Perspective

Chitosan as a biomass-based bridge: Integrating CO_2 capture and electrochemical upcycling

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Abstract

The urgent need to mitigate CO_2 emissions has spurred CO_2 capture and utilization (CCU) technologies. Electrochemical CO_2 reduction reaction (CO_2RR) offers a sustainable route to valuable chemicals, but suffers from low CO_2 concentration, poor mass transport, and low selectivity. Chitosan, a renewable biomass polymer, uniquely addresses these issues: it serves as a precursor for heteroatom-doped porous carbons and metal nanoparticle supports with high electrocatalytic activity, while its amine groups enable efficient CO_2 chemisorption. This dual functionality makes chitosan an ideal "bridge" integrating CO_2 capture and electroreduction. This perspective highlights recent advances in chitosan-derived electrocatalysts and adsorbents, and proposes an

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integrated capture-conversion system.

Keywords: Electrochemical CO_2 reduction reaction, CO_2 capture, chitosan, amine-functionalized materials

INTRODUCTION

Electrochemical CO_2 reduction reaction (CO_2RR) can convert waste CO_2 into fuels and chemicals using renewable electricity[1]. However, its industrial viability is limited by poor CO_2 solubility, sluggish mass diffusion, competing hydrogen evolution reaction (HER), and low selectivity toward multi-carbon (C_{2+}) products at high current densities[2-4]. The innovative electrode designs are urgently needed, which enhance local CO_2 concentration, stabilize intermediates, and facilitate mass/electron transfer[5-6]. Chitosan, a natural polysaccharide from crustacean shells, is rich in amino and hydroxyl groups. It exhibits strong CO_2 adsorption via hydrogen bonding and acid-base interactions, making it an excellent platform for CO_2-selective adsorbents[7-10]. Recent studies have shown that chitosan-derived porous carbons and amine-functionalized foams achieve efficient CO_2 capture[9-14]. In electrocatalysis, chitosan serves as a carbon/nitrogen source, a structure-inducing agent for 3D metal nanosheets, and an ion-conductive binder[7,15-18]. These properties suggest chitosan can act as a “biomass bridge” integrating upstream CO_2 capture with downstream electroreduction.

In this article, the key characteristics and working mechanisms of chitosan-derived materials applied in CO_2 capture and CO_2RR are summarized and critically analyzed. By comparing the structural features, surface chemistry, and functional roles of chitosan in adsorption versus catalysis, there are identified common design principles that can be leveraged to bridge these two processes. A new insight into creating CO_2-rich microenvironments for enhanced kinetics and selectivity is offered. This integrated approach not only addresses key industrial hurdles but also opens a sustainable pathway for valorizing both biowaste and CO_2 emissions. We hope this perspective inspires further research into biomass-derived multifunctional materials for carbon capture and

utilization, accelerating the transition toward a circular carbon economy.

CHITOSAN-DERIVED ELECTROCATALYSTS FOR CO_2RR

Chitosan-derived electrocatalysts achieve high Faradaic efficiencies (FEs) for various products: CO (> 90%)[17], formic acid (~100%)[7], methane (> 63%)[8], ethanol (74.3%)[6], and C_{2+} products (88.2%)[15]. It plays multiple unifying roles--carbon/nitrogen precursor, structure-directing agent, and binder--addressing key CO_2RR challenges.

