Two novel Pb(II) coordination polymers (CPs) based on 4-(4-oxopyridin-1(4H)-yl) and 3-(4-oxopyridin-1(4H)-yl) phthalic acid: Band gaps, structures, and their photoelectrocatalytic properties in CO2-saturated system

Zhi Shuo Yan[a], Ji Ying Long[a], Yun Gong[a,*], Jian Hua Lin[a,b,**]

[a] Department of Applied Chemistry, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, PR China
[b] State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

ABSTRACT

Based on 4-(4-oxopyridin-1(4H)-yl) phthalic acid (**H2L1**) and 3-(4-oxopyridin-1(4H)-yl) phthalic acid (**H2L2**), two novel Pb(II) coordination polymers (CPs) formulated as [Pb4Cl4·(L1)2·H2O]n (CP **1**), [Pb3Cl4·L2·H2O]n (CP **2**) were solvothermally synthesized and characterized by single-crystal X-ray diffraction. The two novel Pb(II) CPs (CPs **1** and **2**) possessed different structures. Density functional theory (DFT) calculations revealed the two CPs had different band structures yet the characteristic of semiconductors in common. Their valence band (VB) and conduction band (CB) positions were determined by Mott-Schottky and UV–visible diffuse reflectance analyses. The photoelectrocatalytic performance of the two CPs towards CO2 reduction were tested by photocurrent responses at various applied potentials. And the $E = -1.4\,V$ vs SCE ($-0.74\,V$ vs NHE) was selected as the required potential according to the regulation of photocurrent responses at various tested potentials in CO2-saturated system. The photoelectrocatalytic performance of CP **2** was superior to that of CP **1** owing to the well-matched CB position of CP **2** and CO2 reduction potentials at the required potential of $-1.4\,V$ vs SCE ($-0.74\,V$ vs NHE). In addition, the photoelectrolytic experiment were performed 1 h in the CO2-saturated 0.2 M Na2SO4 solution at the required potential of $-1.4\,V$ vs SCE ($-0.74\,V$ vs NHE) with and without illumination, and we initially demonstrated the influence of visible light in the CO2-saturated photoelectrocatalytic measurement system and the reason of stability in 1 h chronoamperometry.

1. Introduction

Hydrocarbon fuels, as traditional form of energy, are widely used in our human society due to their availability, high energy density and convenient transportation. With the continually increased energy demand up to 2050, the worldwide energy consumption per hour will reach up to 1.1×10^{18} kJ, more than 80% of which is obtained from natural fossil resources [1]. If this energy consumption pattern is still continuous, it will giving rise to serious problems about the global climatic change and future energy shortage [2]. Importantly, the key point is that this increased demand for the limited present natural resources is unsatisfied, and the accompanied crisis is the large quantities of CO2 generated from the fossil consumption as well as released to our atmosphere, which can result in the large-scale global warming and the environment-unstability [3]. Therefore, in order to meet both the environmental and energy needs, developing new approaches to recycle CO2 in a sustainable process is currently an active research topic [4]. However, catalyzing CO2 still remains challenges, because CO2 is a stable molecule possessing the structure of linear-configured two double bonds between carbon and oxygen atoms, in which the carbon-oxygen double bond energy is $750\,kJ\,mol^{-1}$ ($E_{C^=O} = 750\,kJ\,mol^{-1}$), its conversion into useful chemicals especially having additional values without any catalyst and input energy is not possible owing to its high kinetic and thermodynamic stability itself [5]. In the present research state, three mainstream methods can achieve the aim to catalyzing CO2: (i) photocatalytic CO2 reduction, (ii) electrocatalytic CO2 reduction, and (iii) photoelectrocatalytic CO2 reduction which simultaneously has the advantages of both photocatalysis and electrocatalysis [6].

