

Carbon Dioxide Conversion to Nanomaterials: Methods, Applications, and Challenges

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Abstract

Anthropogenic carbon dioxide (CO₂) emission is one of the biggest global threats we are confronted with in the 21st century. Lack of prompt action to mitigate the atmospheric CO₂ level could lead to global catastrophic events. Due to the significance of the aforementioned threat, multiple nations have agreed to enact carbon capture, storage, utilization, and sequestration (CCUS) technologies at academic and industrial scales with the aim of lowering atmospheric CO₂ level. Though there are many reviews on CCUS technologies, there is a lack of comprehensive reviews on CO₂ conversion to more economically valuable products such as nanomaterials. Carbon dioxide capture and conversion into nanomaterials is an interesting research topic in many ways as it contributes to our fundamental knowledge of material conversion, provides alternative ways to reduce atmospheric pollution, and yields lucrative products, which has not been explored broadly. Aside from the positive outcomes, we have a moral obligation to rectify a global threat caused by anthropogenic emission. Herein, we present current methods of converting CO₂ into organic and inorganic nanomaterials with a focus on operating conditions and challenges, as well as nanomaterials' potential in specifically biomedical applications as opposed to extensively reviewed energy related uses. Moreover, our review emphasizes the toxicity issues related to using such nanomaterials in biological settings based on literature and other comparable studies.

Keywords: CO₂ capture, conversion, carbon nanotube, nanomaterial, biomedical application

1. Introduction

The impact of greenhouse gases (GHGs) on climate change has attracted enormous attention in recent decades. On one hand, climate models have indicated that GHGs, including carbon dioxide (CO₂), have played a critical role in helping to maintain global surface temperatures at inhabitable levels for the existence of humankind on Earth.¹ On the other hand, the subtle balance between the atmospheric concentrations of GHGs and global temperature has been perturbed by the same species during the industrial revolution in the 1900s, and now we foresee a self-created situation whereby the elevated CO₂ level could jeopardize our existence on Earth.^{2,3} Accelerated anthropogenic CO₂ emission can initiate a cascade of disasters globally, and unfortunately, we are already victims of warm winters,⁴ prolonged droughts,^{5,6} unprecedented magnitudes of wild fires,⁷ rising sea levels,⁸ and an increase in global temperature indicated by the fact that 2020 was recorded as the hottest year. The projected socioeconomic impact of increasing CO₂ levels in the near future is detrimental,⁹ and immediate global actions must be taken to mitigate the threats as we have already passed the threshold level (i.e., 350 ppm) of CO₂ in the atmosphere; the current CO₂ level in the atmosphere is 415 ppm, according to the Mauna Loa Observatory.¹⁰

The imminent danger of ever rising CO₂ levels was first pinpointed by scientists in the 1950s, but policy makers were not convinced to take stern action to control anthropogenic emission until the late 1990s,¹¹ especially that coming from burning coal, oil, and natural gases. However, global commitments such as the Kyoto protocol and Paris agreement have fueled the movement and, as a result, CCUS technologies were introduced aiming to achieve net-zero greenhouse gas emission by 2050.¹² The abbreviation CCUS stands for carbon capture, utilization, and storage, aka carbon sequestration. Though each emission reduction technology¹³ is crucial for the global commitment toward the aforementioned goals, some countries may face unique challenges based on their geological structure and the capital demand to implement CCUS technologies. For example, carbon capture and underground storage is a viable option for countries like the United States, where vast storages like depleted oil and gas reservoirs and underground water aquifers are available compared to countries with limited natural storage facilities. In order to compensate for such a discrepancy, fundamental and field studies related to economically and environmentally feasible CCUS technologies should be developed.

Among CCUS technologies studies, some have shown promise in converting the major global warming contributors like CO₂ into valuable products. The significance of the value-added products may be further enhanced if the products are nanomaterials, which may have superior chemical, physical, electrical, and/or material properties compared to their bulk counterparts. Nanomaterials can open up new opportunities in many fields; most notably of late, nanotechnology played an important role in the success of the Pfizer and Moderna vaccines for COVID-19.¹⁴ Over the past decades, various synthetic methods including phase separation¹⁵ have been developed to incorporate CO₂ gas in the production of nanomaterials such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), nanosheets, graphene, nanostructured graphite, carbon nanoparticles, carbon nano-onions, and nano-honeycomb/platelet structures, as well as inorganic nanostructures. There are quite a few interesting review articles covering different approaches that turn CO₂ into fuels and value-added chemicals (**Table 1**). However, there are no review papers on conversion of CO₂ into nanomaterials. Herein, we reviewed various methods reported in the literature to convert CO₂ into nanomaterials, which have the potential to be used in therapeutic, diagnostic, and regenerative applications. In order to realize the full potential of such CO₂-converted-nanomaterials, the operating cost and efficiency of conversion approaches must be economically realistic, and ideally,

such methods have to be powered by renewable energy sources. Additionally, the plausible toxicity effects of CO₂-based nanomaterials should be addressed thoroughly prior to utilizing them in different biological systems.

Table 1. Summary of CO₂ conversion literature reviews.

Author	CO₂ conversion product	Year	Ref.
Huang et al.	Polycarbonate, methanol, dimethyl carbonate, and dimethyl ether	2014	16
Lahijani et al.	Fuel gas (carbon monoxide)	2015	17
Romanov et al.	CaCO ₃ , MgCO ₃ , Na ₂ CO ₃ , K ₂ CO ₃ , and organic carbonates (polycarbonate, dimethyl/ethyl carbonate)	2015	18
Ganesh et al.	Methanol, fertilizers (urea), formic acid, polycarbonates, carbon monoxide, and ethylene	2016	19
Li et al.	Methane, carbon monoxide, methanol, formic acid, ethanol, acetaldehyde, hydrogen, ethane, ethylene, propane, and propene	2016	20
Alper et al.	Methane, methanol, formic acid and derivatives, polymer, organic carbonates, urethanes, carbamates, lactones, pyrenes, epoxides, ethylene, carbon monoxide, higher hydrocarbons, fine chemicals, and inorganic products (calcite, hydrotalcite, MgCO ₃)	2017	21
Sharma et al.	Carbon monoxide, methane, ethylene, formic acid, and ethanol	2017	22
Zheng et al.	Carbon monoxide, formic acid, methanol, ethylene, ethanol, salicylic acids, urea, carboxylic acids, and organic and inorganic carbonates	2017	23
Al-Rowaili et al.	Methanol	2018	24
Artz et al.	Organic carbonates, synthesis gas, carboxylic acids, methanol, methane, Fischer-Tropsch products, and oxygenates	2018	25
Li et al.	Methane and C ₂₊ hydrocarbons	2018	26
Liu and Gadikota	Calcium carbonate	2019	27
Nitopi et al.	Carbon monoxide (syngas), carbon monoxide, coal, methane, methanol, ethylene, ethanol, propanol, acetaldehyde, and formic acid	2019	28
Chauvy et al.	Chemicals, fuels, durable materials (methane, methanol, formic acid, formaldehyde, acetic acid, methyl tertiary-butyl ether, dimethyl carbonate, dimethyl ether, synthetic natural gas, olefin, carbonates, and carbamates), polymers, carbon fibers, composites, fine chemicals, mineral carbonation (Na ₂ CO ₃ , NaHCO ₃ , CaCO ₃ , MgCO ₃), construction materials, algae, and enzyme-based products	2020	29

	(hydrocarbons, lipids, fatty acids, isobutanol, isopropanol, and methyl ketone)		
Wen et al.	Aromatics like toluene, xylene, ethylbenzene, trimethylbenzene, methyl ethylbenzene, propyl benzene, etc.	2020	30
Lin et al.	Methane, methanol, carbon monoxide, formaldehyde, formic acid, and acetic acid	2021	31
Liu et al.	Hydrocarbons	2021	32
Murthy et al.	Methanol	2021	33
Tahir et al.	Methane, methanol, and other fuels	2021	34
Xue et al.	Methane, methanol, carbon monoxide, formaldehyde, acetic acid, ethanol, and hydrogen	2021	35

2. CO₂ Conversion into Carbon Nanomaterials

Varieties of carbon nanomaterials have been produced from CO₂ conversion, including CNTs, CNFs, carbon nanosheets, nanoparticles, nano-onions, porous nanomaterials, graphite honeycombs, and graphene grafted CNFs (Table 2).

Table 2. Nanomaterials produced from CO₂ conversion.

Nanomaterial		Reference
Carbon-Based	CNTs and CNFs	36-54
	Carbon nanosheets	55
	Graphite honeycombs	56
	Carbon nanoparticles	57
	Carbon nano-onions	58
	Carbon nano-platelets	59
	Porous nano-carbons	60
	Graphene grafted CNFs	61
Inorganic	NaHCO ₃ nanofibers and nanoflowers	62
	CaCO ₃ nanoparticles	63,64

2.1 Chemical Vapor Deposition (CVD)-based carbon nanotubes (CNTs) and carbon nanofibers (CNFs)

Early approaches developed to utilize CO₂ in chemical synthesis were based on chemical vapor deposition (CVD), which is a common method to fabricate high quality semiconductors. Using the CVD process, Wang et al.³⁶ successfully prepared three dimensional (3D)-carbon nanotube foams (CNTFs) via direct conversion of CO₂ with a Mg/Ni template. Briefly, CO₂ gas was fed to the reaction as a 1:3 gas mixture of CO₂ and argon gases, and reacted with Mg at 800 °C for 1 to 2 hours to obtain the cylindrical CNTs, in which Ni nanoparticles acted as the catalyst in CNT fabrication. Electron microscopy analysis of the as-prepared CNTFs revealed a 3D network of CNTs (Figure 1a-b). Moreover, the CNTFs have shown good electrical and mechanical properties that are suitable for semiconductor applications.

