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Highly efficient manganese oxide decorated graphitic carbon nitrite electrocatalyst for reduction of CO_2 to formate

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Highlights

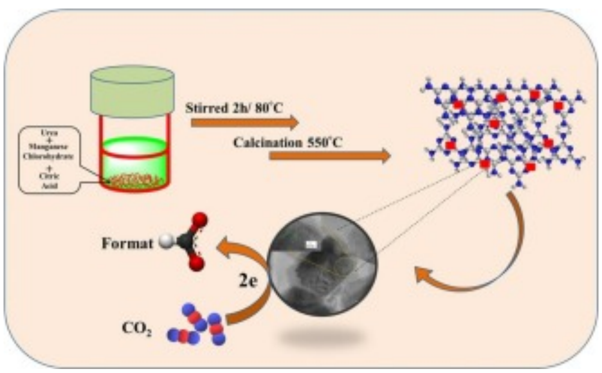
- An economical fabrication of manganese oxide (MnO_2) supported on graphitic carbon nitride (g-C_3N_4).
- Ultralow potential for hydrogenation of CO_2 with Faradic efficiency of 65.28% at −0.52 V Vs RHE.
- Ultra-high current/potential stability for electrochemical and chemical hydrogenation of CO_2.
- Envisioned and progressive catalysts for CO_2 reduction.

Abstract

Herein, an effective electrocatalyst exploiting non-noble metal oxide-containing of manganese oxide (MnO_2) supported on graphitic carbon nitride (g-C_3N_4) for reduction of CO_2 over a wide range of potential. The MnO_2 decorated g-C_3N_4 nanocomposite was synthesized by precipitation, followed by calcination to attain uniform distribution of the MnO_2. The MnO_2 was found α-MnO_2 crystal structure with a size of ~0.5–2 nm having interlinear lattice spacing of 0.243 nm seen on the layer of g-C_3N_4 (50−100 nm). The high defective sites observed on MnO_2/g-C_3N_4 (I_D/I_G) is 1.91 than pristine g-C_3N_4 (I_D/I_G) is 0.054. The core spectrum analysis of XPS showed N, C, O and Mn atoms in the as-synthesized composite. The electrocatalysts were executed for electrocatalytic hydrogenation of CO_2 at lower onset potential of −0.14 V vs. RHE into C_1 products having Faradaic efficiencies (FE) of 8, 47.45 and 65.28% at an applied potential of −0.14, −0.34 and −0.54 V vs. RHE, respectively. The catalyst has further used for the chemical hydrogenation of CO_2. and the good yield of formic acid was 9603.28 μmol obtained. The enrichment of the electrocatalytic activities was observed due to the synergetic effect of both MnO_2 and g-C_3N_4. This methodology will be applicable for industrial applications and it will help control environmental issues.

Graphical abstract

The MnO_2 decorated gC_3N_4 nanocomposite synthesized by precipitation followed by calcination method for electrochemical and chemical hydrogenation of CO_2. This proposed system applies to various industries and to solve the energy and environmental issues.



