiOI and those of Bi₇O₉I₃ and Bi₅O₇I. Interestingly, the peak position at 29.8° of BiOI notably shift in the negative direction to 29.0° of Bi₇O₉I₃ and 28.2° of Bi₅O₇I, respectively, which is attributed to the expansion of lattice and structural distortion, owing to the variability of oxygen and bismuth in different chemical compositions.^[28] The preparation processes of three bismuth oxyiodides are similar. The difference of chemical compositions among them is attributed to the different dosages of KI and the absence/presence of the calcination process.



Fig. 1. XRD patterns of Bi₅O₇I, Bi₇O₉I₃ and BiOI catalysts.



Fig. 2. (a) nitrogen adsorption-desorption isotherms and (b) pore size distributions of BiOI, Bi₇O₉I₃ and Bi₅O₇I.

Additionally, nitrogen adsorption-desorption isotherms were performed to study surface areas and pore structures of bismuth oxyiodides (Fig. 2). BiOI and Bi₇O₉I₃ exhibit the type IV isotherms with type H₃ hysteresis loops, which indicate that the mesoporous pores result from aggregations of nanosheets shown in Fig. 3a-e.^[29] The pore size distributions of BiOI and Bi₇O₉I₃ (Fig. 2b) indicate that the main pores are about 19.8 and 27.0 nm, respectively. In contrast, the adsorption isotherm of Bi₅O₇I is specified as type II, suggesting the characteristic of nonporous materials,^[24] which is confirmed by its pore size distribution. The total surface areas of BiOI and Bi₇O₉I₃ are 40.59 and 51.72 m²/g, respectively, but that of 12.67 m²/g on Bi₅O₇I is lower (Table 1), which is attributed to the densification and agglomeration of nanosheets during the heat treatment process of generating Bi₅O₇I from Bi₇O₉I₃.^[30]

Morphologies of bismuth oxyiodides

As shown in Fig. 3, the three samples are composed of nanosheets. BiOI represents

a sphere-like structure built of nanosheets at a micro-scale (Fig. 3a-c), while the $Bi_7O_9I_3$ and Bi_5O_7I nanosheets assemble irregularly (Fig. 3d-h). The overall thickness of BiOI, $Bi_7O_9I_3$, and Bi_5O_7I is 20 nm, 15 nm, and 40 nm, respectively. The increase of thickness from $Bi_7O_9I_3$ to Bi_5O_7I is owing to the heat treatment process of the phase transformation. Meanwhile, the reducing ratio of iodine in $Bi_7O_9I_3$ nanosheets leads to a decrease in the width of Bi_5O_7I nanoplates.



Fig. 3. SEM/TEM images of (a-c) BiOI, (d & e) Bi₇O₉I₃ and (f-h) Bi₅O₇I catalysts.

Surface chemical compositions and chemical states

The surface compositions and chemical states of the bismuth oxyiodides samples were investigated by X-ray photoelectron spectroscopy (XPS) spectra shown in Fig. 4. The spectra of Bi 4f for three samples are similar; and there are two significant peaks of binding energies (BEs) at about 158.6 and 163.9 eV, which are assigned to Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively, indicating the presence of Bi³⁺ in all samples.^[31] However, the two signals for BiOI slightly shift to higher BEs, which suggests that bismuth is bound with less oxygen that has a stronger electronegativity compared with iodine.^[23-24] For I 3d spectra, two peaks of BEs at about 618.8 and 630.3 eV are assigned to I 3d_{5/2} and I 3d_{3/2}, respectively. Besides, the O 1s spectrum of Bi₅O₇I is deconvoluted into three peaks at 529.35, 529.93 and 530.86 eV, respectively (Fig. 4c). The two peaks at 529.35 and 529.93 eV are ascribed to Bi-O and I-O bonds, respectively,^[31-32] while the other at 530.86 eV is associated with the external hydroxyl groups or water molecules adsorbed on the surface of samples.^[32] According to XPS analysis, the surface chemical compositions of bismuth oxyiodides are determined (Table 1), and they are close to the theoretical values. The surface molar ratio of Bi/I for Bi₅O₇I is 4.38, which is maximum compared with those for BiOI (1.26) and $Bi_7O_9I_3$ (1.85), whereas, the opposite trend in I/O molar ratios of appears. The trends of molar ratios of Bi/I and I/O are in agreement with the Energy Dispersive X-ray Spectrometer (EDS) results. From BiOI through Bi₇O₉I₃ to Bi₅O₇I, the mass contents of bismuth (Bi wt.%) increase from 63.55 to 69.21 to 81.22 wt.%, while I wt.% decrease from 30.64 to 22.69 to 11.29 wt.%; moreover, the atomic contents of Bi (Bi at.%) firstly decrease from 33.45 to 32.58 at.% then increase to 41.03 at.%, while I at.% decrease from 26.56 to 17.59 to 9.37 at.%. However,

atomic contents reflect surface atomic concentration of catalysts, so atomic contents and specific surface areas should be taken into account together to calculate actual amounts of active sites, which is an extremely complex work. Therefore, the chemical compositions of bismuth oxyiodides can influence the local chemical environments of Bi atoms, leading to the differences on the electrocatalytic properties during CO_2RR .