The energy demanding steps involved in CVD fabrication such as high temperature and pressure over a long period, as well as low scalability, are certainly not attractive features of an economically feasible CO₂ utilization approach. Hence, recent developments in the CVD technique focus on moderate reaction conditions and exploitation of highly efficient catalysts for the conversion of CO₂ into valuable products. According to an improved CVD method devised by Kim et al.,⁵⁴ CO₂-derived CNTs (CCNTs) were obtained under mild conditions (500-700 °C and 1 atm), in which 100% CO₂ gas reacted with NaBH₄ and metallic Ni, which served as the reducing agent and catalyst, respectively. Additionally, the proposed synthetic route is a one-step continuous CVD method which addresses the low scalability concerns associated with previous CVD fabrications. Furthermore, the mesoporous structure of as-prepared CCNTs has contributed to the enhanced electrical properties compared to the commercial activated carbon (YP-50F) used for supercapacitors (**Figure 1c-d**). Recently, the same group reported a further improved CVD method to form CNTs from atmospheric CO₂, which were coated with boron atoms (**Figure 1e-f**) to overcome the material failures that were found in commercial CNTs, making CCNTs more appealing.⁵³ The boron coating on CCNTs has provided anti-oxidative and anti-combustion properties to the nanostructure, which are required for high-temperature (e.g., 1,000 °C) applications.

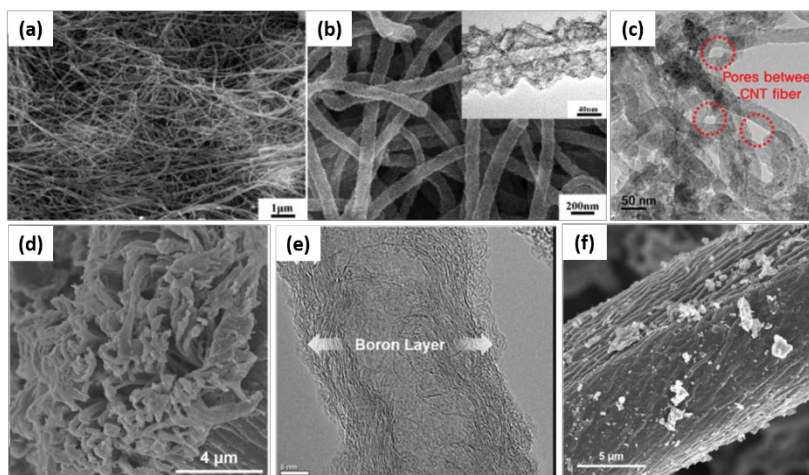


Figure 1. The electron microscopic images of carbon nanotubes (CNTs) and carbon nanotube foams (CNTFs) prepared by direct conversion of CO₂ gas using the chemical vapor deposition (CVD) method. (a) Microstructures of CNTF; (b) High-resolution morphology of CNTF. Inset: TEM image of the single CNT. Reproduced from ref³⁶. Copyright 2015 Elsevier. TEM (c) and SEM (d) images of CNT fibers and inter-fiber pore structures. Reproduced from ref⁵⁴. Copyright 2020 Royal Society of Chemistry. HRTEM image (e), and SEM image (f) of the boron-coated CNT (CB-CNT). Reproduced from ref⁵³. Copyright 2020 American Chemical Society.

2.2 Electrochemical methods-based CNTs and CNFs

In parallel to the CVD methods, electrochemical approaches have gained a prominent stake in CO₂ utilization research. In fact, some of the electrochemical methods developed to convert CO₂ into nanomaterials have been advanced to the start-up company level to show their scalability

and cost-effectiveness. Particularly, the Licht group^{51,52} is one of the pioneers in research on electrochemical conversion of CO₂ into valuable nanomaterials. Their work has been recognized as a breakthrough technology to receive the Carbon XPRIZE award in 2019, which enabled them to establish the C2CNT (CO₂ to carbon nanotube) Company. Their promising technology is based on molten carbonate electrolysis, in which CO₂ gas is reacted with highly soluble Li₂O to form molten Li₂CO₃, which can be electrochemically cleaved into CNTs (and/or CNFs) and oxygen gas while regenerating Li₂O in the electrolysis chamber, which consists of a nickel (Ni) anode and a galvanized steel cathode. The C2CNT approach is estimated to be a profitable method to obtain CNTs/CNFs compared to conventional methods. According to the Licht's group estimation, Li₂CO₃-based molten electrolysis would cost approximately \$2,000 per metric ton of CNF, considering the electric cost of \$0.10 per kW h, \$ 6,000 per ton of lithium carbonate, and \$140 per metric ton of CNF for the electrolyte.⁵¹ Conventional methods such as CVD or electrospun production could cost nearly \$25,000 per ton of CNF, which emphasizes the economic benefits of the molten carbonate electrolysis method. The early methods developed by the Licht group produced both CNFs and CNTs (**Figure 2a-e**), which could be attributed to the changes in mass diffusion, electrolysis conditions, and presence of nucleating agents such as Ni during the electrosynthesis of CO₂-based nanomaterials.^{49,50} Further improvements in their technology that led to C2CNT synthesis were able to produce CNTs at 100-fold price reduction compared to the CVD methods⁵⁰ which is also less expensive than polymer-based electrospun carbon fibers.⁴⁹

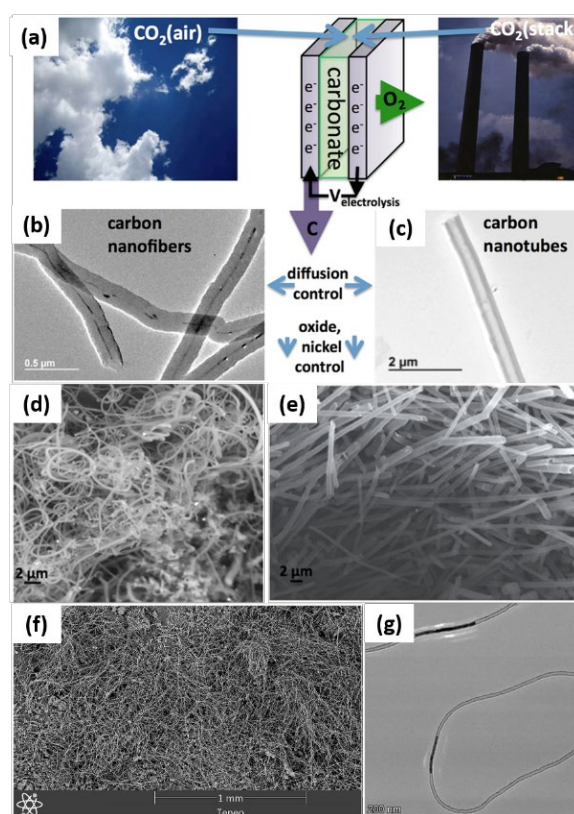


Figure 2. Scheme for the electrolytic synthesis of carbon nanostructures: (a) Source of CO₂ as dissolved air or smoke stack concentrations of CO₂, diffusion controls on formation of (b) CNTs or (c) CNFs, high oxide concentrations produce (d) tangled morphologies while low concentrations produce (e) straight nanotubes. Adapted from ref⁵⁰. Copyright 2016 Creative Common CC BY

license. (f) SEM of the CNT wool product produced at the cathode from CO₂ during replicate syntheses of 770 °C Li₂CO₃ electrolysis. Reproduced from ref⁴⁷. Copyright 2017 Elsevier. (g) Thin walled and small diameter CNTs obtained with calcium metaborate addition. Adapted from ref⁴⁵. Copyright 2016 Creative Common CC BY license.

The flexibility of coupling the C2CNT technology with well-known CO₂ generating industries like cement production has been evaluated as an economically viable and environmentally friendly initiative to mitigate CO₂ greenhouse emission as a major contributor.⁴⁸ It is estimated that 9 kg of CO₂ is emitted during 10 kg of cement production,⁴⁸ which can be fed to the C2CNT technology as CO₂ feedstock to produce valuable CNTs. As a result of further advancements in the C2CNT technology, Johnson et al.⁴⁷ in 2017 showed the first electrochemical conversion of CO₂ into macroscopic CNT-based wools, which have great potential to be used as nanocomposite materials in many industries. Replacing the Ni/steel electrodes used in the original molten carbonate electrolysis method with Monel cathodes and Nichrome anodes, macroscopic CNT wools **Figure 2f**), were obtained. The cost to prepare a ton of CNTs in this method is calculated to be \$660, which is economically advantageous compared to \$100,000 per ton of CNTs prepared by CVD and direct spin methods.⁴⁷ Continuous method development by the Licht group has produced magnetic CNTs through electrochemical splitting of CO₂.⁴⁶ The presence of Fe or Ni during the molten carbonate electrolysis is attributed to the ferromagnetic nature of as-prepared CNTs, which have a potential in biomedical and recoverable catalysis applications. Moreover, Wang et al. reported an advanced electrochemical method to produce thin walled and small diameter CNTs using the CO₂ gas directly captured from air without pre-concentration (direct air capture) with a higher yield.⁴⁵ The addition of calcium metaborate during the molten carbonate electrolysis was identified as the reason for the formation of thin walled CNTs (**Figure 2g**), with a yield higher than 90% as compared to the control reactions (~ 15%).

Other research groups have also made tremendous progress with the molten salt electrolyte method to produce economically valuable carbon-based nanomaterials from atmospheric CO₂.³⁷⁻⁴⁴ In essence, the aim of their work is to lower the cost involved in the molten salt electrolyte method while enhancing the value of CO₂-derived CNTs. Pint's group⁴⁴ also utilizes the molten salt electrochemical approach to convert CO₂ into CNTs, and they were able to optimize functionality of electrochemical setup by applying a thin layer of Al₂O₃ on a Ni anode using atomic layer deposition (ALD). The coated anode has shown resistance against electrochemical corrosion and also prevented subsequent deposition of Ni on the cathode, which could otherwise deteriorate the quality of CNTs as well as produce non-CNT products. There is a distinct improvement in the quality of CNTs produced with the Al₂O₃ coated anodes compared to the uncoated controls (**Figure 3**). Such structural modifications in the electrode systems have immensely benefited the lifetime of the electrochemical conversion process to produce homogeneous CNTs consistently.