For photocatalytic CO_2 reduction (also denoted as artificial photosynthesis), it consists of two reactions: (i) to extract electrons from water through water oxidation, (ii) to generate carbonaceous radicals using electrons generated from water oxidation for CO_2 reduction. This approach is considered advanced in the relative mild conditions, i.e., it can occurs at room temperature and pressure without extra artificial energy input [7]. In artificial photosynthesis, the catalysts should have an appropriate conduction band (CB) for the reduction half-reaction and a valence band (VB) for the oxidation half-reaction, where the electrons are excited from the VB to CB with an equal amount of holes generated in the VB. Such electron-hole pairs separate from each other and transport to the catalyst surface for surface catalytic redox reaction, i.e., reduction of CO_2 into hydrocarbon fuels such as methanol (CH_3OH), carbon monoxide (CO) and methane (CH_4) or useful chemicals such as formic acid (HCOOH), formaldehyde (HCHO), and oxidation of sacrificial agent or H_2O [8]. Moreover, the photo-induced electron-hole pairs are excited by absorbing a flux of photos with energy higher than the band gap of the catalyst under visible light. However, if band gap of the catalyst is not suitable for visible light absorption, i.e., if band gap of the catalyst is higher than light spectrum energy (~1.5 eV), few photo-induced electron-hole pairs can be produced, on the contrary, if band gap of the catalyst is lower than light spectrum energy (~1.5 eV), electron-hole recombination can not be easily suppressed [9]. Consequently, proper band gap and appropriate CB edge of catalysts are prerequisites for CO_2 reduction.

With respect to photocatalytic CO_2 reduction, the electrochemical catalysis have several advantages: (i) the process can be controlled by adjusting potentials and reaction time at room temperature and pressure, (ii) the electrolytes can be recycled, (iii) the electrochemical reaction can be magnified to large-scale chemical industry production [10]. However, in the current research state, the electrochemical reaction consumes vast energy and the energy utilization efficiency is very low, In addition, the product is usually not pure species but mixed components [11]. Theoretically, the CO_2 electroreduction system requires a thermodynamic potential of approximately −0.25 to −0.52 V (vs NHE at pH 7) for the conversion into various hydrocarbons. [12]

Photoelectrocatalysis is considered as an integration of photocatalysis and electrocatalysis, on the one hand, the applied potential can facilitate the separation of photo-induced carriers in the photocatalytic process, on the other hand, extra light irradiation can reduce the overpotential in the electronic process. In this configuration, the catalysts serve as not only the electrocatalysts but also the light harvesting materials. In fact, the conversion of solar and electricity to chemical energy is complicated because multiple products can be formed in the field of CO_2 reduction [13]. All in all, the photoelectrocatalytic mechanism is still under investigation.

For CO_2 reduction itself, it is well-known that CO_2 reduction is a multi-step process involving both activation and dissociation of CO_2. The key initial step is the activation by the given catalysts [14]. Notably, the threshold energy for one electron-induced dissociation of CO_2 to form a CO_2^- radical needs a very negative redox potential, i.e., $CO_2 + e^- \rightarrow CO_2^-$ ($E^0{}_{redox} = -1.9$ V vs NHE) [15]. In fact, a multi-electron process is more available due to low energy requirement per electron. Generally, the CO_2 reduction includes two-, six-, and eight- electron reduction pathways in aqueous and non-aqueous phases with different chemicals/CO_2 potentials, forming into CO, HCOOH, CH_3OH, and CH_4. It is even more challenging in kinetics and the mechanism is still complicated [16].