Firstly, chitosan is a precursor to offer carbon and nitrogen source. Upon pyrolysis, chitosan forms 3D porous carbon that stabilizes metal nanoparticles (In, Ni) via strong metal-support interactions[7,17]. Its amino groups are incorporated into the carbon lattice as pyridinic-N, pyrrolic-N, and graphitic-N, which enhance CO_2RR performance. For example, pyridinic-N activates CO_2; ternary N, P, B doping creates P-N and B-N bonds that optimize *CO binding energy, steering selectivity toward CH_4[8]. In In/N-dG, N-doping enriches electron density on In sites, lowering the $*HCOO^-$ barrier and achieving near-unity FE for formate [Figure 1A][7]. Secondly, chitosan is a structure-inducing agent in electrodeposition. Chitosan chelates metal ions (Cu^{2+}, Ag^+, Sn^{2+}) and directs the growth of vertically aligned 3D nanosheet arrays or hexagonal prismatic microrods on gas diffusion layers[5-6,15]. This 3D morphology increases electrochemical surface area (ECSA), exposes more active sites, facilitates CO_2 diffusion, and protects the hydrophobic layer. The 3D Cu-CS-GDL[15] and 3D-CuAg-GDE[5] showed superior performance in electroreduction CO_2 to C_{2+} products [Figure 1B]. Chitosan also combines with rGO to form chi-rGO/SnO_2 composites with 80-fold higher C_{dl} and 88% formate FE[16]. Finally, Chitosan is a ion-exchange binder, which can replace fossil-based ionomers (Nafion, Sustainion)[15,18-19]. In the latest report, chitosan was coated on the surface of Cu NPs, replacing Nafion directly and reducing the oxidation rate of Cu, while its hydrophilic, ion-conductive nature adjusts the catalytic microenvironment with increasing the local CO_2/CO concentration and suppressing HER. At a current density of 1.6 A cm^{-2}, FE(C_{2+}) reached 90 ± 1.7%, and at

2.2 A cm^{-2}, it reached 83 ± 3.2% [Figure 1C][19].

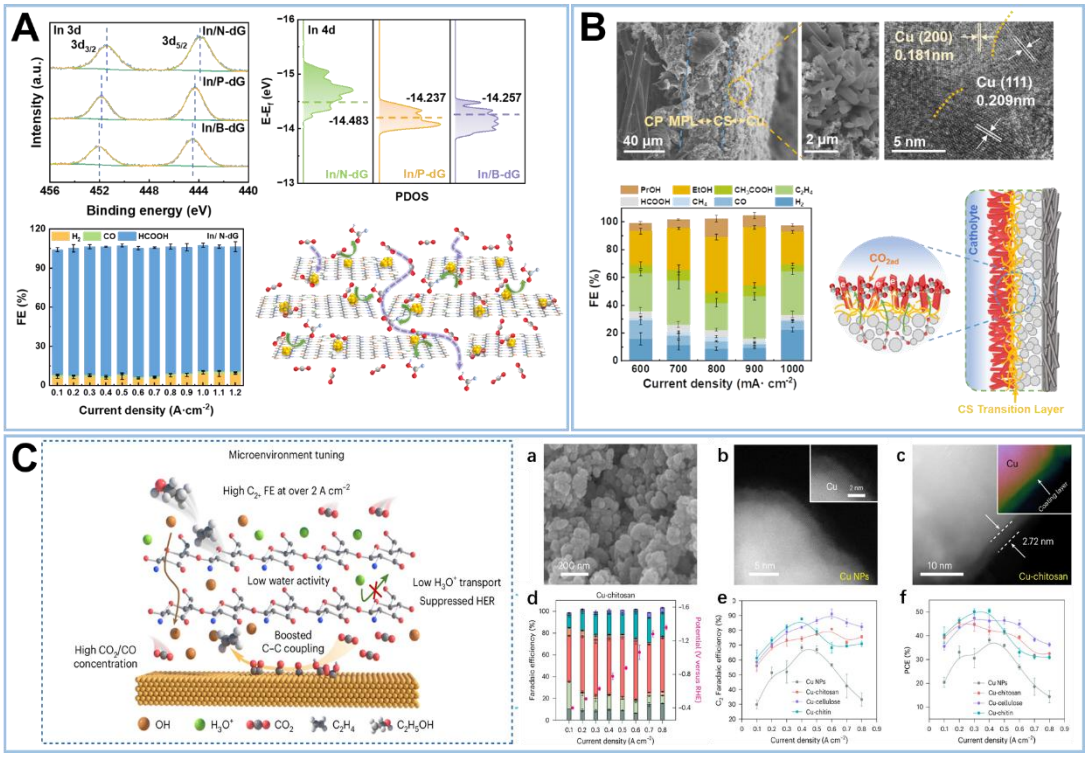

Figure 1. Chitosan-Derived Electrocatalysts for CO_2RR. A) In/N-dG electro-catalyze CO_2 transform to formate[7]; B) 3D Cu-CS-GDL electro-catalyze CO_2 transform to C_{2+} products[15]; C) Cu-chitosan, Cu-cellulose and Cu-chitin electro-catalyze CO_2 transform to C_{2+} products[19]. In/N-dG represents the catalyst consisting of indium nanoparticles anchored on the chitosan-derived graphene substrate, and 3D Cu-CS-GDL represents the catalyst with 3D Cu film growing on the chitosan over gas diffusion layer (GDL).