One of the caveats in the molten salt electrolysis of CO₂ is the operating cost as it needs high temperature (e.g., 750 °C in most of the reported methods), and the negative impact of the associated cost is further amplified if that energy comes from a non-renewable energy source. One way to address the cost-benefit relationship is to produce smaller CNTs from CO₂, which have a higher market value compared to larger CNTs. To achieve this goal, Douglas et al. re-designed the electrochemical reaction by combining an ALD grafted Ni anode with an Fe catalyst deposited stainless steel cathode to produce CO₂-based small CNTs (diameter ~10 nm) with a narrow size-distribution.⁴³ Further, they reported that the diameter of as-synthesized CNTs can be adjusted by

simply varying the thickness of the Fe catalyst on the cathode. Their calculation for a lab scale process demonstrates that it would cost \$50 to prepare 1 kg of CNTs, which is 2 times lower than the production cost of market products. The profit margin can be further improved if alumina is replaced by zirconia used for thermal insulation and using geothermal or carbon neutral energy sources.^{42,43} Demonstrating the flexibility of the molten salt electrolysis approach, Douglas et al. were able to use scrap materials (steel and brass) as the cathode materials to replace the stainless steel electrode to produce CCNTs. Using metal scrap materials may not only lower the cost of the overall process but it may also provide a solution to another environmental burden, low-value non-degradable waste accumulation.⁴² Joint research from the Licht and Pint groups showcased another advancement in the electrochemical lysis of CO₂, namely, solar thermal electrochemical process (STEP), whereby the process is heated and powered by photovoltaic cells.⁴¹ Such a research milieu may contribute to lowering the cost and commercializing the applications of molten salt electrolysis.

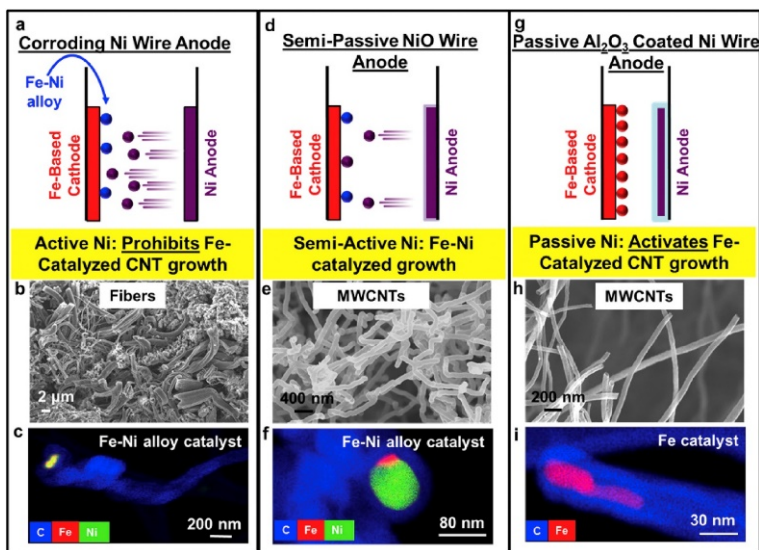


Figure 3. Schematic illustrations of the three anodes and their corrosive nature in electrolyte, SEM images of the carbons grown from each anode, and STEM EDS analysis of the catalysts left inside CNTs for (a-c) bare Ni anodes, (d-f) thermally passivated Ni anodes, and (g-i) ALD alumina passivated Ni anodes. Reproduced from ref⁴⁴. Copyright 2017 Elsevier.

In parallel, lowering the cost of the electrochemical method by substituting the expensive Li₂CO₃ electrolyte with earth abundant and inexpensive alternatives is attractive. As such, Hu et al.⁴⁰ were able to electrochemically deposit CCNTs at 750 °C with high quality and purity using molten CaCl₂-NaCl-CaO salts and a glassy carbon/graphite and RuO₂-TiO₂ electrode couple as shown in **Figure 4a**. In a similar attempt, Li and coworkers³⁹ reported the conversion of CO₂ to CNTs when Li-Ca-Ba and Li-Ba carbonates were used in **Figure 4b-c**. Furthermore, in a separate study, they demonstrated that CaCO₃, SrCO₃, and BaCO₃ could also be used as the electrolytes instead of expensive LiCO₃.³⁸ The structural properties of CNTs prepared with earth abundant alkaline carbonates were comparable with that made of LiCO₃.

2.3 Other carbon-based nanostructures

Beyond CNT-based structures, production of other nanostructures has also been reported by various groups, wherein CO₂ gas is utilized as the C-source.⁵⁵⁻⁶¹ Based on the same molten salt electrochemical method, Chen and coworkers were able to obtain a unique honeycomb-shaped porous structure made from nanosheets (**Figure 5a-b**).⁵⁵ One key difference in their method compared to the other prevailing electrochemical approaches is that they used Li₂CO₃-Na₂CO₃-K₂CO₃-Li₂SO₄ as the electrolyte, which enabled them to use a flue gas mixture containing SO₂ without pre-treatments.⁵⁵ In general, desulfurization of the flue gas mixture prior to introduction to the electrochemical system is a must as SO_x gases can have corrosive reactions with the electrochemical components, hence adding extra cost to the process. Moderate reaction conditions (475 °C and Ni/SnO₂ electrodes) combined with the novel electrolyte further enhances the cost-effectiveness of the method introduced by Chen et al. to convert flue gases into valuable nanomaterials. In a separate study, the same group successfully demonstrated the production of crystalline graphite (**Figure 5c**) at 775 °C using CO₂ and SO₂ flue gas mixture in a Li₂CO₃-Na₂CO₃-K₂CO₃-Li₂SO₄ electrolyte mediated electrochemical reaction.⁵⁶ The as-produced graphite showed the same honeycomb structure similar to their previous study (**Figure 5d-i**) and crystalline features appeared in the nanostructure as the reaction temperature increased, which was confirmed by powder X-ray diffraction (PXRD) patterns. Furthermore, Chen and coworkers claimed that their approach utilized the lowest temperature to produce catalyst-free graphite as other existing methods use temperatures of 3,000 °C and above, making their method strongly appealing.⁵⁶

Other morphologies such as carbon nanoparticles,⁵⁷ nano-onions,⁵⁸ and nano-platelets⁵⁹ have been derived from CO₂ following the molten carbonate electrochemical reaction as shown in **Figure 6a-c**. These carbon nanostructures hold a significant economic value compared to coal, especially the nano-onion structure, which is 20,000 times more valuable than coal according to Liu et al.⁵⁸ Furthermore, they estimated that the cost of preparation of carbon nano-onions in the molten carbonate electrolysis was \$1,000 per ton, which is significantly lower than other comparable methodologies.⁵⁸ Similar calculations for graphene platelets show \$1,000 profit with the CO₂-based graphene preparation method compared to the industrial methods.⁵⁹ The search for alternative and cost-effective routes to electrochemical conversion has revealed that direct reduction of CO₂ gas can form interesting nanostructures.^{60,61} One-step reduction of CO₂ by LiH involves moderate reaction conditions (addition of water, ball milling, or heating) to form porous nano-carbon structures within 30 s (**Figure 6d**). Another method developed by Baik et al. yielded graphene via thermal reduction of CO₂ in the presence of metallic Mg and Ni as shown in **Figure 6e**.⁶¹

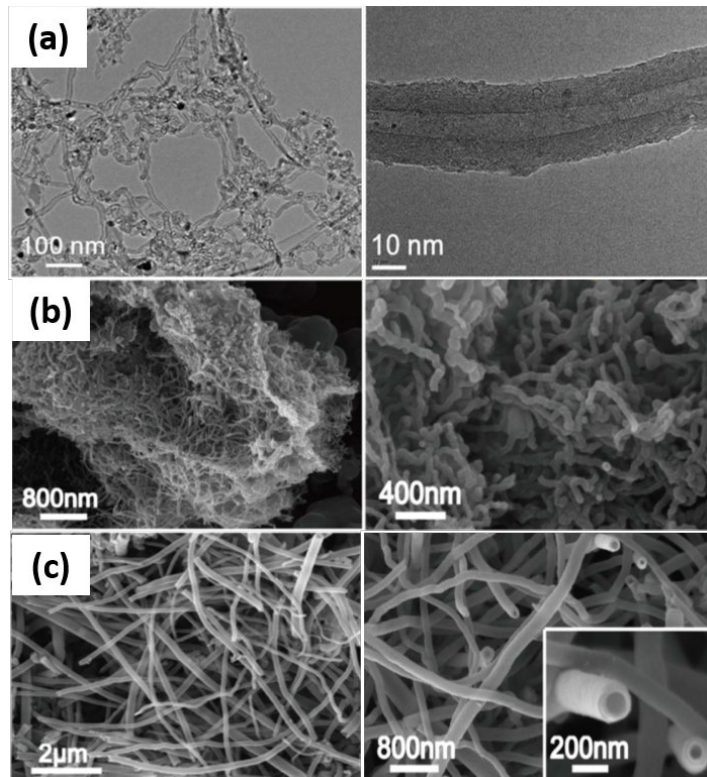


Figure 4. CNTs prepared using (a) molten $\text{CaCl}_2\text{-NaCl-CaO}$ salt-based electrochemical route. Reproduced from ref⁴⁰. Copyright 2017 Royal Society of Chemistry. (b) Li-Ca-Ba carbonates, and (c) Li-Ba carbonates. Reproduced from ref³⁹. Copyright 2018 Royal Society of Chemistry.

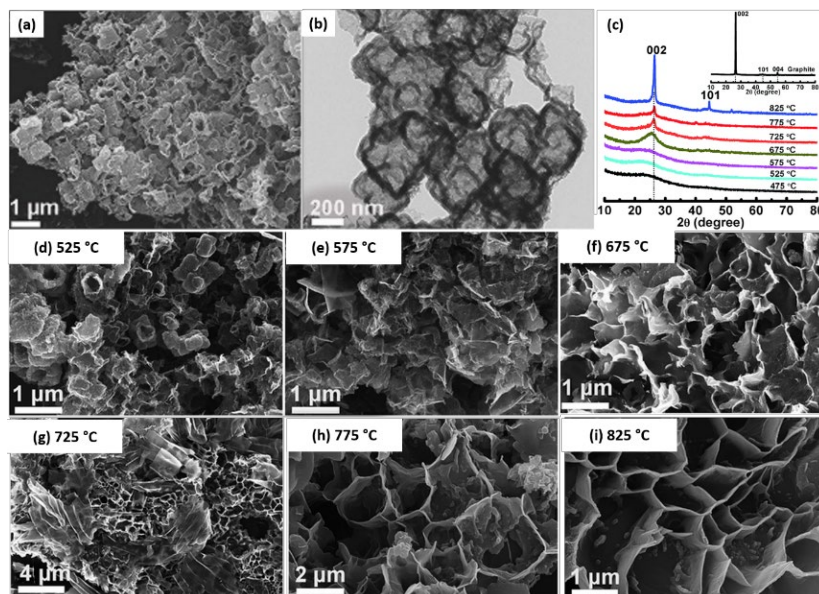


Figure 5. (a) SEM and (b) TEM images of the honeycomb-shaped nanostructure obtained from SO_2 containing flue gas mixture at 475 °C. Reproduced from ref⁵⁵. Copyright 2017 John Wiley and Sons. (c) Powder X-ray diffraction patterns, SEM images of the electrolytic carbon materials

obtained at (d) 525 °C, (e) 575 °C, (f) 675 °C, (g) 725 °C, (h) 775 °C, and (i) 825 °C. Reproduced from ref⁵⁶. Copyright 2017 Royal Society of Chemistry.

