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Full Length Article

Specific anion effects on copper surface through electrochemical treatment: Enhanced photoelectrochemical CO_2 reduction activity of derived nanostructures induced by chaotropic anions

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ABSTRACT

Copper derivatives are the most prominent CO_2 reduction electrocatalyst. Herein, the metallic copper has been electrochemically treated with some of common ionic salts such as N_3^-, HPO_2^-, S^{2-}, F^-, Cl^-, Br^- and I^- based on the dissolution of a metallic working electrode in an aqueous solution to derive the surface roughness incorporated with nanostructures. Diverse surface morphology can be obtained when the ionic radii of anions are changed. Surface study reveals various roughness shapes based on the size and polarity of the anions, where the ions with higher ionic radii have higher impact on the Cu surface. In comparison, polyatomic oxyanion such as HPO_2^- even with large ionic radii do not have enough strength to create the surface roughness than that of oxygen-free anions with large ionic radii. The photoelectrochemical behavior of the modified surfaces toward CO_2 reduction is studied at a wide potential window in bicarbonate aqueous solution. Based on our investigations, treated surfaces by I^-, Cl^- and S^{2-}give a more surface roughness, while I^- and N_3^- offer higher catalytic activity toward CO_2 reduction due to possible complexing ability of these anions with Cu cations, followed by formation of the co-catalyst semiconductor and facilitate electron transfer. This methodology can be applied to investigate the effect of ions on transition metals along with obtaining different surface morphologies tailored to different applications.

1. Introduction

CO_2 conversion into useful chemicals has attracted considerable attention in recent years as a potential strategy aimed at controlling the green house emission and economic benefits [1]. CO_2 can be practically converted through a various chemical, photochemical or electrochemical transformations [1–8]. Electrochemical systems can be easily operated near room temperature where directly controllable by adjusting the applied electrode potential without a noticeable footprint and chemical feeding [5,6]. Electrochemical reduction combined with photochemistry have taken advantages of both processes which, decrease the energy barrier and enhance the faradaic efficiency [9,10]. In this regard, numerous heterogeneous and homogenous catalysts for photoelectrochemical CO_2 reduction have been designed and a lot of reviews have been published in recent years [3–14].

Semiconductor nanostructures as heterogeneous catalysts have been concerned in the past decades because of their remarkable chemical and physical properties tailored to various fields such as electronic devices, catalysts, sensors and etc. In particular, numerous types of transition metal derivatives have been extensively engaged for the photo/electrocatalytic energy conversions such as CO_2 reduction [3–20]. In this sense, the electrocatalytic activity of Cu is highly representative. Cu is well known as a low-cost eco-friendly element and has been more considered, where the high photoelectrocatalytic activity toward CO_2 reduction reaction at low overpotentials can be achieved on the derived Cu-based nanostructures. Additionally, the useful chemicals such as methanol, ethanol or ethylene could be obtained with low side reactions and catalyst deactivation on Cu-based catalysts [3–8,21–27]. Essentially, pristine Cu is not a photoactive material and such property can be displayed by Cu_xO. Moreover, combination of Cu with other photoactive materials is a resourceful way to enhance the photocatalytic activity toward CO_2 reduction [21,22,26–31]. However, some challenges in terms of catalyst preparation, photoactivity and stability are still persisted.

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Electrochemical synthesis as a highly efficient route encloses many advantages such as simplicity, low synthetic temperature, low cost and environmental friendliness for the fabrication of various nanostructures, such as nanoparticles, nanoclusters, nanowires nanorods, nanosheets, composite nanostructures and so on. The high purity of the nanostructures with possibility of a particular particle-size control have been attained by adjusting the solvent electrolyte and applied potential with or without typical templates [32–34]. However, the template-based electrochemical synthesis can somewhat be complicated and costly compared to template-free methods. On one hand, in a template-free system the derived nanostructures directly synthesized and tightly grafted onto metal or other conductive material supports without utilizing binders, projected for special surface morphologies and catalytic performance. This fixation of nanostructures through direct electrochemical synthesis offers high fraction of active sites with less catalyst detachment from the electrode substrate and avoiding particle agglomeration [35].

Currently, we performed an electrochemical synthesis method for the fabrication of photo/electrochemical energy conversion materials without the assistance of additives and templates in aqueous solution. Exactly, the surface of copper is tuned via electrochemical modification in presence of background electrolyte salts. The ions play a significant role in various fields where, a first example of specific ion interactions is the Hofmeister effect [36] in the field of protein precipitation. Thereafter, it was effectively applied to other fields of biology such as colloidal dispersion of macromolecules [37]. Different anions or cations of electrolyte salt have been introduced as dopant materials in the electrochemical synthesis process of doped-organic polymers [38]. Additionally, the corrosive power of different ionic species in conception of mesoporous solids [39,40], specific impact on synthesis, morphology, activity and electrical property of inorganic nanoparticles [35,39,41,42] have been discussed for a very long time. In an aqueous electrolyte solution, solvation of anions are more considerable than that of cations since the small H atoms of water molecules have the superficial hydrogen bond with anions, while the O atom has interacted with cations [40]. Furthermore, the anions have exhibited higher tendency to accumulate at the salt-aqueous solution/air interface than that of cations because of their higher size and polarizability [43]. However the interaction of anions on meal surface in an electrode/aqueous interface through an electroplating process has not been discussed anymore. In our previous work, we investigated the effect of an organosulfur compound on the metallic copper electrode in a solution containing KCl electrolyte to prepare a photoelectrocatalyst designed for CO_2 reduction reaction [44]. Now, taking into account of anions/metal surface interactions, the impact of some typical anions on the construction of surface roughness along with various shapes of nanostructures at Cu metal is studied and the resulted modified surface is applied for photoelcrocatalytic CO_2 reduction.