Fig. 4. XPS spectra of (a) Bi 4f, (b) I 3d and (c) O 1s regions of BiOI, Bi₇O₉I₃ and Bi₅O₇I.

| Table 1. Chemical c | compositions and textural | l properties of variou | is bismuth oxyiodides |
|---------------------|---------------------------|------------------------|-----------------------|
| | | | |
| catalysts. | | | |

| Catalyst | Molar ratio of elements | | | \mathbf{D} : $\mathbf{ret} 0/[a]$ | L+ 0/ [8] | D : -+ 0/ [b] | Lat 0/[b] | $\mathbf{S} = (m^2/\alpha)^{[\mathbf{c}]}$ | V (3/->[c] | |
|---|-------------------------|--------------------|---------------------|-------------------------------------|------------------------|----------------------|-------------------------|--|---------------------------------|---|
| | Bi/I ^[a] | I/O ^[a] | Bi/I ^[b] | I/O ^[b] | B1 Wt.% ¹⁻³ | 1 wt.% | B1 at. % ¹⁻¹ | 1 at.% ¹³⁴ | S_{BET} (III /g) ^r | $\mathbf{v}_{\text{total}} (\text{CIII} / g)^{c_2}$ |
| BiOI | 1.26 | 0.66 | 1.36 | 0.24 | 63.55 | 30.64 | 33.45 | 26.56 | 40.59 | 0.32 |
| Bi ₇ O ₉ I ₃ | 1.85 | 0.35 | 2.04 | 0.15 | 69.21 | 22.69 | 32.58 | 17.59 | 51.72 | 0.60 |
| Bi ₅ O ₇ I | 4.38 | 0.19 | 9.11 | 0.01 | 81.22 | 11.26 | 41.03 | 9.37 | 12.67 | 0.20 |

^[a] Measured by XPS spectra; ^[b] Measured by EDS spectra; ^[c] Obtained from nitrogen adsorption-

desorption isotherms.



Fig. 5. (a) FT-IR and (b) Raman spectra of (A) BiOI, (B) Bi₇O₉I₃ and (C) Bi₅O₇I.

FTIR and Raman spectra

FTIR spectra of various bismuth oxyiodides samples are shown in Fig. 5a. In the spectra of BiOI and Bi₇O₉I₃, the peaks at 3359 and 1620 cm⁻¹ are assigned to the stretching vibration and bending vibration of hydroxyl groups due to the adsorption of free water molecules on the surface of samples.^[31,33] The peaks at 771 and 492 cm⁻¹ are ascribed to the asymmetrical stretching vibration and symmetrical A_{2u} -type vibration of Bi-O bond.^[33] Especially, the peak at 771 cm⁻¹ for BiOI and Bi₇O₉I₃ shifts to 610 cm⁻¹ for Bi₅O₇I, which is consistent with previous reports,^[34] on account of the formation of the enhanced chemical interaction of Bi-O bond accompanied with reductive iodine during the transform process from Bi₇O₉I₃ to Bi₅O₇I.

Raman spectra of bismuth oxyiodides samples are shown in Fig. 5b. In the spectra of $Bi_7O_9I_3$ and BiOI, the bands at 95.0 and 147.0 cm⁻¹ are ascribed to the A_{1g} and E_{1g} of Bi-I stretching, respectively.^[35] However, they shift to 123.9 and 183.0 cm⁻¹ for Bi_5O_7I due to that the enhanced interaction between bismuth and iodine brings about an increase in bond energy. Furthermore, peaks at 300-600 cm⁻¹ for Bi_5O_7I result from the

change of Bi-O environment.^[17,31]

Electrocatalytic performances

The electrocatalytic performances over BiOI, Bi₇O₉I₃ and Bi₅O₇I catalysts for CO₂RR were evaluated in a gas-tight two-compartment electrochemical cell with CO₂-saturated 0.5 M KHCO₃ solutions. The linear sweep voltammetry (LSV) curves of all catalysts were conducted in Ar- or CO₂-saturated KHCO₃ solutions, respectively (Fig. 6a). The catalytic activities on BiOI and Bi₅O₇I in the potential region of -1.4 to - 0.4 V vs. RHE are higher than that on Bi₇O₉I₃. As shown in Fig. 6b-d, the constant-potential electrolysis measurements were carried out to evaluate the stability of