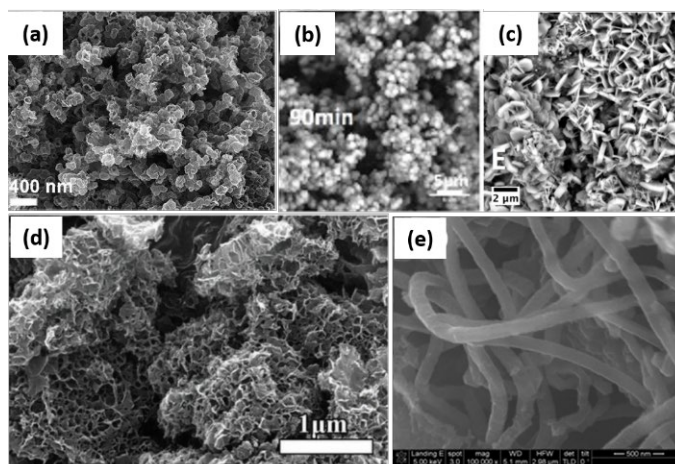


Figure 6. SEM images of (a) carbon nanoparticles, (b) nano-onions, and (c) nano-platelets produced from electrochemical conversion of CO₂ gas. Reproduced from ref⁵⁷⁻⁵⁹. Copyrights 2017 Elsevier, 2019 John Wiley and Sons, and 2020 Elsevier. (d) Porous nano-carbons, and (e) graphene obtained via LiH and Mg reduction of CO₂, respectively. Reproduced from ref^{60,61}. Copyrights 2020 John Wiley and Sons and 2020 Elsevier.

3. CO₂ Conversion into Inorganic Nanomaterials

In contrast to the significant progress made in CO₂ conversion into carbonaceous nanomaterials, there is a lack of methods developed to transform CO₂ into inorganic nanomaterials (**Table 2**). However, Li's group reported capturing CO₂ gas using amino acids and converting into NaHCO₃ nanostructures.⁶² Nanofibers and nanoflowers of NaHCO₃ have been obtained when CO₂ gas was reacted with glycine and alanine sodium salts, respectively.⁶² Carbon mineralization is another approach to capture, store, and convert CO₂ mostly into inorganic microstructures as shown in **Figure 7**. During carbon mineralization, CO₂ reacts with the earth abundant minerals of Ca or Mg to produce energetically favorable carbonates that can be easily stored long-term with less economic burden.⁶⁵⁻⁷⁰ However, production of CaCO₃ nanoparticles shown in **Figure 8a-b** was also reported, whereby CO₂ reacted at 50 °C with a mixture of choline chloride and calcium chloride, which is collectively called Calcoline.⁶³ In a separate study, the same researchers have shown the versatility of their one-step CO₂ capturing reaction to form “Apacite” (apatite-calcite) nanocomposites as shown in **Figure 8c-d**.⁶⁴ As-prepared Apacite nanocomposites are biocompatible nanomaterials, and thus can be used in biomedical applications as biomimetic materials for bone reconstruction and regeneration. A comparison of advantages and disadvantages of methods used to convert CO₂ into nanomaterials is presented in **Table 3**.

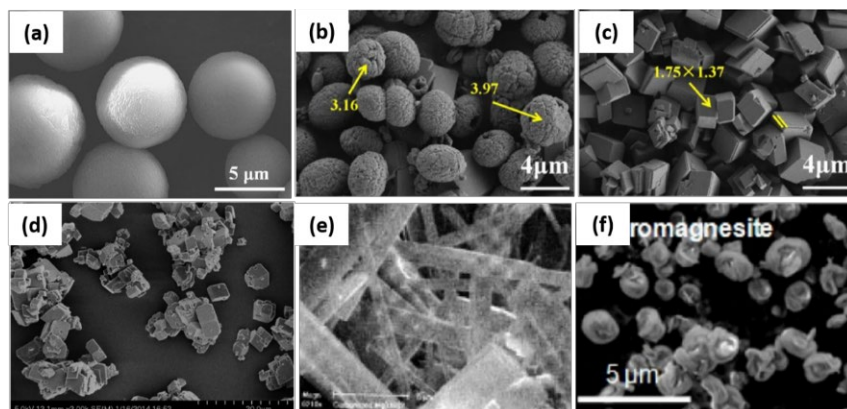


Figure 7. SEM images of CaCO_3 crystals obtained with CO_2 captured by (a) CaCl_2 and (b-c) $\text{Ca}(\text{OH})_2$, respectively. Reproduced from ref^{69,70}. Copyrights 2020 and 2021 Elsevier. SEM images of different microstructures of magnesium carbonates by carbon mineralization: (d) MgCO_3 , (e) $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, and (f) $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ obtained by capturing CO_2 with sodium salts of glycine and alanine. Reproduced from ref⁶⁶⁻⁶⁸. Copyrights 2003 John Wiley and Sons, 2014 American Chemical Society, and 2014 Royal Society of Chemistry.

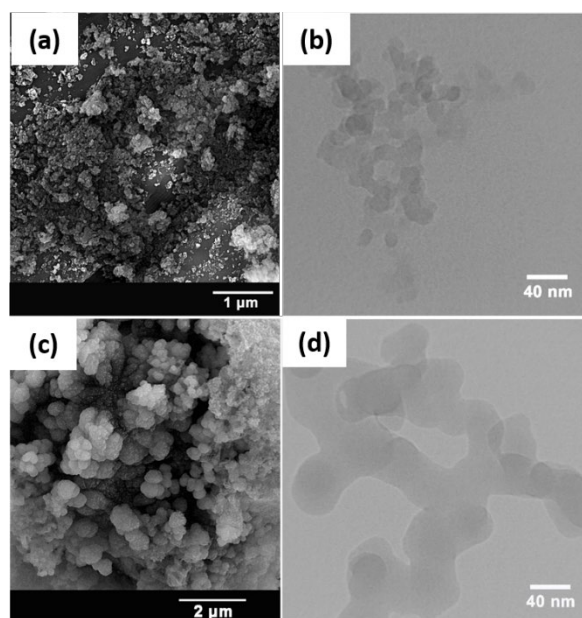


Figure 8. (a) FESEM and (b) TEM micrographs of CaCO_3 nanoparticles obtained from fresh Calcoline reacting with direct capture of CO_2 gas. Reproduced from ref⁶³. Copyright 2018 Elsevier. (c) FESEM micrograph, and (d) TEM micrograph Apacite nanocomposites. Reproduced from ref⁶⁴. Copyright 2018 Elsevier.

Table 3. Comparison of advantages and disadvantages of methods used to convert CO_2 into organic and inorganic nanomaterials.

Nanomaterial	Method	Pros	Cons	Ref
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Organic Nanomaterials				
CNT and CNF	CVD	<ul style="list-style-type: none"> • Versatile • Scalable • Extendable to fabricate a broad class of materials • Produced CNTs with high electrical and mechanical properties 	<ul style="list-style-type: none"> • Using CO₂ and argon gas mixtures • High temperature (800 °C) • Long reaction time (1-2 h) • Possible contamination by Mg/Ni catalysts 	36
		<ul style="list-style-type: none"> • Mild reaction conditions (500-700 °C, 1 atm) • Efficient catalyst • One-step reaction • Potential to be scaled up • Products with superior electrical properties 	<ul style="list-style-type: none"> • 100% CO₂ gas used • Long reaction time (1-2 h) • Possible contamination by Ni/NiCl₂ catalysts 	54
		<ul style="list-style-type: none"> • Tunable method to deposit other elements • Products resistant to high temperatures 	<ul style="list-style-type: none"> • Energy demanding process (500 and 600 °C) 	53
	Electrochemical method (molten carbonate electrolysis)	<ul style="list-style-type: none"> • Less energy demand as solar thermal energy is used to split CO₂ • Choice of using a variety of cheap electrodes to lower the operating cost • Pure oxygen generated as a byproduct 	<ul style="list-style-type: none"> • Producing mixed products • Wide size distribution in CNFs • Possible contamination by Ni/Al/Ir ions • High temperature to prepare the molten salt (700-800 °C) 	51,52
		<ul style="list-style-type: none"> • 100-fold cost reduction compared to CVD method • Morphology control over CNTs vs. CNFs • Direct conversion of atmospheric CO₂ • Potential of combining with cement industry to co-generate cement and CNTs 	<ul style="list-style-type: none"> • High temperature demand to prepare the molten salt (750 °C) • Possible contamination by Ni ions 	46-48,50

		<ul style="list-style-type: none"> • Possibility to grow CNT-based wool and magnetic CNTS 		
		<ul style="list-style-type: none"> • Hollow CNT production • First method to produce doped electrochemical CNTs • High conductive CNTs with boron doping • Reduced electrolyte cost as Li_2CO_3 partially replaced by other inorganic carbonates (Na_2CO_3, CaCO_3) • CO_2 the only consumable reactant • Overall process cheaper than CVD 	<ul style="list-style-type: none"> • Tangled and poly-dispersed CNTs formed • Low yield of CNTs when Li_2CO_3 is replaced with CaCO_3 • High reaction temperature (770°C) 	45,49
		<ul style="list-style-type: none"> • ALD electrodes produced highly crystalline, multi-walled CNTs • The ALD electrode resistant against electrochemical corrosion • High yield (99%) • Narrow size distribution 	<ul style="list-style-type: none"> • High reaction temperature (750°C) • Possible contamination by Ni, Cr, and Zn ions 	44
		<ul style="list-style-type: none"> • High valued CNTs with small diameters (10 nm) • Expensive electrodes replaced by metal scrap materials • Inexpensive approach 	<ul style="list-style-type: none"> • High reaction temperature (750°C) • Catalyst coarsening during long reaction time 	42,43
		<ul style="list-style-type: none"> • Low cost using cheap alternatives (Na, Ca, Sr, and Ba) • No Ni or other metal ion catalyst used 	<ul style="list-style-type: none"> • High reaction temperature (750°C) • Possible formation of carbon spheres 	38,40
Nanosheet	Electrochemical method	<ul style="list-style-type: none"> • Conversion of SO_2 containing flue gas without desulfurization 	<ul style="list-style-type: none"> • A boundary between cathode and anode required 	55