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Introduction

The interest in energy and sustainability in the world has dynamically changed due to industrialization and globalization. The current energy sources and demand have a considerable gap contributing to energy crises [1]. Furthermore, the susceptibilities of the existing energy system stem typically dependent on fossil fuels, up to 80% of our chief energy is gain from fossil fuels, non-renewable, reducing capitals that, on combustion, it emits greenhouse gases [2]. The global average surface temperature has increased (including ocean, earth surface and north-south poles) ≈ +0.93 °C to +1.2 °C. Since decade and is the highest in the last 30 years, this happened due to a considerable amount of widespread CO_2 released (33 Gigatonnes GT in 2018) into the planet has contributed to unexpected environment and climate change [3]. This awareness is directed to considerable attention in the utilization of CO_2 molecules, specifically as a low-cost feedstock for the creation of useful chemicals and fuels. The capture of CO_2 and utilization or/and hydrogenation becomes an additional mainly focused area in recent decades because of the easy accessibility of CO_2 in the environment and the prospect to reduce its concentration on the planet is continuously grown in the environment [4]. Based on the way of CO_2 reduction, technologies are like thermochemical [5], bioelectrochemical [6], photochemical [7] and electrochemical [8]. Among those, electrochemical having advantages like high selectivity of the product as it is a potential controlled technique. Moreover, the electrochemistry of CO_2 is complicated as product formation. Its selectivity depends on the number of electrons and protons desirable for species like CO, HCHO, HCOOH, MeOH, C_1-C_3 feedstock, CH_4, N_2H_4CO etc., [9] which are applicable in research and development as well as an industrial field for process development [10]. Even though an electrocatalytic CO_2 reduction journey is very complicated and critical because of its slower electro-kinetics, noted to overpotential, compete with hydrogen evaluation reaction (HER), strapped towards the product selectivity and slower rate of CO_2 conversion [11]. Considering the above issues, the researchers have tried to develop or design a more sustainable, stable and selective electrocatalyst, which will be exhibiting more efficient CO_2 electro-reduction [12]. Literature reflects electrochemical hydrogenation of CO_2, several electrocatalysts have been used for the formation of products like CO, formate, formaldehyde, alcohol, urea and C_1-C_3 products [13]. Among those products, formic acid is important and valuable chemicals used in fuel cell reactions and industrial and sustainable energy applications. In literature, various catalysts are reported for selective formate formation from electrochemical reduction of $CO_{2.}$ including Bi, Sn, Pb, Cd and In, mostly in P block metals and metal oxides [14] (Scheme 1).

The above-mentioned catalysis suffers from toxicity, high cost and required more cathodic potential to reduce CO_2 with lower Faradic efficiency (FE). Furthermore, MnO_2 and Mn_3O_4 are fascinating low-cost nanomaterials with a variable oxidation state that makes useful material and used in various electrochemical applications viz., catalysis, sensors, supercapacitors, and alkaline and rechargeable batteries [15]. In addition to this, some reports also available on electrochemical reduction of CO_2, For example, Liu et al. reported the selective synthesis of Ni foam modified with MnO_2 to the formation of nanosheets MnO_2 was found be highly active for the electrochemical CO_2 to CO conversion at lower potential and high current density [16]. Chen et al. elucidated the Mn-doped SnO_2 shows highly efficient electrocatalyst towards the CO_2 conversion into formic acid due to Mn doping with SnO_2 creates oxygen vacancies, which was exposed the more active sides. Spectroscopic and DFT calculations were found to be a more active site because of CO_2 reduction in ultra-lower potentials on the surface of Mn-SnO_2 [17]. Furthermore, Strasser et al. have used 3d-transition based (M-N-C) electrocatalyst (Mn, Fe, Co, Cu and Ni) for CO_2 utilization reactions. It was found that homogeneous dispersion M-N_x sites increase the interactions of CO_2 molecule and lower valance electron-rich metal center, and exhibited lower potential and increasing the current density [18].

In recent reports, graphitic carbon nitride (g-C_3N_4) has attracted more attention due to excellent properties like high surface area, more extended catalytic durability, and small bandgap with *sp*^{2}-hybridized nitrogen and carbon with pi (л)-conjugated system. In addition to this, g-C_3N_4 has strong covalent bonds, which gives extra stability to the material and its synthesis is simple and uses low-cost starting materials [19]. These enormous properties of g-C_3N_4 have been used in electrochemical applications as water splitting, supercapacitor, oxidation-reduction, batteries, photo-electrocatalytic, sensors, solar cells etc. [20]. Again, the few carbon nitride layers have been used for the electrochemical reduction of CO_2 and the formation of CO products with FE ~80% [21]. Even though very few reports are available for the reduction of CO_2 on the electrocatalysts using MnO_2 and g-C_3N_4 both having low FE, higher cathodic potential, low stability etc. and only given CO as the product; consequently, there is an urgent need to develop electrocatalyst for liquid product formation from CO_2. Herein, we have fabricated the MnO_2 decorated g-C_3N_4 by using citric acid and urea molecules. The hexagonal like structure of MnO_2/g-C_3N_4 are having active sites, edges with high surface area, and more stable towards the CO_2 conversion into formate at low overpotential with 65.28% FE. The chemical hydrogenation of CO_2 and obtained yield was 9603.28 μmol. The electrocatalyst showed high electrocatalytic activity applicable to the industrial applications from CO_2 to the useful product like formate.

