Recycling electroplating sludge to produce sustainable electrocatalysts for the efficient conversion of carbon dioxide in a microbial electrolysis cell

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ABSTRACT

Electrochemical reduction is one of the most promising methods for converting carbon dioxide (CO_2) into valuable chemicals, but its disadvantages include its low efficiency and need for a high electrode overpotential. In this study, a novel catalyst derived from thermally treated electroplating sludge (TES) was investigated for use in the electrochemical reduction of CO_2 by means of full utilization of the chemical features of electroplating sludge. This new catalyst can reduce CO_2 with a peak potential of −0.3 V (versus SCE), as measured using a linear sweep voltammogram, suggesting its' good electrocatalytic activity. Furthermore, this catalyst is feasible for use in converting CO_2 in a microbial electrolysis cell; the main products were methane, ethylene, carbon monoxide and acetate with faraday efficiencies of 37.3%, 25.9%, 7.8% and 6.8% at an external potential of 0.6 V, respectively. The catalytic performance of the TES-based catalyst is much better than that of catalysts derived from municipal and dyeing sewage sludge. Electrokinetic data and electrochemical in situ infrared spectra reveal that the notable reactivity for CO_2 reduction may arise from a competition between the slow combination of pairs of $CO_2^{\cdot-}$ ions and the fast kinetic activation toward protonation on the metal or metal oxide surface of the TES. This study presents a new approach to recycling solid waste to produce an inexpensive catalyst that performs CO_2 conversion well.

1. Introduction

Carbon dioxide (CO_2), a notorious greenhouse gas, is known to be increasingly emitted into the atmosphere, where it causes global warming. Reducing atmospheric concentration of CO_2 has therefore become a critical issue [1–3]. Several approaches are currently used to reduce CO_2, such as carbon capture and sequestration, chemical usage, photoelectrochemical, thermochemical, electrochemical and biochemical reduction [4–8]. Of these approaches, electrochemical reduction is considered a promising method of recycling carbon not only because it can provide a compact, continuous conversion system near power plants and industrial factories [9]. However, as many researchers have found, a high overpotential is required for the electrochemical reduction of CO_2 [9,10]. Therefore, it is very important to develop catalysts that are capable of reducing CO_2 at low overpotentials over long periods of time [11]. Most metals, including Cu, Ni, Fe, Pb, Sn and their complexes, are able to function as catalysts in electrochemical systems for CO_2 reduction [12–16]. For example, Kuhl and Li et al. demonstrated that polycrystalline Cu is one of the best catalysts available for reducing CO_2 directly to the

hydrocarbons methane and ethylene [10,11]. However, the rising cost of metals is the main obstacle to their large-scale practical application.

Electroplating sludge (ES) is unwanted heavy-metal waste from the treatment of electroplating wastewaters, which could pollute the environment if they are not disposed properly. The features of ES include a high level of enrichment with organic matter and metals (Fe, Cr, Cu, Ni, Pb, Mn, Sn, Ag etc.) in a variety of forms, such as mixed oxides, hydroxides, sulfates, silicates and phosphates, which have the potential to be precursors to advanced catalysts [17,18]. Previous studies found that ES can be converted into a catalyst for propane oxidation by mixing it with red mud [19,20]. Recently, Zhang et al. demonstrated that ES alone can be thermally converted into a mixture of various metals, metal oxides and carbons that effectively causes the decomposition of the greenhouse gas SF_6 and the selective catalytic reduction of NO [21,22]. The catalytic activity of the resultant ES-based catalysts was attributed to their enriched metal and metal oxide contents; these species are also potential active sites for the electrochemical reduction of CO_2 [5,10]. Therefore, it is our belief that ES could be a potential catalyst for the electrochemical reduction of CO_2 due to its enrichment with various metal species.

The aims of this study were to examine the feasibility and efficiency of using thermally treated ES to convert CO_2 by means of electrochemical reduction. To reveal the possible active sites of the resultant catalyst, the morphology, structure, and electrochemical behavior of the catalyst were characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and cyclic voltammetry (CV). Furthermore, the electrochemical reduction of CO_2 was catalyzed by ES-derived catalysts for the first time in a bioelectrochemical system known as a microbial electrolysis cell (MEC). In a MEC, because of the potential generated by organic matter at bioanodes, less power is required for the cathodic reactions to occur than is required in a common electrolytic cell, which makes MECs a novel and sustainable technology that has been proposed for use in the renewable and sustainable production of valuable chemicals from waste [23–25]. In this study, the feasibility and efficiency of an ES-based catalyst for the reduction of CO_2 were examined in such a system, and the results were compared with those of catalysts derived from municipal and dyeing sludge.

