







Electrocatalytic and catalytic CO₂ hydrogenation on ZnO/g-C₃N₄ hybrid nanoelectrodes

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Highlights

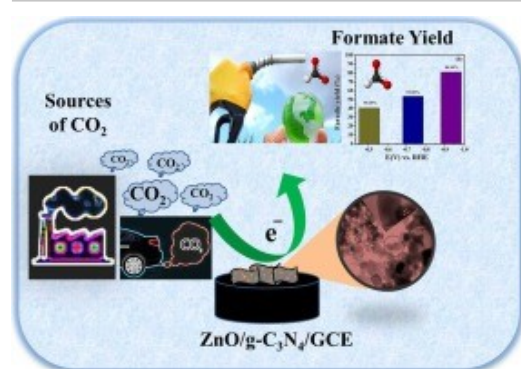
- The ZnO/g-C₃N₄ hybrid fabricated by synthesis of g-C₃N₄ followed by anchoring of ZnO NPs.
- Active N-centres from g-C₃N₄ and non-stoichiometric ZnO confirmed from spectroscopic and microscopic techniques.
- Synergetic effect of g-C₃N₄ with ZnO NPs supports for high performance towards CO₂ reduction.

Abstract

The enhancement of efficiency of electrocatalysts towards the electrochemical reduction of CO₂ reaction is always an exploring area of the present days. Herein, we have synthesized g-C₃N₄ and ZnO decorated g-C₃N₄ hybrid nanostructures by precipitation followed by calcination method. The as-synthesized nanostructures were well characterized by various spectroscopic techniques. X-ray diffraction suggests the synthesized material in the hexagonal Wurtzite structure. Whereas,

scanning electron microscopy and transmission electron microscopy concludes the formation of a g-C₃N₄ layer with 23.7–71.4 nm and hexagonal decorated ZnO with 2.3±0.5 nm, respectively. Furthermore, the electrochemical reduction of CO₂ was observed at -0.504 V vs. RHE in the aqueous KHCO₃ medium. The bulk electrolysis has been further carried out at -0.504, -0.734 and -0.934 V vs. RHE and obtained Faradic yield as 40.20, 53.60 and 80.99% respectively. Also, the same catalyst was used for the thermal reduction of CO₂ in the batch reaction to confirm the activity and which gave excellent yield (10 mM) of the formate. Based on above investigations, a plausible reaction mechanism for hydrogenation of CO₂ to formate synthesis over ZnO/g-C₃N₄ catalyst is also proposed. This methodology has been applicable for industrial applications for large scale production and hope will overcome the environmental and energy issues i.e., CO₂ to formate as a fuel.

Graphical abstract



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Introduction

Recently large amount of carbon dioxide (CO₂) being released into the atmosphere, which causes “Global Warming” and other severe environmental issues, which is having a very close correlation with the consumption of fossil fuels for economic and societal development purposes as an energy resource. Presently, searching solutions for the energy crisis and also saving the environment is one of the significant global challenges [1]. To solve this threat, capturing or recycling CO₂ into useful chemicals as an alternative feedstock would be a great substitute. Since the last few years, chemical, electrochemical and photo-electrochemical reduction of CO₂ has been carried out using various catalysts [2]. Among those electrochemical reduction has been an effective way to convert CO₂ into valuable products like carbon monoxide (CO), formaldehyde (HCHO), formic acid (HCOOH), methanol (CH₃OH), methane (CH₄), ethane (C₂H₄) etc., because of its applied potential merits like selectivity of product, environmentally friendly, cost-effective, easy to handle, etc. [3],

[4], [5]. However, during the electrochemical reduction of CO₂ variety of issues acts as an obstacle like its poor solubility, larger overpotentials, surface poisoning of electrocatalysts, the stability of electrocatalyst and crossover hydrogen generations and other counter reactions [6]. Along with this, another issue associated with CO₂ is that various product formation depends on the choice of electrocatalytic systems, supporting electrolytes and medium used [7]. Moreover, in the early years, most of the research has been carried out on bulk systems like metal electrocatalysts, which possessed many unsolved issues [8]. This problem has been solved by substitute the bulk catalytic systems by different types of nanostructures including metal, metal alloys, hybrid nanostructures on the support of carbon based materials, polymers, porous materials having different sizes and shapes [9].