Section snippets

Material

Manganese Chloride ($MnCl_2$) 99.99%, Sodium hydroxide (NaOH) 99.99% (Alfa Asear), Urea $CO(NH_2)_2$ 99.99%, Citric acid $C_6O_8H_7$ 99.99% (SD Fine chemicals), Potassium bicarbonate $KHCO_3$ (Sigma Aldrich), Nitrogen gas N_2 99.99%, Carbon Dioxide CO_2 gas 99.99% (Vijay Scientific Ltd, India), de-ionized water. All the chemicals were used are of AR grade without further purification.…

Synthesis of MnO_2 nanoparticles (NPs)

The MnO_2 NPs have been synthesized by using an earlier reported method [22]. In a typical procedure, 0.5 g (3.2 mM) of $KMnO_4$ was…

Characterization of MnO_2/g-C_3N_4 nanocomposite

The MnO_2/g-C_3N_4 has been synthesized using simple precipitation followed by calcination method and characterized by structural and morphological techniques and used for further applications. The XRD pattern for g-C_3N_4 and MnO_2/g-C_3N_4 is displayed in Fig. 1(a), where the characteristic peaks at 12.90 (weaker) and 27.8° are having plane (002) for exfoliated g-C_3N_4 and thus indicating successful exfoliation (JCPDS87-1526) [23]. The peak slightly shifted towards the more positive angle due to the…

Conclusion

In summary, we have developed $MnO_2/g\text{-}C_3N_4$ nanocomposite by using simple precipitation followed by the calcination method. The synthesized nanocomposite well characterized by various characterization techniques, including XRD of $MnO_2/g\text{-}C_3N_4$ depicts $\alpha\text{-}MnO_2$ crystal structure, Raman spectra of $MnO_2/g\text{-}C_3N_4$ and $g\text{-}C_3N_4$ with I_D/I_G ratio are 1.21 and 0.79 respectively. The TEM images showed the hexagonal type of morphology of MnO_2 with ~0.5–2 nm in size with the interlayer distance of 0.243 nm between…

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.…

CRediT authorship contribution statement

Balaji B. Mulik: Data curation, Validation, Writing - original draft. **Ajay V. Munde:** Data curation, Methodology, Writing - original draft. **Balasaheb D. Bankar:** Data curation, Formal analysis, Writing - original draft. **Ankush V. Biradar:** Conceptualization, Funding acquisition, Supervision, Writing - review & editing. **Bhaskar R. Sathe:** Conceptualization, Investigation, Methodology, Project administration, Supervision, Writing - review & editing.…

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2023, Journal of Colloid and Interface Science

> *Citation Excerpt :*
>
> …As shown in Fig. S1c, the lattice spacings of MnO were 0.156 nm, 0.222 nm, and 0.256 nm for (220), (200), and (111) crystal planes, respectively [25,30]. The lattice distance of 0.196 nm and 0.230 nm could be attributed to (120) and (330) planes of MnO2 [31,32]. Moreover, the lattice spacing of 0.276 nm for Mn3O4 corresponded to the (103) crystal plane (Fig. S1d) [25,33]….

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2023, International Journal of Hydrogen Energy

> *Citation Excerpt :*
>
> …The Nyquist plot is used to obtain the reduced charge transfer resistance (RCT), which verifies the kinetics improvement and separation efficiency of charge carriers of the two photoelectrodes [59]. The information on RCT can be obtained from the diameter of the semicircle/arc of the Nyquist plot [63]. The RCT during the catalytic process is directly proportional to the diameter of the arc i.e smaller the diameter, the smaller the RCT [64]….

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