CHITOSAN-BASED MATERIALS FOR CO_2 CAPTURE

Chitosan's high nitrogen content (~7 wt%), abundant -NH_2/-OH, and low cost enable both physisorption and chemisorption of CO_2[7,14,20]. Thus, chitosan-based adsorbents combine high surface area, nitrogen functionality, and amine-rich surfaces for efficient, reversible CO_2 capture[9-13].

Chitosan can transform to porous carbons via carbonization/activation. Lin *et al.* used hydrothermal treatment with P123 and $NaNH_2$ to obtain 3D porous carbons with

lamellar stacking, achieving CO_2 adsorption capacities of 5.92 mmol/g at 0 °C and 4.06 mmol/g at 25 °C[9]. Guo *et al.* carbonized chitosan in molten LiCl/KCl followed by $KHCO_3$ activation and urea doping, producing N-doped hierarchically porous carbons (S_{BET} up to 2,658 m^2/g and N content up to 10.77 wt%). The best sample (C0700) had a CO_2 uptake of 4.10 mmol/g at 25 °C and 1 bar with excellent stability and selectivity [Figure 2A][11]. Chitosan acts as a renewable C/N source, creating micro/mesopores during decomposition, and residual N-groups serve as basic adsorption sites.

Amine-functionalized chitosan-based composites can further enhance CO_2 capture ability. The FA/CS_1-50PEI was modified by chitosan and PEI, forming an ordered 3D network, which achieved a maximum CO_2 adsorption capacity of 1.96 mmol/g at 40 °C and retained 93% capacity after 10 cycles [Figure 2B][10]. Zhang *et al.* prepared a chitosan foam by emulsion templating followed by dopamine/PEI co-deposition, yielding ACF with 389.2 m^2/g and 3.59 mmol/g CO_2 uptake at 60 °C, plus high selectivity (90.3) and cyclic stability[12]. Mota *et al.* impregnated chitosan onto SBA-15, where interconnected microporosity allowed better CO_2 diffusion to chitosan chains, outperforming MCM-41[13]. Chitosan serves as a structural scaffold, provides initial amine sites, and acts as a matrix for additional amines (PEI, dopamine), boosting uptake via carbamate formation.

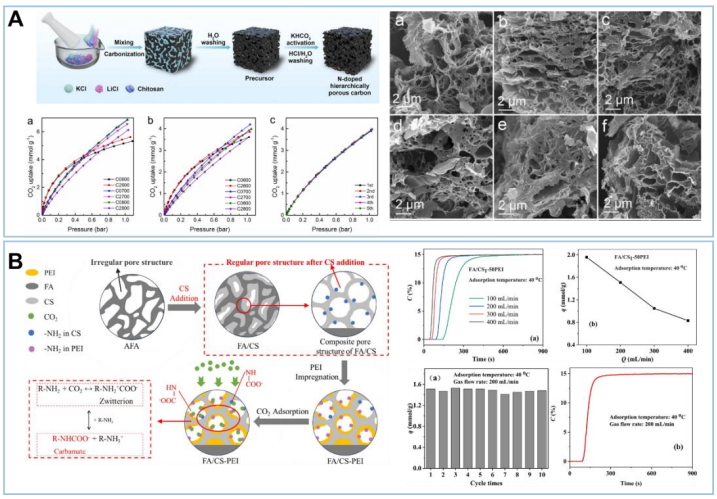

Figure 2. Chitosan-Based Materials for CO_2 Capture. A) N-doped hierarchically porous carbons capture CO_2[11]; B) FA/CS_1-50PEI achieved a maximum CO_2 adsorption

capacity[10]. FA/CS_1-50PEI represents the adsorbent of polyethyleneimine (PEI)-impregnated fly ash (FA) modified by chitosan, with the CS/FA ratio of 1 and PEI impregnation ratio of 50.