	(molten carbonate electrolysis)	<ul style="list-style-type: none"> • Cheap method as moderate temperature (475 °C) and Ni/SnO₂ electrodes were used • S-doped carbon nanostructures with high capacitance and cycling stability 	to avoid undesirable reactions of O ₂ with carbon or sulfide/sulfur.	
Honeycomb (graphite)	Electrochemical method (molten carbonate electrolysis)	<ul style="list-style-type: none"> • SO₂ containing flue gas mixture used 	<ul style="list-style-type: none"> • High temperature required to get crystalline products 	56
Carbon nanoparticles	Electrochemical method (molten carbonate electrolysis)	<ul style="list-style-type: none"> • High electrocatalytic active product 	<ul style="list-style-type: none"> • Long reaction time to dope sulfur in the molten salt (12 h) at 550 °C 	57
Nano-onions	Electrochemical method (molten carbonate electrolysis)	<ul style="list-style-type: none"> • High synthesis yield • More valuable products 	<ul style="list-style-type: none"> • High reaction temperature (770 °C) 	58
Nano-platelets	Electrochemical method (molten carbonate electrolysis)	<ul style="list-style-type: none"> • High yield production • Low electric potential (0.7-2 V) involved 	<ul style="list-style-type: none"> • High temperature reaction (770 °C) 	59
Porous nano-carbon	Reduction of CO ₂ by LiH	<ul style="list-style-type: none"> • Benign and efficient • Low temperature • Quick reaction time • Potential to scale up 	<ul style="list-style-type: none"> • Temperature up to 470 °C and pressurized CO₂ (1-30 bar) needed 	60
Graphene	Reduction of CO ₂ by metallic Mg and Ni	<ul style="list-style-type: none"> • Reduction at atmospheric pressure • One-step reaction • Improved electrochemical properties 	<ul style="list-style-type: none"> • High temperature demand (680 °C) 	61
Inorganic Nanomaterials				
Nanofibers and nano-flowers	CO ₂ to NaHCO ₃ conversion by amino acid salt solution	<ul style="list-style-type: none"> • Water-based solvent • Recyclable absorbent • Scalable • A quick process (30 min) at room temperature 	<ul style="list-style-type: none"> • Current studies are limited to pure CO₂ or flue gas 	62

		<ul style="list-style-type: none"> Value-added nanomaterials 		
CaCO ₃ nanoparticles	Conversion by choline chloride-calcium chloride (Calcoline) eutectic solution	<ul style="list-style-type: none"> Atmospheric CO₂ conversion at mild conditions (50 °C, 6 h) Value-added calcite products 	<ul style="list-style-type: none"> Considerable reduction (23%) in the recyclability of the choline solution after one cycle 	63,64

4. Potential Applications of CO₂-based Nanomaterials

Conversion of CO₂ into nanomaterials for energy and chemical industrial uses has been one of the driving forces in CCUS related research fields.^{36,41,45,46,53-55,58,59,61} As such, carbon nanotubes/foams from direct conversion of CO₂ have been used as electrode materials in the supercapacitor industry and shown excellent device performance with superior stability over 10,000 cycles.^{36,53,54} The excellent material properties such as light weight, high surface area, and high energy and power density of the CO₂-based nanomaterials are ascribed to their superior performance in energy storing devices. The physicochemical stability of the CO₂-based CNTs during post conversion processing has further enabled the material optimization and production of boron-coated CNTs with high-temperature oxidation tolerance. Such materials have potential applications in solid oxide fuel cells.⁵³ It has also been demonstrated that the ferromagnetic characteristics can be bestowed on CNTs to turn these materials into recoverable catalysts, which are useful in chemical industries.⁴⁶ Furthermore, CO₂-based CNTs can be used as composite materials,⁴⁹ conductive pastes,⁴⁵ and anodes in Li-ion batteries.⁴¹ Beyond CNTs, exploring the potential of other CO₂-based nanomaterials has been a topic of investigation.^{55,58,59,61} Particularly, graphene obtained from CO₂ conversion can be used as a lubricant, battery anode, or concrete additive.⁵⁹ Similar to CNTs, graphene has been chemically functionalized to prepare functional materials suitable for sulfur cathodes and thin interlayers of Li-S battery.⁶¹ Challenges related to energy and chemical uses in general are how to achieve high activity and selectivity for a specific application,^{24,28} and large-scale manufacturing at low cost is still a major challenge as well.

In contrast to energy and chemical applications, biological applications of CO₂ converted nanomaterials are limited. However, their potential in such a milieu can be inferred from the carbon-based nanomaterials, such as CNTs and graphene, which were obtained through regular synthetic routes. CNTs and graphene have been utilized in a wide range of biological applications including biosensing, drug and gene delivery, imaging, phototherapy, tissue engineering, and regenerative medicine (**Figure 9**).^{65,71} In particular, their superior physicochemical properties, such as higher surface area to volume ratio, electrical conductivity, and ease of chemical modification, provide a great platform to attach clinically relevant target molecules onto the carbon surface to design biosensors, namely, glucose,⁷² acetylcholine,⁷³ organophosphates,⁷⁴ DNA,⁷⁵ and various cancer diagnostic biomarkers.⁷⁶⁻⁷⁸ Similarly, selective targeting and sustained drug release of carbon nanomaterials offered ample opportunity to develop cancer drugs as well as gene

therapy.⁷⁹⁻⁸¹ Moreover, CNTs are capable of producing heat upon near infra-red (NIR) irradiation to inhibit tumors while CNT mediated photoacoustic imaging due to absorption in NIR enables monitoring the progress of the photothermal treatment (PTT).⁸² Similar PTT applications of graphene have also been reported for the destruction of cancer cells. The unique mechanical and electrical properties of carbon nanomaterials also make them ideal candidates in regenerative medicine applications.⁶⁵ Specifically, incorporation of CNTs and graphene into artificial composites can enhance the overall conductivity and flexibility of the composites, which in turn improves the signal transmission, growth, and functionality of the artificial tissues.⁸³

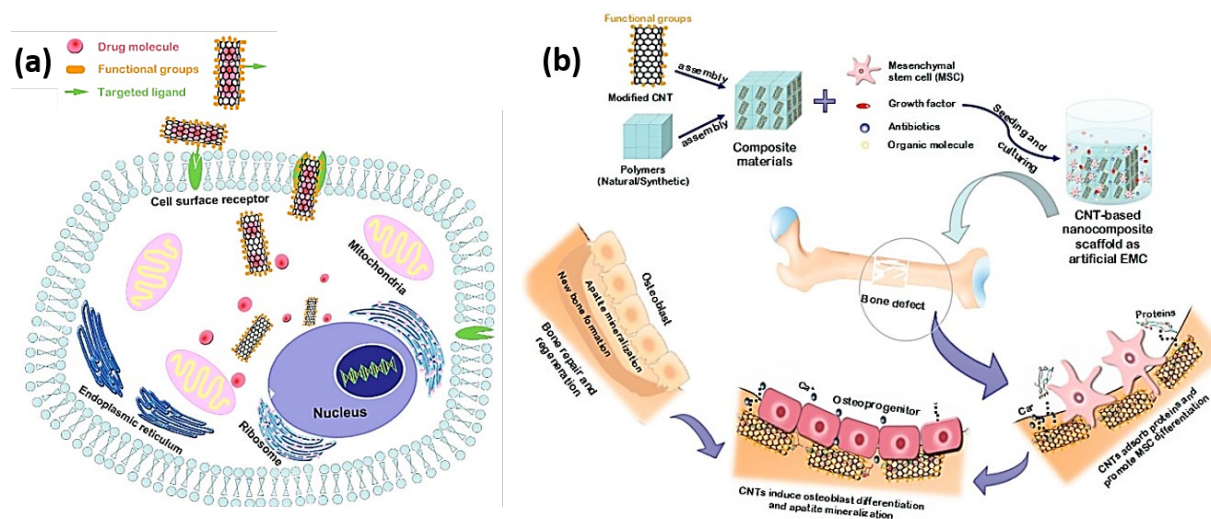


Figure 9. (a) A CNT-based drug delivery system. Due to the poor cell penetration of many small molecules and an increasing number of large molecules, CNTs functionalized with a targeted ligand were able to penetrate cell membranes through an ion channel and transport-specific drug molecules into targeted cells. (b) Schematic diagram describing the role of carbon nanotubes (CNTs) as scaffold composites in bone tissue engineering and regeneration. Adapted from ref⁶⁵. Copyright 2019 Creative Common CC BY license.