Fig. 6. (a) LSV curves in Ar- or CO₂-saturated 0.5 M KHCO₃ solutions over bismuth oxyiodides; current densities at varied applied potentials over (b) Bi₅O₇I (c) BiOI and (d) Bi₇O₉I₃.

catalysts during CO₂RR, which provided the steady-state current at each applied potential. The gas and liquid products of CO₂RR were quantified by gas chromatography (GC) and ¹H nuclear magnetic resonance (NMR). Only H₂, CO and formate are identified, which is consistent with most studies on Bi-based electrocatalysts.^[4,6a,6b,7b]

The FEs of formate, CO, and H₂ are shown in Fig. 7a-b. The main products are formates; the lowest FE of formate (FE_(formate)) is 71.4% at -0.79 V on Bi₇O₉I₃, while the highest value is 89.0% at -0.89 V on Bi₅O₇I. The FEs of CO are as low as 1-2%. H₂ is the major by-product, and its amounts vary from 8% to 27% with the various potentials and catalysts. As displayed in Fig. 7c, the partial current densities of formate $(i_{(formate)})$ on all catalysts elevate with the increasing overpotentials. As shown in Fig. 7b-c, among three samples, Bi₅O₇I exhibits the excellent electrocatalytic properties with FE_(formate) of 89.0% at -0.89 V and $j_{(formate)}$ of 14.9 mA/cm². This consequence is owing to more metal Bi on Bi₅O₇I from Bi³⁺ by electrochemical reduction.^[6b] Although metal Bi is considered as the active site for CO₂RR, there is no positive correlation between the electrocatalytic performances and Bi wt.% among three catalysts. The Bi wt.% of Bi₅O₇I is larger compared with that of BiOI (or Bi₇O₉I₃), which is considered as the major reason for that $FE_{(formate)}$ and $j_{(formate)}$ on Bi₅O₇I are higher than those on BiOI (or Bi₇O₉I₃) at applied potentials. However, the Bi wt.% of BiOI is lower compared with that of Bi₇O₉I₃, but *j*(formate) on BiOI is greater than that on Bi₇O₉I₃ owing to the elevated I wt.% from 22.69 wt.% to 30.64 wt.%. We believe that this phenomenon is due to that iodine can accelerate the

activation of reactants and/or intermediates to enhance catalytic properties.^[36] Therefore, the synergistic effect of bismuth and iodine is responsible for electrocatalytic performances during CO₂ reduction.

In addition, the stability of Bi_5O_7I was evaluated at -0.99 V for 18 h (Fig. 7d). It exhibits a stable cathodic current density of 17-19 mA/cm² and the FEs gradually decline by 7%.



Fig. 7. (a) FEs of formate, CO and H₂ over bismuth oxyiodides; (b) FEs and (c) partial current densities of formate on BiOI, $Bi_7O_9I_3$ and Bi_5O_7I ; (d) long-term stability on Bi_5O_7I at -0.99 V vs. RHE for 18 h.

Conclusions

In summary, three bismuth oxyiodides with varied chemical compositions are

fabricated to evaluate the electrocatalytic performances for CO₂RR. Compared with BiOI and Bi₇O₉I₃ catalysts, Bi₅O₇I exhibits excellent electrocatalytic properties in a wide potential range, reaching a highest FE_(formate) of 89% at -0.89 V vs. RHE with $j_{(formate)}$ of 13.2 mA/cm². The electrocatalytic properties during CO₂RR on bismuth oxyiodides mainly depend on the contents of bismuth that are active sites for generating formate. They are also associated with the contents of iodine that can accelerate the activation of reactants and/or intermediates to enhance catalytic properties. The synergistic effect of bismuth and iodine is responsible for electrocatalytic performances during CO₂ reduction in aqueous solutions. This work provides a new understanding on the influence of the chemical compositions on Bi-based electrocatalysts to promote CO₂ reduction.

Experimental Section

Preparation of bismuth oxyiodides electrocatalysts

Bi₅O₇I nanosheets were prepared according to a previous report by Chang *et al.* with a few modifications.^[31] In a typical procedure, 1.46 g of Bi(NO₃)₃ 5H₂O was dissolved in 40 ml of ethylene glycol, then 0.50 g of KI was added to the above solution. The resulting solution was stirred at room temperature for 0.5 h, and then transferred into a Teflon-lined stainless-steel autoclave. The autoclave was heated to 413 K and maintained at that temperature for 24 h. The solid product was collected by centrifugation, thoroughly washed twice with distilled water and ethanol, dried at 353 K overnight, and finally calcined at 723 K in a tube furnace with an air flow for 4 h.