Literature reflects various electrocatalysts have been reported for C₁ feedstock generation from CO₂. For instance, Yang et al. reported the cube-like nanoparticles of Cu were effectively used for electrochemical reduction of CO₂ to ethylene, ethanol and n-propanol are the major products with an onset potential of -0.53V vs. RHE in 0.1 M KHCO₃ with Faradic yield of 50% [10]. Qiao et al., also reported Bi decorated on polyethylene glycol using a simple chemical reduction method having product selectivity towards formate with Faradic yield of 81.3% at a potential of -0.83 vs. RHE in aqueous solution [11]. Co₃O₄ nano-fiber based electrocatalytic systems reported by Kus et al. for electrochemical CO₂ hydrogenation in acetonitrile-water solution to improve the solubility and also electrode fabricated by an electro-spinning method having high surface area is responsible for the higher electrocatalytic activity, i.e., proposed Faradic yield for the formation of CO and formate is 90% at a potential of -1.5V vs. NHE [12]. Furthermore, Cu-rich bronze (α -bronze) and a Sn-rich bronze (η -bronze) nanoparticles were developed to reconnoiter the outcome of alloy configuration on product selectivity for electrocatalytic CO₂ hydrogenation. Whereas, the selective CO production with a Faradic yield of 90% was observed on α bronze alloy, whereas formate production observed on η -bronze with Faradic yield of 70%. The kinetic analysis also exposed to know the vital role of Sn towards enhancement in performance [13]. A large number of reported systems are available on hybrid electrocatalysts, including InO₂ decorated GO [14], NiO/MWCNTs [15], Au-Cu bimetallic nanoparticles [16] etc. The enhancement in reduction performance of CO₂ has observed due to the synergistic, geometric, structural and electronic effects at the multi-component interfaces of electrocatalysts.

The current trend in this line has been shifted towards Zn and its non-stoichiometric oxides because of having enormous properties viz., it has n-type semiconductor with a bandgap of ~3.37eV and excitation binding energy of 60eV. Structurally it is hexagonal Wurtzite kind whereas Zn atoms are tetrahedrally coordinated to four O and d-electrons of Zn atoms hybridized with the O p-electrons. In addition to this, it has better thermal stability, high surface area, low cost/nontoxic and, most importantly, its high earth-abundance [17]. Therefore, it is widely used for electrocatalytic applications like electrochemical sensing, water-splitting reactions, biological sensing and real sample (antibacterial activity) analysis, drug detection, electrochemical CO₂ reduction, determination of dyes and pesticides from the soil and other real sample, etc. [18], [19],

[20]. Furthermore, electrochemical reduction of CO₂ is having important applications of above listed. For example, Zn and its oxides selectively give carbon monoxide (CO) C₁ feedstock with high Faradic efficiency [21].