2. Experimental section

2.1. Materials and instruments

All sodium or potassium ionic salts containing F^-, Cl^-, Br^-, I^-, S^{2-} N_3^-, HPO_2^- and bicarbonate were used with analytical grade. Cu disc with purity of >95% was purchased from Kaveh cupper industrial, Iran. CO_2 with purity of ~99.9% was prepared from medical and industrial gases production of Saman Co., Iran. It should be mentioned that we did not find a significant difference in catalytic property of derived Cu by replacing K^+ with Na^+ and vice versa. Therefore, in this work we just consider the impact of anions.

The XRD analysis of the samples was performed with a STOE powder diffractometer (Germany) using Ni filtered CuKα (k = 1.5 4056 Å). AFM images and UV-Vis spectra were taken by NT-MDT (Russia) and SPECORD 250 of Analytikjena (Germany), respectively. Scanning electron microscopy (SEM) images and elemental analysis were obtained with a MIRA3 TESCAN HV: 20.0 kV. The electrochemical synthesis and studies including cyclic voltammetry (CV) and choronoamperometry were carried out using a μAUTOLAB modular electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PGSTAT type III driven by GPES software in conjunction with a conventional three-electrode system in an electrochemical cell (an Ag/AgCl/3 M KCl and platinum rod as reference and counter electrode, respectively). All experiments were done at room temperature (~298 ± 3 K).

2.2. CO_2 reduction procedure

Electrochemical and photoelectrochemical study of CO_2 reduction reaction were taken by a three electrode system in a conventional electrochemical cell as described above, containing 4 ml 0.25 M $NaHCO_3$ aqueous solution. Before of each experiment, the electrolyte was carefully purged by CO_2 gas for 5 min to obtain the CO_2 saturated solution. During the electrochemical investigation, CO_2 atmosphere was kept above the solution with pressure of 0.2 bar. The visible light irradiation was applied by a 1 watt LED lamp located in front of the working electrode behind the glassy cell.

2.3. Surface modification of copper through electrochemical treatment

A copper disc with diameter of 1 cm was used as working electrode to obtain the roughness surface. CV was performed at Cu(0)/Cu(1) redox potential window (0.1 to −0.6 V vs. Ag/AgCl, 0.7 to 0.0 V vs RHE) containing 1 M of F^-, Cl^-, Br^-, I^-, S^{2-} N_3^- or HPO_2^- as supporting electrolyte in an aqueous solution. After 50 CV cycles the treated Cu discs were rinsed with deionized water and calcinated by ramping up the temperature from ambient to 300 °C with 15 °C per min and then kept for another 15 min at 300 °C. After that the resulted roughness surface were performed for photoelectrochemical CO_2 reduction in the 0.25 sodium bicarbonate aqueous solution. After annealing the modified surface was studied bay XRD, AFM, EDX and SEM.

3. Results and discussion

3.1. Characterization

Erosion of Cu surface effected by different ionic salts was powered by CV at Cu(0)/Cu(1) redox potential window in the presence of 1 M aqueous solution of various ionic salts. With increasing the cycle numbers, Cu(0) at outer layer of electrode is oxidized to Cu (1), supported by aqueous electrolyte. Fig. 1 shows the XRD patterns of different Cu_xO catalysts. The sharp diffraction peaks at 2θ of 43.35° and 50.43° mainly ascribed as Cu(0) substrate. Cu_2O diffraction peaks are detected at 36.24°, 41.78°, 61.51° and 74.57°. The electroplated surfaces in the presence of Br^-, I^-, S^{2-} and HPO_2^- display the small diffraction peaks at 2θ of 38.92° and 48.23°, signify the CuO diffraction peaks. Other diffraction peaks for modified surfaces can be seen, which most prominent of them are listed as follow: in the presence of Br^- at 29.95° defined as CuBr [45], I^-: 25.7°, 35.8°, 67.6°, 77.7° defined as CuI [46], N_3^-: 49.32°, 56.45°, 67.94° defined as Cu_3N [47] and S^{2-}: 25.8°, 27.2°, 35.4°, 37.9°, 46.5°, 66.8°, 73.9° demarcated as Cu_2S [44,48]. The comparison of ionic radii of these anions [49] and their atomic percentage (obtained from EDX analysis) at the surface of Cu disc electrode