In order to meet the requirements for CO_2 reduction, many studies have been conducted to find suitable alternatives, for example, semiconductors, proteins, metal complexes, organic materials, transition metals and coordination polymers. Among these candidates, Coordination polymers (CPs), as one group of Metal-organic frameworks (MOFs), are hybrid materials that consist of secondary building units (SBUs) such as metal ion clusters or organic linkers, which have drawn great interests due to their rational design of pore sizes, structural diversity, and various functionality. And CPs can be applied in many fields such as gas adsorption/desorption, catalysis, drug delivery, host-guest chemistry, and supramolecular chemistry and so on [17]. The CPs, which possess the SBUs of metal ion clusters accepting electrons from the organic linker under light irradiation, can provide active sites for CO_2 reduction. Moreover, if the metal ion clusters of CPs have the d^{1o} mode, the performance of their CO_2 reduction will be relative good due to their inherent catalytic activity towards CO_2 [18].

In this work, we successfully synthesized two novel Pb(II) CPs formulated as $[Pb_4Cl_4·(L_1)_2·H_2O]_n$ (CP **1**), $[Pb_3Cl_4·L_2·H_2O]_n$ (CP **2**) based on 4-(4-oxopyridin-1(4H)-yl) phthalic acid (**H₂L₁**) and 3-(4-oxopyridin-1(4H)-yl) phthalic acid (**H₂L₂**), respectively. The UV–vis absorption and diffuse reflectance spectra, the electrochemical behaviors have been investigated. Density functional theory (DFT) calculations reveal both CPs **1** and **2** possess the characteristic of semiconductors. And their VB and CB positions are determined by Mott-Schottky and UV–visible diffuse reflectance analyses.

In the aspect of CO_2 reduction, for the first time, we prepared the working electrode of the two novel Pb(II) CPs, which were measured in CO_2-saturated 0.2 M Na_2SO_4 solution, and explored the photoelectrocatalytic performance of the two CPs towards CO_2 reduction tested by photocurrent responses at various applied potentials. The $E = -1.4$ V vs SCE (−0.74 V vs NHE) was selected as the required potential. The photoelectrocatalytic performance of CP **2** was superior to that of CP **1** due to the well-matched CB position of CP **2** and CO_2 reduction potentials at the required potential of −1.4 V vs SCE (−0.74 V vs NHE). In addition, the photoelectrolytic experiment were performed 1 h in the CO_2-saturated 0.2 M Na_2SO_4 solution at the required potential of −1.4 V vs SCE (−0.74 V vs NHE) under illumination and non-illumination, and we initially demonstrated the influence of visible light in the CO_2-saturated photoelectrocatalytic measurement.

2. Experimental sections

2.1. General considerations

All the staring chemicals and solvents were directly purchased from commercial resources and without further purification. The melting point was determined using an uncorrected X-4 melting point apparatus of Beijing Kaifu Company. Elemental analyses (C, H and N) were performed with a Vario MICRO CHONS II Element Analyzer. Infrared spectra were recorded with KBr pellets in the range 4000–400 cm^{-1} on a Nicolet iS50 FT-IR spectrometer. Powder X-ray diffraction (PXRD) data were collected on Tongda TD-3500 diffractometer using Cu Kα radiation (λ = 0.154 nm). Thermogravimetric analyses (TGA) were implemented on a NETZSCHSTA 449 C instrument from room temperature to 750 ℃ under the steady flowing of N_2 with a heating rate of 10 ℃ min^{-1}. UV–vis spectra were measured on a HITACHI U-4100 UV–vis spectro-photometer. The morphologies of the samples were observed by scanning electron microscopy (SEM, JSM-7600F, JEOL) under different magnification of top and cross-sectional view.

2.2. Computational methods for theoretical band structure

The band structures and orbital calculations of CPs **1** and **2** were carried out through the CASTEP program in the Materials Studio 7.0, which were supported by density functional theory (DFT). And two-step methodology was used for the calculation. The first step was to optimize their crystal structures. And the second step was to calculate the band structures and density of states (DOS) for the optimized structures based on their crystallographic data [19]. All the calculations were done using the GGA-PBE functional and ultrasoft pseudo-potentials based on reciprocal space with a 500 eV of kinetic energy cutoff and 1.0×10^{-5} eV/atom of SCF tolerance thresholds. The sets of