Moreover, as a one of the active component g-carbon nitride (g-C₃N₄) is having highly polymeric class and consists of carbon and nitrogen with different types of allotropes with sheet-like structure, synthesized by simple way from commercially accessible and low-cost materials [22]. It is one of the most stable at any of the experimental conditions and also consist of high surface area, small and tunable band gap with sp^2 hybridization of nitrogen and carbon having highly stable pi (π) conjugated system. Because of having strong covalent convoluted bonds having stability to composite also additional scope for metal ion entered into the heptazine ring cavities and which significantly alters the properties of its composite [23], [24], [25]. Due to these properties, g-C₃N₄ is having a large and diverse number of applications as an electrocatalyst for a variety of transformations in the field of energy conversion and storage. Some of the significant examples include, Dudney et al. reported lithiated g-C₃N₄ as an anode material for batteries [26]. Herein, Li and the graphite C₃N moieties of C₃N₄ reacts and which results in the formation of Li-CH=NR and Li-N=CR₂ molecules, which enhances their conducting performance along with anode properties. Also, Wu et al. demonstrated the small pore size and homogenous distribution of particles showing improved capacitance of the material with pyridinic and pyridone N atom on GO. The enhanced capacitance of GO-OOH-N is endorsed with the N content, which also helps a carboxylation on GO [27]. Furthermore, Zhang et al. introduced Co into the structure of (CN)_x through a chemical reaction and its surface and interface further alteration speed up the photocatalytic OER via. promotional charge transfer for water splitting reaction [28]. Dai et al. demonstrated the improvement in electrocatalytic activity of ORR was endorsed due to the synergetic effect of g-C₃N₄ and nitrogen-doped graphene while both electrocatalysts have individually low current density with higher potential [29]. The literature survey reflects that g-C₃N₄ and its hybrids having very few numbers of reports on electrochemical reduction, specifically on hydrogenation of CO₂. For example, Peng and coworkers reported a reduction of CO₂ into CH₃OH selectively via. facile coupling of ZnO with g-C₃N₄ and proposed its activity by explaining the role of g-C₃N₄ [30]. Studies also have been done on photoelectrocatalytic reduction of CO₂ using Ti₃C₂/g-C₃N₄ and also narrated the effect of hetero-junctions by Jing et al.[31] Herein, our invention is for combined studies of CO₂ to formic acid by using high-pressure reactor for chemical approach and optimum lower potential for electrochemical reduction of CO₂ on ZnO/g-C₃N₄.

Herein, we have prepared ZnO/g-C₃N₄ composite by simple one-step precipitation followed by calcination at 550 °C for 3 h by using urea and citric acid as a precursor. The aim of the present work is to further demonstrate the catalytic and electrocatalytic performance of this ZnO on g-C₃N₄ based hybrid systems towards CO₂ hydrogenation. The electrochemical/chemical reduction product was observed formate and which was confirmed by the HPLC technique with ultrahigh Faradic yields.

Section snippets

Synthesis of ZnO nanoparticles

In this synthesis of ZnO, ZnSO₄ 50mL (10mM) and NaOH (5M) 50mL were taken in 250 round bottom flask (R.B.) and it was stirred for 2h the white precipitate was formed at room temperature. The reaction mixture was filtered by the membrane filter paper of size 0.2μm. The precipitate has been washed three times with deionized water and finally with absolute ethanol to remove unreacted ZnSO₄, NaOH and other counter ions along with its organic impurities. The final product has been calcined at...

Results and discussions

The absorbance/reflectance properties of one-step synthesized composite have studied by UV-vis absorption spectra. Accordingly, the ZnO/g-C₃N₄ and g-C₃N₄ independently dispersed in dimethylformamide (DMF) with ~0.2wt% and absorbance was conceded within the range of wavelength of 200–800nm as shown in (Fig. 1a). The g-C₃N₄ shows absorption band at the lower wavelength of λ_{max}~225 and ~345nm due to inter-ligand π→π* and n→π* transitions attributed to the free non-bonding electrons of...

Conclusion

In summary, we have successfully synthesized ZnO decorated g-C₃N₄ by simple precipitation followed by the calcination method. The as-synthesized materials were further well-characterized by FTIR, UV-vis, XRD, SEM-EDAX and TEM analysis etc. Higher and rough surface area of the material showing an excellent electrocatalytic and catalytic activities towards the reduction of CO₂ at lower onset potential with high Faradic efficiency of 80.99%. Furthermore, the chemical hydrogenation of CO₂ was...

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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...Apart from that, XPS is conducted to further examine the electronic states of ZnO. As shown in Fig. 4c and d, typical peaks at 530 eV and 531.7 eV in O 1s spectra which corresponds to the lattice oxygen and oxygen defects, respectively, can be detected in all nano ZnO catalysts [46,47]. However, the peak shift of p-ZnO-800 in the Zn 2p_{3/2} spectra suggests a decreased Zn-O bond length, which can also be considered as a convincing evidence for the existence of oxygen vacancies in p-ZnO-800 [48]....

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