In contrast to the carbonaceous nanomaterials, inorganic nanomaterials from CO₂ hold great potential in a wide variety of biological applications due partly to their bulk counterparts such as sodium bicarbonate (baking soda) and calcium and magnesium carbonates, which have been utilized in various fields over many years. Baking soda is a well-known ingredient in bakery products and carbonated drinks, and an essential component in animal feed to regulate the rumen pH. Also, its applications can be found in non-food industries including cosmetics and personal care products, laundry detergents, and pigments. Due to its ability to release CO₂ gas upon decomposition, sodium bicarbonate is used in most dry fire extinguishers, and also as an inexpensive inorganic chemical blowing agent. In addition, previous studies have shown that sodium bicarbonate can absorb SO₂ and NO_x gases and hence it has been attractive as a sorbent material to purify flue gases.⁸⁴ Beyond the aforementioned uses of sodium bicarbonate, it has served as a biocompatible material in the pharmaceutical industry to treat metabolic acidosis, heartburn, and uric acid renal stones.^{85,86} Unique physical properties like abrasiveness have made sodium bicarbonate a suitable material to remove coatings in aerospace industry and more importantly, it is an irreplaceable dental biomaterial to treat and prevent oral diseases.⁸⁷ Multiple

in vitro, animal, and human studies have demonstrated antimicrobial effects of sodium bicarbonate against *Streptococcus mutans* and other Gram-negative bacteria associated with dental plaque biofilms.⁸⁸⁻⁹⁰ Moreover, the hardness of sodium bicarbonate is comparable with dentin, which further improves its biocompatibility as a dentifrice material to reduce oral bacterial plaque and gingivitis. In terms of prevention of caries, chemical properties of sodium bicarbonate play a vital role as a pH buffering agent to maintain critical pH of enamel after consumption of food causing enamel demineralization.⁸⁷ Therefore, both physical and chemical properties of sodium bicarbonate synergistically make it a superior biomaterial in oral hygiene. With current research in nanobiotechnology, unprecedented uses of sodium bicarbonate are revealed. It can be fabricated into nanofibers with polymers and drug molecules of interest to produce biodegradable drug carriers and artificial cell scaffolds, which can sustainably release encapsulated drugs at pH-sensitive locations by dissolving NaHCO₃ nanofibers, while providing a scaffold to grow new tissues (Figure 10).⁹¹

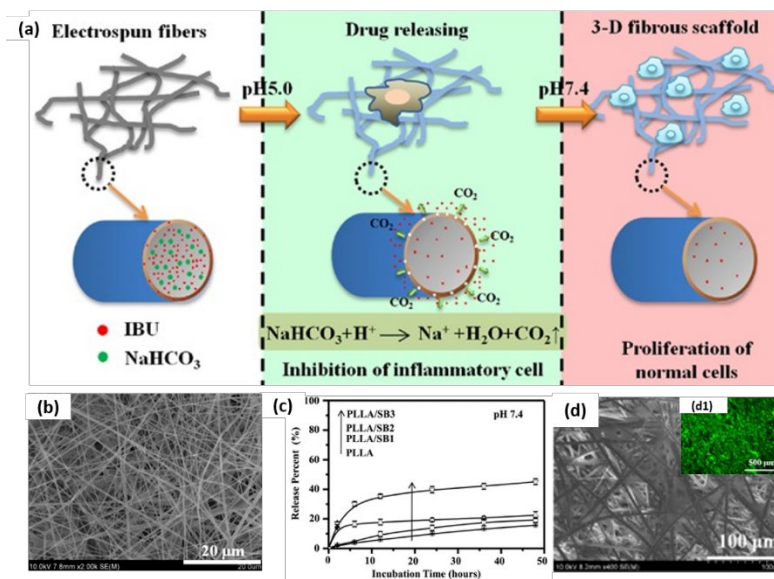


Figure 10. Schematic illustration of electrospun drug carrier and cell scaffold containing fibers of poly(L-lactide) (PLLA), sodium bicarbonate (SB), and ibuprofen (IBU) (a) and the corresponding SEM image (b), *in vitro* drug releasing profiles of different assembly with increasing SB content (c), and SEM image showing the cell growth on the scaffold. The inset (d1) shows dead/live cell assay of adhered cells. Reproduced from ref⁹¹. Copyright 2013 John Wiley and Sons.

Similarly, calcium carbonate and magnesium carbonate-based nanomaterials obtained from CO₂ conversion could have a potential to be used in many industries. In fact, CarbonCure Technologies is one of the North American cement and concrete industries, which was established based on CO₂ converted nano-limestone to meet the global demand with “greener cement,” while reducing the atmospheric emission of GHGs. With regard to biomedical applications, both calcium and magnesium carbonates are known materials in bone tissue engineering, even at bulk levels due to their favorable bioactivity and biocompatibility with negligible cell toxicity.⁹²⁻⁹⁵ As such, Li and coworkers⁹⁵ have prepared rhombohedron and fusiform shaped CaCO₃ nanoparticles to study their potential in osteogenesis. Their results suggest that there is a slight shape and dose dependent

viability effect on human bone-marrow mesenchymal stem cells (hBMSCs), while promoting osteogenic differentiation, growth of collagen, and osteogenesis-related genes significantly at low doses of calcium. Moreover, chemical and mechanical compatibility of CaCO_3 allows it to be integrated in nanocomposites with other bioactive materials like collagen, hydroxyapatite (HA), carbon nanofibers, and polymers to yield synergetic benefits.⁹²⁻⁹⁴ By forming hydroxyapatite-calcite (most stable polymorph of CaCO_3) nanocomposite, Kumar and coworkers⁹⁴ were able to overcome the poor bioresorbable property observed when only HA is used as the bone construction material. Also, Savelyeva et al.⁹³ coated vaterite (a polymorph of CaCO_3) on electrospun polymeric fibers to produce porous scaffolds to support and spread normal human dermal fibroblasts with no cytotoxicity as shown in **Figure 11**. Promising results of 3D-printed silica, carbon, and calcite composites by Memarian et al.⁹² showed great cell adhesion, growth, and osteogenic differentiation with MSCs. Interestingly, Karimi and coworkers⁶⁴ demonstrated that nano calcite can be obtained from atmospheric CO_2 to form apatite (apatite+calcite) nanocomposites, which were proven to have high bioactivity, non-toxicity, and osteogenic properties. Similar to CaCO_3 , nano MgCO_3 from CO_2 capture may have biological uses as MgCO_3 in bulk phase and nanostructures prepared using other methods have already shown cosmetic and bone regenerative applications.^{96,97}

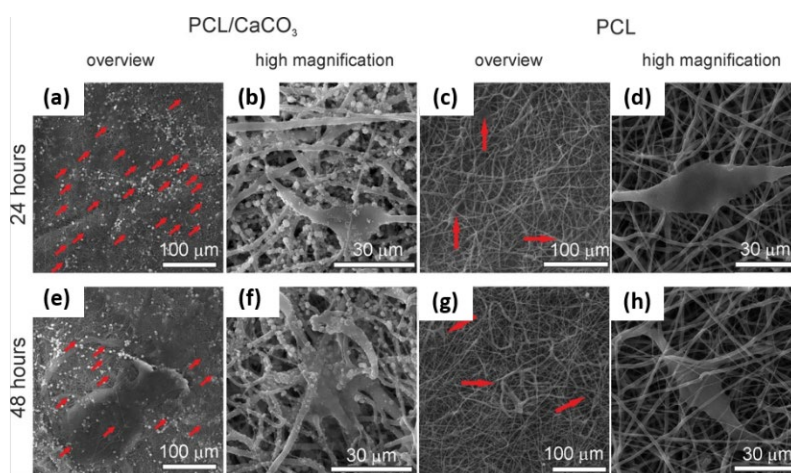


Figure 11. SEM images of polycaprolactone (PCL) and CaCO_3 scaffolds after culturing normal human dermal fibroblasts (NHDF) for 24 h (a, b) and 48 h (e, f); and control PCL scaffolds after culturing NHDF for 24 h (c, d) and 48 h (g, h). Red arrows highlight the cells. Reproduced from ref⁹³. Copyright 2017 John Wiley and Sons.

5. Challenges and Perspectives

In order to realize the applicability of CO_2 derived nanomaterials in biological systems, evaluating their biocompatibility through careful *in vitro* and *in vivo* toxicity studies is critical. It has been one of the hurdles carbon-based nanomaterials have had to overcome as numerous studies have shown their toxicity, especially those associated with CNTs. The main culprit of carbonaceous nanomaterial toxicity is reactive oxygen species (ROS) generation after exposure in biological systems, which initiates many adverse cytotoxic events such as DNA damage, lysosomal damage, and mitochondrial dysfunction that may lead to cell death as shown in **Figure 12**. Previous studies showed that the morphology, chemical properties, and even the reaction

conditions used to prepare carbon nanomaterials had a direct impact on their degree of toxicity. In particular, the dimension of the carbon-based nanomaterials such as CNTs has a direct correlation with its cytotoxicity. Generally, longer CNTs are more toxic than shorter ones as the shorter CNTs may be easily enveloped by macrophages whereas the longer ones tend to accumulate and intensify ROS production.⁹⁸ In contrast, thinner CNTs pose a higher risk as they can pierce cells compared to their thicker counterparts. Also, a greater oxidative stress has been observed with smaller carbon nanomaterials due to the higher surface activity.⁹⁹ Other morphological features such as shape may also impact cell viability. Spherical shaped nanomaterials such as fullerenes and carbon nanoparticles are comparatively safer than elongated versions as they could easily cause cell membrane damage.⁸³

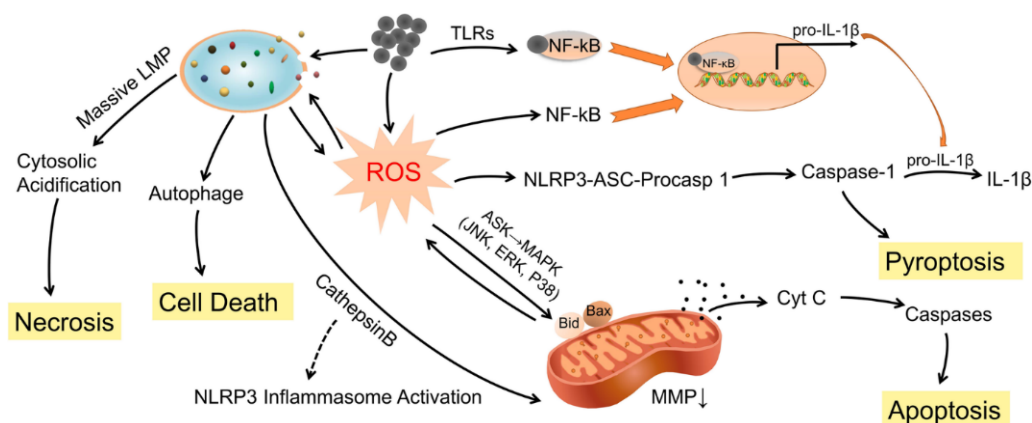


Figure 12. The mechanisms by which carbon-based nanoparticles induce cytotoxicity of macrophages. Exposure of macrophages to carbon nanomaterials triggers a cascade of cellular and molecular events, such as ROS generation and lysosome damage, which serve as the mechanisms underlying carbon nanomaterial-induced cell death, including necrosis, apoptosis and pyroptosis. Adapted from ref⁸³. Copyright 2019 Creative Common CC BY license.