BiOI nanosheets were synthesized with the same method as Bi_5O_7I except that 0.83 g of KI was added and the absence of the calcination process. $Bi_7O_9I_3$ nanosheets were obtained except the absence of the calcination process.

Characterization

XRD patterns were recorded on a Rigaku SmartLab3KW diffractometer using a Cu K α ($\lambda = 0.154$ nm) radiation source operated at 40 kV and 30 mA. SEM images were taken on a Hitachi S4800 equipped with an EDS at 5 kV. TEM analysis was performed on a JEOL JEM-2100 at 200 kV. XPS spectra were acquired with a PHI 5000 Versa Probe spectrometer with Al Kα radiation (1486.6 eV). The spectra of Bi 4f, I 3d and O 1s were recorded. The charging effect was corrected by adjusting the BE of C 1s to 284.6 eV. Nitrogen adsorption-desorption isotherms were conducted at 77 K on a Quantachrome Autosorb iQ station. Prior to the measurement, the samples were degassed at 393 K for 5 h. The total surface areas were obtained by the Brunauer-Emmett-Teller (BET) equation from the adsorption isotherms at P/P₀ between 0.05 and 0.30, and the total pore volumes were calculated from the adsorption isotherms at P/P_0 = 0.99. The pore size distributions were calculated by density functional theory (DFT) method from the adsorption branches of the isotherms. FTIR spectra were recorded on a Bruker ALPHA spectrometer. Raman spectra were collected using a LabRAM UV Raman microspectrometer with the green line of an argon laser as the excitation source.

Electrochemical measurements

To fabricate the working electrode, 5.0 mg of catalyst and 50 μ L of Nafion solution (5 wt.%) were ultrasonically mixed in 450 μ L of isopropyl alcohol for 30 min to form a homogeneous catalyst ink. Then, the suspension was dropped on a carbon paper (1 cm \times 1 cm) with the catalyst loading of about 1.0 mg/cm². All electrochemical experiments were performed on a Biologic VMP3 potentiostat controlled by EC-Lab®

software in a gas-tight two-compartment electrochemical cell. The cathode compartment and anode compartment contained 25 mL of electrolyte with a ~ 25 mL of headspace and were separated by a proton exchange membrane (Nafion[®] 115). The CO₂-saturated KHCO₃ (0.5 M, pH = 7.2) aqueous solution was used as the electrolyte. A graphite rod electrode and an Ag/AgCl (3.5 M KCl) electrode were used as the counter electrode and reference electrode, respectively. All measured potentials against the Ag/AgCl reference electrode were converted to the RHE reference scale according to the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.205 V + 0.0591 × pH.

The LSV curves were obtained in Ar-saturated or CO₂-saturated 0.5 M KHCO₃ solutions. Before each controlled-potential electrolysis, the electrolyte was purged with a CO₂ flow (99.99%) for at least 30 min. During electrolysis, the CO₂ flow (4.5 mL/min) was injected into the cathodic compartment, from which the effluent gas was analyzed online by a GC (Nanjing Hope, GC-9860-5C). The chromatography was equipped with a divinylbenzene column (Valcoplot HayeSep Q) connected to a flame-ionization detector (FID), and was also equipped with a Molsieve 5A column successively connected in series to a thermal conductivity detector (TCD), a nickel catalytic converter and another FID. The gas products such as CO/CH₄ and hydrocarbons were quantified by two FIDs, and hydrogen was analyzed by TCD. The liquid products were analyzed by ¹H NMR recorded on a Bruker AVANCE AV-300 by extra adding 0.1 mL of DMSO/D₂O (2.80 mmol/L) standard solution to 0.5 mL of the electrolyte.

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Keywords: bismuth oxyiodide • carbon dioxide reduction reaction • electrocatalysis •

nanostructures

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Bismuth oxylodides nanosheets for CO_2 electroreduction to formate with three chemical compositions (Bi₅O₇I, Bi₇O₉I₃ and BiOI) were fabricated via a solvothermal method. Bi₅O₇I exhibits an excellent electrocatalytic performance compared with BiOI and Bi₇O₉I₃, while the partial current densities of formate on BiOI are higher than those on Bi₇O₉I₃. Their electrocatalytic properties are attributed to the synergistic effect of bismuth and iodine.