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ORIGINAL ARTICLE

Electro-reduction of CO_2 onto ZnO–Cu nano composite catalyst

Srijita Basumallick[1]

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Abstract
Present communication reports a simple method of preparation of ZnO–Cu nano composite, a reverse water gas shift (RWGS) type low-cost catalyst for electro-catalytic reduction of CO_2. The composite catalyst has been characterized by EDX, SEM, EDX atom mapping and XRD. The observed distinct reduction peaks at − 0.7 V and − 1.1 V versus Ag/AgCl in cyclo voltammogram (CV) are explained by cathodic reduction of CO_2 to CO preferably onto ZnO surface and electro-reduction of CO/CO_2 onto Cu surface. This electro-reduction peak at low over-potential indicates formation of small molecular organic fuels like methane and methanol onto catalyst surface. A signature of methanol oxidation peak at 0.79 V versus Ag/AgCl is detected in the anodic scan of the CV at 5th cycle. The catalytic stability has been explained from chrono-amperometric study.

Keywords CO_2 reduction · ZnO–Cu composite catalyst · Reverse water gas shift reaction

Introduction

Large-scale reduction of CO_2 to fuel is one of the promising routes of restoring CO_2 balance and meeting energy need (Robert 2016). Reduction of CO_2 to alcohol or gaseous hydrocarbon fuel is neither thermodynamically nor kinetically a favourable process. Thermodynamic barrier is overcome by use of solar energy (Photo-reduction) or by applying electrical energy (electro-reduction). But to overcome kinetic barrier, development of an efficient photo/electro-catalyst for CO_2 reduction is required. This is a major challenge to arrive at the goal. It is known ZnO–Cu is a cost-effective industrial catalyst (Fujita et al. 1992) for chemical reduction of CO_2 to methanol. But this requires a high temperature. Thus it is not recommended as an energy-efficient method.

Again, in spite of exhaustive studies on the mechanism of CO_2 reduction by reverse water gas shift (RWGS) type catalyst, the role of ZnO in this catalyst is not well understood (Jianga et al. 2018; Christina 2014).

Among the most studied electro-catalysts/photo catalysts for reduction of CO_2, the Cu-based materials (Hirunsit et al. 2015; Basumallick and Santra 2014), particularly Cu(I) oxide, has been studied exhaustively as a direct solar energy-driven photo-catalyst. Photo catalytic reduction of CO_2 to formaldehyde and methanol using Cu_2O was first studied by Tennakone et al. (1989). Exhaustive experimental works on electro/photo-reduction of CO_2 by Hori (2008), Andrews et al. (2013) and Yano et al. (2004) using Cu-based catalysts clearly established that such reduction, particularly reduction products, mainly depend on pH of the solution. This may be owing to the proton assisted (Bonin et al. 2014) electronation reaction.

We have studied (Basumallick and Santra 2014) electro-reduction of CO_2 using depolymerized chitosan-coated Cu_2O nano catalyst and noted methanol formation. It has been also used as photo-reduction (An et al. 2014; Basumallick 2016; Richardson et al. 2011) of CO_2 despite its instability and conversion to CuO.

ZnO is a low-cost material and chemically and photochemically stable. It is also used in combination with Cu as an industrial catalyst (Fujita et al. 1992; Le 2009) for reduction of CO_2 to methanol (Le 2009; Hirunsit et al. 2015)

In this research, we report an easy method of preparation of ZnO–Cu nano composite catalyst, their characterization by EDS, SEM, EDX atom mapping and XRD. We have studied electro-reduction of CO_2 by cyclo-voltammetric (CV) and chrono-amperometric methods with a view to understand the role of different components of the composite catalyst.

✉ Srijita Basumallick
srijitabasumallick@gmail.com

[1] Department of Chemistry, Asutosh College Under Calcutta University, 92, SP Mukherjee Road, Kolkata 700026, India

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Conducting Polymer Based Sensors for Detection and Estimation of CO_2

Srijita Basumallick*
Assistant Professor, Department of Chemistry, Asutosh College under Calcutta University, 92, S P Mukherjee Rd. Kolkata, India

Abstract

CO_2 is a greenhouse gas causing global warming, therefore, its detection and estimation by some smart sensors are extremely important. This review paper made an attempt to present current state of affairs on development of conducting polymer based smart sensors for detection and estimation of CO_2. This is followed by a discussion on merits and demerits of spectroscopic techniques for sensing CO_2. Applications of conducting polymer particularly, poly aniline (PANI), sulfonated poly aniline (SPANI) and poly pyrrole (PPY) and their nano composites with metal oxides in CO_2 sensing have been presented. Mechanisms of CO_2 sensing by these polymers and their composites have been discussed.

Keywords: *Conducting polymer sensors; estimation and detection of CO_2, green house gas, smart sensors.*

****Author for Correspondence*** E-mail: srijitabasumallick@gmail.com

INTRODUCTION

Detection and estimation of CO_2 by an user friendly and low cost sensor is one of the challenging problems of the day. Basically, materials or composites with selectivity towards CO_2 are relatively a few. This may be owing to the almost chemical inertness of CO_2 at ambient temperature.