One of the major challenges associated with carbon nanomaterials is their poor water solubility compared to the noble metal nanoparticles. In order to improve water solubility, which is a prerequisite for biological applications, chemical functionalization of CNTs is needed. According to previous reports, the functionalized CNTs show less toxicity compared to the intrinsic ones due partly to improved water solubility that leads to less aggregation within the *in vivo* systems.¹⁰⁰ Among many functional routes, PEGylation (-PEG) and carboxylation (-COOH) have attracted great interest due to the biocompatibility of as-functionalized materials. Specifically, PEGylated CNTs are prone to generate less ROS and hence are much safer for biomedical applications.⁸³ Another significant safety concern of carbon nanomaterials is related to how these nanomaterials were processed as metal impurities such because Fe and Ni used as the catalysts can pose serious health consequences. Generally, the CNTs obtained from different approaches have undergone several cycles of purification which could minimize the impurity levels; however, even trace amounts of Fe trapped within the CNTs could generate free radicals via the Fenton reaction and oxidative stress in cells.¹⁰¹ Therefore, it is important to produce carbon nanomaterials using metal-free catalysts if the products are intended to be used in theranostic applications.

Compared to carbon-based nanomaterials, inorganic nanomaterials from CO₂ capture and conversion have fewer safety concerns, since NaHCO₃, CaCO₃, and MgCO₃ are relatively less toxic and the excess can be easily excreted from a normal healthy body.¹⁰²⁻¹⁰⁵ However, possible cytotoxic effects due to unique structural properties at the nanoscale must be studied carefully before using them in biomedical fields. As such, Horie et al.¹⁰⁵ demonstrated that soluble CaCO₃ nanoparticles can cause intercellular calcium release but with negligible levels of ROS. In an adverse event, excess metal ion levels can be avoided by chelation therapy, whereby FDA approved chelating agents, like ethylenediaminetetraacetic acid (EDTA), which strongly bind to the metal ions. Regardless of the organic or inorganic nature of CO₂-based nanomaterials, detailed toxicology studies are needed before reaching their applications in biomedical fields as the industrial flue gases are contaminated with organic pollutants and toxic heavy metals, which could easily deteriorate the biocompatibility of pristine nanomaterials.

6. Conclusions

In this review, we focused on various methods of converting CO₂ into nanomaterials, which have potential applications in both biomedical and non-biomedical fields. Upon the cost-benefit analysis of each method, we weighed the operating conditions, such as temperature, pressure, and the requirement of pre-concentrating the flue gas, with respect to their potential benefits. One of the common advantages of CO₂-based nanomaterial synthetic processes is that the major reactant (i.e., CO₂) is an undesired byproduct of many industries, and hence is a readily available, cost-free starting material. However, the presence of organic pollutants and toxic metals, and energy intensive processes could impact the cost-benefit analysis. Our review also discussed the toxicity issues of CO₂ converted nanomaterials, which have to be addressed before employing this special class of materials in biomedical applications. Safety concerns are an important consideration for biomaterials used in biomedical fields opposed to the energy applications, mainly due to their physicochemical behavior. Additionally, there is a substantial lack of knowledge in toxicology of materials derived from CO₂ capture making it hard to recommend them as of now for biomedical applications. However, their potential in biological applications such as therapeutic, diagnostic, regenerative medicine, are very attractive and CO₂ conversion methods may be continuously refined to yield biocompatible products and future toxicology studies may clear the uncertainty.

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References

1. Manabe, S., Role of greenhouse gas in climate change. *Tellus A* **2019**, 71, (1), 1620078.
2. Davis, W. J., The relationship between atmospheric carbon dioxide concentration and global temperature for the last 425 million years. *Climate* **2017**, 5, (4), 76.
3. Abram, N. J.; McGregor, H. V.; Tierney, J. E.; Evans, M. N.; McKay, N. P.; Kaufman, D. S., Early onset of industrial-era warming across the oceans and continents. *Nature* **2016**, 536, (7617), 411–418.
4. Towers, S.; Chowell, G.; Hameed, R.; Jastrebski, M.; Khan, M.; Meeks, J.; Mubayi, A.; Harris, G., Climate change and influenza: the likelihood of early and severe influenza seasons following warmer than average winters. *PLoS Curr.* **2013**, 5.
5. Wang, L.; Yuan, X.; Xie, Z.; Wu, P.; Li, Y., Increasing flash droughts over China during the recent global warming hiatus. *Sci. Rep.* **2016**, 6, (1), 1–8.
6. AghaKouchak, A.; Feldman, D.; Hoerling, M.; Huxman, T.; Lund, J., Water and climate: Recognize anthropogenic drought. *Nature News* **2015**, 524, (7566), 409.
7. Abatzoglou, J. T.; Williams, A. P., Impact of anthropogenic climate change on wildfire across western US forests. *PNAS* **2016**, 113, (42), 11770–11775.
8. Mimura, N., Sea-level rise caused by climate change and its implications for society. *P. Jpn. Acad. B-Phys.* **2013**, 89, (7), 281–301.
9. Smith, M. R.; Myers, S. S., Impact of anthropogenic CO₂ emissions on global human nutrition. *Nat. Clim. Change* **2018**, 8, (9), 834–839.
10. Global Monitoring Laboratory. <https://www.esrl.noaa.gov/gmd/ccgg/trends/monthly.html> (accessed January 11,2021).
11. Revelle, R.; Suess, H. E., Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO₂ during the past decades. *Tellus* **1957**, 9, (1), 18–27.
12. Breidenich, C.; Magraw, D.; Rowley, A.; Rubin, J. W., The Kyoto protocol to the United Nations framework convention on climate change. *Am. J. Int. Law* **1998**, 92, (2), 315–331.
13. Li, B.; Duan, Y.; Luebke, D.; Morreale, B., Advances in CO₂ capture technology: A patent review. *Appl. Energy* **2013**, 102, 1439–1447.
14. Chung, Y. H.; Beiss, V.; Fiering, S. N.; Steinmetz, N. F., COVID-19 vaccine frontrunners and their nanotechnology design. *ACS Nano* **2020**, 14, (10), 12522–12537.
15. Wang, X.; Akhmedov, N. G.; Hopkinson, D.; Hoffman, J.; Duan, Y.; Egbebi, A.; Resnik, K.; Li, B., Phase change amino acid salt separates into CO₂-rich and CO₂-lean phases upon interacting with CO₂. *Appl. Energy* **2016**, 161, 41–47.
16. Huang, C.-H.; Tan, C.-S., A review: CO₂ utilization. *Aerosol Air Qual. Res.* **2014**, 14, (2), 480–499.
17. Lahijani, P.; Zainal, Z. A.; Mohammadi, M.; Mohamed, A. R., Conversion of the greenhouse gas CO₂ to the fuel gas CO via the Boudouard reaction: A review. *Renew. Sustain. Energy Rev.* **2015**, 41, 615–632.
18. Romanov, V.; Soong, Y.; Carney, C.; Rush, G. E.; Nielsen, B.; O'Connor, W., Mineralization of carbon dioxide: a literature review. *ChemBioEng Rev.* **2015**, 2, (4), 231–256.

19. Ganesh, I., Electrochemical conversion of carbon dioxide into renewable fuel chemicals—The role of nanomaterials and the commercialization. *Renew. Sustain. Energy Rev.* **2016**, *59*, 1269–1297.
20. Li, K.; Peng, B.; Peng, T., Recent advances in heterogeneous photocatalytic CO₂ conversion to solar fuels. *ACS Catal.* **2016**, *6*, (11), 7485–7527.
21. Alper, E.; Orhan, O. Y., CO₂ utilization: Developments in conversion processes. *Petroleum* **2017**, *3*, (1), 109–126.
22. Sharma, P. P.; Zhou, X. D., Electrocatalytic conversion of carbon dioxide to fuels: a review on the interaction between CO₂ and the liquid electrolyte. *Wiley Interdiscip. Rev. Energy Environ.* **2017**, *6*, (4), e239.
23. Zheng, Y.; Zhang, W.; Li, Y.; Chen, J.; Yu, B.; Wang, J.; Zhang, L.; Zhang, J., Energy related CO₂ conversion and utilization: advanced materials/nanomaterials, reaction mechanisms and technologies. *Nano Energy* **2017**, *40*, 512–539.
24. Al-Rowaili, F. N.; Jamal, A.; Ba Shammakh, M. S.; Rana, A., A review on recent advances for electrochemical reduction of carbon dioxide to methanol using metal–organic framework (MOF) and non-MOF catalysts: challenges and future prospects. *ACS Sustain. Chem. Eng.* **2018**, *6*, (12), 15895–15914.
25. Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W., Sustainable conversion of carbon dioxide: an integrated review of catalysis and life cycle assessment. *Chem. Rev.* **2018**, *118*, (2), 434–504.
26. Li, W.; Wang, H.; Jiang, X.; Zhu, J.; Liu, Z.; Guo, X.; Song, C., A short review of recent advances in CO₂ hydrogenation to hydrocarbons over heterogeneous catalysts. *RSC Adv.* **2018**, *8*, (14), 7651–7669.
27. Liu, M.; Gadikota, G., Integrated CO₂ capture, conversion, and storage to produce calcium carbonate using an amine looping strategy. *Energy Fuels* **2019**, *33*, (3), 1722–1733.
28. Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E.; Chan, K.; Hahn, C., Progress and perspectives of electrochemical CO₂ reduction on copper in aqueous electrolyte. *Chem. Rev.* **2019**, *119*, (12), 7610–7672.
29. Chauvy, R.; De Weireld, G., CO₂ Utilization technologies in Europe: A short review. *Energy Techn.* **2020**, *8*, (12), 2000627.
30. Wen, C.; Jiang, J.; Chilibi, C.; Tian, Z.; Xu, X.; Wu, J.; Wang, C.; Ma, L., Single-step selective conversion of carbon dioxide to aromatics over Na-Fe₃O₄/hierarchical HZSM-5 zeolite catalyst. *Energy Fuels* **2020**, *34*, (9), 11282–11289.
31. Lin, J.; Tian, W.; Zhang, H.; Duan, X.; Sun, H.; Wang, S., Graphitic carbon nitride-based Z-scheme structure for photocatalytic CO₂ reduction. *Energy Fuels* **2020**, *35*, (1), 7–24.
32. Liu, J.; Li, K.; Song, Y.; Song, C.; Guo, X., Selective hydrogenation of CO₂ to hydrocarbons: Effects of Fe₃O₄ particle size on reduction, carburization, and catalytic performance. *Energy Fuels* **2021**, *35*, (13), 10703–10709.
33. Murthy, P. S.; Liang, W.; Jiang, Y.; Huang, J., Cu-based nanocatalysts for CO₂ hydrogenation to methanol. *Energy Fuels* **2021**, *35*, (10), 8558–8584.
34. Tahir, M.; Ali Khan, A.; Tasleem, S.; Mansoor, R.; Fan, W. K., Titanium carbide (Ti₃C₂) MXene as a promising Co-catalyst for photocatalytic CO₂ conversion to energy-efficient fuels: A review. *Energy Fuels* **2021**, *35*, (13), 10374–10404.