FUTURE PERSPECTIVES: TOWARD INTEGRATED CAPTURE AND CONVERSION

Comparing chitosan materials for capture and electrocatalysis reveals striking commonalities: chitosan is a renewable C/N source, a structural scaffold for hierarchical porosity, and a functional matrix with abundant amine groups. For CO_2 capture, the key is maximizing accessible basic sites and microporosity. For CO_2RR, the same amine backbone enables N-doping, 3D metal growth, and ion conduction. It suggests that chelating ability, porous network formation, and electron-donating amines of chitosan can simultaneously address low local CO_2 concentration and poor intermediate stabilization—the two major bottlenecks of CO_2RR.

We propose a conceptual integrated platform--a bifunctional gas diffusion electrode (GDE) with three hierarchical components: (i) a macroporous chitosan foam or carbonized network that captures CO_2 via amine-mediated chemisorption[10,12]; (ii) a meso-/microporous N-doped carbon matrix that further concentrates CO_2 and provides conductivity[9,11,19]; and (iii) embedded bimetallic active sites (e.g., Cu-Ag, Cu-Sn) that electroreduction CO_2 to C_{2+} products[5-6]. This design eliminates separate capture/compression steps, feeding concentrated CO_2 directly to catalytic sites. From the perspective of the mechanism, the intrinsic properties of chitosan create a localized CO_2-rich microenvironment. First of all, the amine groups bind CO_2 reversibly, and generate a local alkaline environment upon quaternization, which suppresses HER and lowers C-C coupling overpotential[15,20]. Moreover, tunable porosity (ultramicropores to macropores) balances adsorption capacity with rapid diffusion[13]. And chelation allows precise anchoring of dual-metal sites, enabling tandem catalysis where CO generated on one metal (e.g., Ag) spills over to adjacent Cu sites for C-C coupling[5]. Finally, nitrogen functionalities (pyridinic-N, pyrrolic-N) stabilize *CO and *CHO intermediates via

hydrogen bonding, lowering asymmetric coupling barriers and steering selectivity toward ethanol or ethylene[8].

The integrated platform bypasses CO_2 solubility/diffusion limitations, shortens diffusion paths, and simplifies electrode fabrication, opening a new paradigm for sustainable CO_2 valorization. However, there are several challenges and opportunities remaining:

1. The trade-off between capture capacity and catalytic activity needs optimization. The high amine loading may block active sites or alter hydrophilicity. Systematic studies on amine density, porosity, and performance are needed.

2. The long-term stability under simultaneous capture/reduction conditions is largely unexplored, which should be figuring out through in-situ characterization (Raman, FTIR, XPS).

3. The scalability to larger electrode areas and industrially relevant current densities (> 500 mA cm^{-2}) must be demonstrated, along with techno-economic and life-cycle assessments.

4. The integrated platform should achieve universal development and application. For instance, this design concept should be extended to the use of other biomass polymers (such as cellulose, alginate) and the application should be expanded to other technical routes such as photo-catalysis or thermal catalysis.

CONCLUSION

In this perspective, we have analyzed chitosan-derived materials for CO_2 capture and CO_2RR, identifying common design principles: chitosan acts as a renewable C/N source, a structural scaffold, and an amine-rich functional matrix. In CO_2RR, it enables N-doped carbon supports, directs 3D metal growth, and serves as an ion-conductive binder. In CO_2 capture, it provides basic adsorption sites, creates porous architectures,

and allows amine functionalization. By comparing these fields, we proposed an integrated bifunctional GDE that combines efficient capture with direct electrochemical upcycling. Chitosan's intrinsic properties create a CO_2-rich microenvironment with stabilized intermediates, enhancing kinetics and selectivity. While challenges in optimization, stability, and scale-up remain, this integrated platform represents a promising pathway toward sustainable CO_2 valorization and a circular carbon economy.

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Author Contributions

Manuscript preparation: JH.B;

Manuscript correction: J.Z, SQ.L.

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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