As a greenhouse gas, it contributes significantly towards global warming [1-3]. During the recent time CO_2 balance [4, 5] of nature has been greatly disturbed, because of rapid urbanization and industrialization. Natural photosynthetic path of CO_2 utilization is not able to restore CO_2 balance [4, 5] of environment. Therefore, monitoring of CO_2 level at different CO_2 emission sources should be made on a regular basis. Presently, CO_2 is precisely monitored by spectroscopic techniques [6-8] but these methods, particularly, IR technique often leads to cross sensing with small organic molecules with –C=O groups and these methods are cumbersome and costly. Again, transitional metal oxide based sensors for detection of CO_2 work well only at high temperature. Sensors based on conducting polymer [9-12] are relatively low cost and operate at room temperature. In spite of limited R&D works on this specific topic, considering its importance an attempt has been made to present a systematic review on the subject.

General Background of Polymer Sensors

CO_2 is chemically almost inactive and behaves like a hard base and prone to accept proton forming carbonic acid, the later reacts with basic centre of a polymer segment. Therefore, polymer based CO_2 sensors generally contain basic nitrogen centre in its skeleton, like poly aniline. Hybrid organic inorganic polymeric materials like alkyl amine functionalized polysilsesquioxanes has been reported [13] as chemicaptive sensor which operates at low temperatures ranging from 15-50°C. During exposure to CO_2, the capacitance of the capacitor with such polymeric material changes [13]. Similar sensing materials are hetero polysiloxanes with 3-amino propyl tri methoxysilne (PTMS) [14, 15]. These sensors work as chemi-capacitive sensors with sensing limit 400-4000 ppm. But presence of moisture interfere sensing activity of these sensors. Therefore, hydrophobic groups are often blended with amino groups of these sensors. It

Chapter 7

Pullulan-Degrading Enzymes and Their Biochemical Features

Srijita Basumallick

Department of Chemistry, Asutosh College under Calcutta University, 92, S P Mukherjee Road, Kolkata 700026, India
srijitabasumallick@gmail.com

Pullulan is a highly ordered branched polysaccharide comprising linear chains of D-glucopyranosyl units, which arrange in between one (1–6) ϱ D link and two (1–4) ϱ D links. Pullulan-degrading enzymes (PDEs), known as pullulanase, break the polymer to smaller oligomers, hydrolyzing glycoside linkages. In this chapter, we discuss different types of pullulanase, their origin (plants/animals/fungi/bacteria), and some common biochemical features with special reference to substrate-binding domains. In addition to these, basic enzymatic features such as substrate specificity and product analysis have also been presented. An attempt has been made to present different mechanisms proposed from time to time on enzymatic degradation of pullulan. Applications of enzymatic hydrolysis of pullulan in the industry for manufacturing maltotriose and glucose have also been discussed.

7.1 Introduction

Pullulan is a highly ordered branched polysaccharide [1,2,3,4 and 5] comprising linear chains of D-glucopyranosyl units arranged in between one (1–6) ϱ D link and two (1–4) ϱ D links (Fig. 7.1). Thus, pullulan-degrading enzymes (PDEs) have the ability [6,7 and 8] to hydrolyze these glyconidic linkages. Enzyme pullulanase (pullulan α-glucanohydrolase; enzyme EC.3.2.1.41) is an extracellular carbohydrase, which was first isolated by Bender and Wallenfels [9] in 1966 from the mesophilic organism

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Alginates in Drug Delivery

Srijita Basumallick

Asutosh College under Calcutta University 92, Kolkata, India

Abstract

Alginate is a biocompatible biopolymer and is widely used as a drug delivery vehicle in different forms. In this chapter, we will discuss the applications of different cross-linked networks of alginates, their microspheres, and hydrogel in relation to drug encapsulation and delivery processes with a brief introduction of chemistry and pharmaceutical chemistry of alginates. Biomedical applications of alginate–chitosan composites with special reference to their unique hydrogel-forming ability have been discussed. In conclusion, we have highlighted the promising features of alginates as an ideal biomaterial for drug delivery.

Keywords: Biocompatible, alginate–chitosan composites, microspheres, hydrogels, cross-linked alginates

8.1 Introduction

Drug delivery materials are selected and designed to overcome the defensive mechanism of our immune system, which resists introduction of foreign materials within its border. Thus, biocompatible materials and materials with natural origin-fulfilling criteria [1–4] of an ideal delivery system should be the first choice. Bio-friendly and biodegradable materials with drug-encapsulating and -release properties are a basic requirement for this purpose. Targeted delivery and controlled release are the most important criteria for designing material for drug delivery. A drug designer addresses many of these criteria in selecting an ideal material for drug delivery. In spite of hundreds of challenges like nature of drugs, their doses, and side effects, delivery materials are selected to minimize the interactions with

Email: srijitabasumallick@gmail.com

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