2. Experimental

2.1. Catalyst Preparation

The electroplating sludge (ES) used in this study was supplied by Guangdong Jiangmen Electroplating Co., Ltd. Before use, the ES was first dried at 100 °C for 24 h; then, the dried sludge was pyrolyzed at 900 °C for 2 h under nitrogen. After cooling, the material was immersed in a 1 mol/L HCl solution and stirred magnetically for approximately 24 h; then, the material was extensively washed with water, filtered and dried at 105 °C, and milled until the particle size was between 0.10 to 0.15 mm. The resultant thermally treated ES was termed TES. For comparison, municipal sludge (from the Guangzhou Liede wastewater treatment plant) and dyeing sludge (collected from local company) were also treated following this procedure to produce thermally treated municipal sludge (TMS) and dyeing sludge (TDS), respectively.

2.2. MEC System

The MEC used in this study was composed of 100 mL two chambers separated by a proton exchange membrane (PEM, Nafion

117, DuPont) (see Fig. S1 in the supporting information). A carbon brush was used as the anode, and carbon cloth ($6.0 \times 7.0 \times 0.1$ cm) coated with 1 mg/cm^2 of a sludge-based catalyst was used as the cathode. The catalyst was coated by mixing 50 mg TES, TMS or TDS with 30 μL water, 5 μL Nafion solutions (5% wt Sigma-Aldrich) and 1 mL ethanol, and the mixture was ultrasonicated for approximately 5 minutes to prepare a homogenous catalyst ink mixture. The obtained slurry was painted on two sides of carbon cloth using a brush and dried overnight at room temperature. Prior to the MEC operation, the carbon brush bioanode was inoculated in a microbial fuel cell (MFC). The MFC reactors were composed of 100 mL two chambers separated by a proton exchange membrane. Carbon brushes were served as anodes, carbon cloth with Pt/C catalyst was served as cathode, and a 1000 Ω external resistance was loaded between the anode and cathode. The reactors were initially inoculated with 20 mL of aerobic activated sludge (Liede wastewater treatment plant, Guangzhou, China), and fed with 80 mL of sodium acetate (1000 mg/L) medium solution, the cathode fed with 0.1 mol/L phosphate buffer and purged with air. The anode medium solution contained KH_2PO_4 (13.6 g/L), NaOH (2.32 g/L), NH_4Cl (0.31 g/L), NaCl (1.0 g/L), a vitamin stock solution (10 mL/L) and a mineral stock solution (10 mL/L). When the stable voltage output ($\sim$500 mV) was achieved from the MFC (Fig. S2), the bioanode was shifted to a MEC system. The MEC system was connected in series with a 30 Ω resistor and an external DC power supply (BEST, PS-1502DD). In the MEC, the anode was filled with 1 g/L sodium acetate solution in 50 mM phosphate buffer containing 10 mL/L mineral solution and 10 mL/L vitamin solution, and the cathode was filled with a CO_2-saturated $KHCO_3$ (0.1 mol/L, pH = 6.8) solution, where a final HCO_3^- concentration of 0.124 mol/L was obtained due to the continuous CO_2 bubbling. The voltage across the resistor was continuously monitored using a 16-channel voltage collection instrument (AD8223, China). All of the tests were conducted in triplicate, and the mean values are presented here.

2.3. Analytical Techniques

X-ray fluorescence (XRF, AxiosmAX Petro, PANalytical Corp., Almelo, the Netherlands) and elemental analysis (Elementar, vario EL cube) were used to identify the major elements in the sludge (w/w %).A Fourier transform infrared spectrometer (FTIR, TENSOR 27) was used to analyze the functional groups of the sludge-based catalysts. XRD patterns of the sludge-based catalysts were recorded using an X-ray diffractometer (XRD, model X'Pert-PRO, PANalytical Corp., Almelo, the Netherlands) with a Cu Kα target (λ = 0.154056 nm). The specific surface areas of the sludge-based catalysts were measured using the Brunauer-Emmett-Teller (BET) method. The nitrogen (N_2) adsorption isotherm was measured at 77 K using a sorptometer (model 1800, Carlo Erba Instruments, Italy). The morphology and structure were characterized using a field-emission scanning electron microscope (FE-SEM, model S-4800, Hitachi, Ltd., Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 instrument (Thermo Fisher Scientific) with 150 W monochromatic Al Kα radiations (1486.69 eV). The reduction product of CO_2 was analyzed in a C18 column (Welch Materials, Inc.) using high-performance liquid chromatography (Agilent 1260 Infinity LC) at 213 nm. The gas products of CO_2 reduction were analyzed by Refinery gas GC (Agilent, 7890A) with FID and double TCD detectors. Five columns were used for gas separation: Agilent 3 ft Q, Agilent 6 ft 5A, Agilent 0.5 m Q, Agilent 6 ft Q+ 8 ft 5A and J&W 113-4362, and external standard method calibration curves were used for the quantitative analysis. Electrochemical in situ FTIR spectroscopy was performed using a Nexus 6700 spectrometer (Thermo, Nicolet 6700) equipped with a liquid nitrogen-cooled