35. Xue, Y.; Zhou, X.; Zhu, Y.; Chen, H., Rational construction of light-driven catalysts for CO₂ reduction. *Energy Fuels* **2021**, 35, (7), 5696–5715.
36. Wang, C.; Li, F.; Qu, H.; Wang, Y.; Yi, X.; Qiu, Y.; Zou, Z.; Luo, Y.; Yu, B., Fabrication of three dimensional carbon nanotube foam by direct conversion carbon dioxide and its application in supercapacitor. *Electrochim. Acta* **2015**, 158, 35–41.
37. Wu, H.; Li, Z.; Ji, D.; Liu, Y.; Li, L.; Yuan, D.; Zhang, Z.; Ren, J.; Lefler, M.; Wang, B., One-pot synthesis of nanostructured carbon materials from carbon dioxide via electrolysis in molten carbonate salts. *Carbon* **2016**, 106, 208–217.
38. Li, Z.; Wang, G.; Zhang, W.; Qiao, Z.; Wu, H., Carbon nanotubes synthesis from CO₂ based on the molten salts electrochemistry: effect of alkaline earth carbonate additives on the diameter of the carbon nanotubes. *J. Electrochem. Soc.* **2019**, 166, (10), D415.
39. Li, Z.; Yuan, D.; Wu, H.; Li, W.; Gu, D., A novel route to synthesize carbon spheres and carbon nanotubes from carbon dioxide in a molten carbonate electrolyzer. *Inorg. Chem. Front.* **2018**, 5, (1), 208–216.
40. Hu, L.; Song, Y.; Ge, J.; Zhu, J.; Han, Z.; Jiao, S., Electrochemical deposition of carbon nanotubes from CO₂ in CaCl₂–NaCl-based melts. *J. Mater. Chem. A* **2017**, 5, (13), 6219–6225.
41. Licht, S.; Douglas, A.; Ren, J.; Carter, R.; Lefler, M.; Pint, C. L., Carbon nanotubes produced from ambient carbon dioxide for environmentally sustainable lithium-ion and sodium-ion battery anodes. *ACS Cent. Sci.* **2016**, 2, (3), 162–168.
42. Douglas, A.; Muralidharan, N.; Carter, R.; Pint, C. L., Sustainable capture and conversion of carbon dioxide into valuable multiwalled carbon nanotubes using metal scrap materials. *ACS Sustain. Chem. Eng.* **2017**, 5, (8), 7104–7110.
43. Douglas, A.; Carter, R.; Li, M.; Pint, C. L., Toward small-diameter carbon nanotubes synthesized from captured carbon dioxide: critical role of catalyst coarsening. *ACS Appl. Mater. Interfaces* **2018**, 10, (22), 19010–19018.
44. Douglas, A.; Carter, R.; Muralidharan, N.; Oakes, L.; Pint, C. L., Iron catalyzed growth of crystalline multi-walled carbon nanotubes from ambient carbon dioxide mediated by molten carbonates. *Carbon* **2017**, 116, 572–578.
45. Wang, X.; Liu, X.; Licht, G.; Licht, S., Calcium metaborate induced thin walled carbon nanotube syntheses from CO₂ by molten carbonate electrolysis. *Sci. Rep.* **2020**, 10, (1), 1–7.
46. Wang, X.; Sharif, F.; Liu, X.; Licht, G.; Lefler, M.; Licht, S., Magnetic carbon nanotubes: Carbide nucleated electrochemical growth of ferromagnetic CNTs from CO₂. *J. CO₂ Util.* **2020**, 40, 101218.
47. Johnson, M.; Ren, J.; Lefler, M.; Licht, G.; Vicini, J.; Liu, X.; Licht, S., Carbon nanotube wools made directly from CO₂ by molten electrolysis: Value driven pathways to carbon dioxide greenhouse gas mitigation. *Mater. Today Energy* **2017**, 5, 230–236.
48. Licht, S., Co-production of cement and carbon nanotubes with a carbon negative footprint. *J. CO₂ Util.* **2017**, 18, 378–389.
49. Ren, J.; Johnson, M.; Singhal, R.; Licht, S., Transformation of the greenhouse gas CO₂ by molten electrolysis into a wide controlled selection of carbon nanotubes. *J. CO₂ Util.* **2017**, 18, 335–344.
50. Ren, J.; Licht, S., Tracking airborne CO₂ mitigation and low cost transformation into valuable carbon nanotubes. *Sci. Rep.* **2016**, 6, (1), 1–11.

51. Lau, J.; Dey, G.; Licht, S., Thermodynamic assessment of CO₂ to carbon nanofiber transformation for carbon sequestration in a combined cycle gas or a coal power plant. *Energy Convers. Manag.* **2016**, 122, 400–410.
52. Ren, J.; Li, F.-F.; Lau, J.; González-Urbina, L.; Licht, S., One-pot synthesis of carbon nanofibers from CO₂. *Nano Lett.* **2015**, 15, (9), 6142–6148.
53. Kim, G. M.; Choi, W. Y.; Park, J. H.; Jeong, S. J.; Hong, J.-E.; Jung, W.; Lee, J. W., Electrically conductive oxidation-resistant boron-coated carbon nanotubes derived from atmospheric CO₂ for use at high temperature. *ACS Appl. Nano Mater.* **2020**, 3, (9), 8592–8597.
54. Kim, G. M.; Lim, W.-G.; Kang, D.; Park, J. H.; Lee, H.; Lee, J.; Lee, J. W., Transformation of carbon dioxide into carbon nanotubes for enhanced ion transport and energy storage. *Nanoscale* **2020**, 12, (14), 7822–7833.
55. Chen, Z.; Deng, B.; Du, K.; Mao, X.; Zhu, H.; Xiao, W.; Wang, D., Flue-gas-derived sulfur-doped carbon with enhanced capacitance. *Adv. Sustain. Syst.* **2017**, 1, (6), 1700047.
56. Chen, Z.; Gu, Y.; Hu, L.; Xiao, W.; Mao, X.; Zhu, H.; Wang, D., Synthesis of nanostructured graphite via molten salt reduction of CO₂ and SO₂ at a relatively low temperature. *J. Mater. Chem. A* **2017**, 5, (39), 20603–20607.
57. Chen, Z.; Gu, Y.; Du, K.; Wang, X.; Xiao, W.; Mao, X.; Wang, D., Enhanced electrocatalysis performance of amorphous electrolytic carbon from CO₂ for oxygen reduction by surface modification in molten salt. *Electrochim. Acta* **2017**, 253, 248–256.
58. Liu, X.; Ren, J.; Licht, G.; Wang, X.; Licht, S., Carbon nano-onions made directly from CO₂ by molten electrolysis for greenhouse gas mitigation. *Adv. Sustain. Syst.* **2019**, 3, (10), 1900056.
59. Liu, X.; Wang, X.; Licht, G.; Licht, S., Transformation of the greenhouse gas carbon dioxide to graphene. *J. CO₂ Util.* **2020**, 36, 288–294.
60. Liang, C.; Pan, L.; Liang, S.; Xia, Y.; Liang, Z.; Gan, Y.; Huang, H.; Zhang, J.; Zhang, W., Ultraefficient conversion of CO₂ into morphology-controlled nanocarbons: A sustainable strategy toward greenhouse gas utilization. *Small* **2019**, 15, (33), 1902249.
61. Baik, S.; Park, J. H.; Lee, J. W., One-pot conversion of carbon dioxide to CNT-grafted graphene bifunctional for sulfur cathode and thin interlayer of Li–S battery. *Electrochim. Acta* **2020**, 330, 135264.
62. Li, B.; Wang, X.; Hopkinson, D.; Hoffman, J.; Egbebi, A.; Resnik, K. P., Amino acids react with carbon dioxide (CO₂) and form nanofibers and nanoflowers. US patent US10,583,388. Date of patent granted: March 10, 2020.
63. Karimi, M.; Jodaie, A.; Khajvandi, A.; Sadeghinik, A.; Jahandideh, R., In-situ capture and conversion of atmospheric CO₂ into nano-CaCO₃ using a novel pathway based on deep eutectic choline chloride-calcium chloride. *J. Environ. Manage.* **2018**, 206, 516–522.
64. Karimi, M.; Kalantarzadeh, R.; Saba, G.; Hafshejani, T. M.; Shamsi, M.; Jahangir, V.; Jodaie, A.; Sadeghinik, A., Apacite nanocomposites: A novel bioactive, biocompatible and osteogenic product originated from atmospheric carbon dioxide processed spontaneously in Calcoline. *Chem. Eng. J.* **2018**, 353, 679–688.
65. Pei, B.; Wang, W.; Dunne, N.; Li, X., Applications of carbon nanotubes in bone tissue regeneration and engineering: Superiority, concerns, current advancements, and prospects. *Nanomaterials* **2019**, 9, (10), 1501.

66. Gadikota, G.; Swanson, E. J.; Zhao, H.; Park, A.-H. A., Experimental design and data analysis for accurate estimation of reaction kinetics and conversion for carbon mineralization. *Ind. Eng. Chem. Res.* **2014**, 53, (16), 6664–6676.
67. Park, A. H. A.; Jadhav, R.; Fan, L. S., CO₂ mineral sequestration: chemically enhanced aqueous carbonation of serpentine. *Can. J. Chem. Eng.* **2003**, 81, (3-4), 885–890.
68. Swanson, E. J.; Fricker, K. J.; Sun, M.; Park, A.-H. A., Directed precipitation of hydrated and anhydrous magnesium carbonates for carbon storage. *Phys. Chem. Chem. Phys.* **2014**, 16, (42), 23440–23450.
69. Yang, T.; Fu, J.; Ma, L.; Du, H.; Yue, X.; Zhao, B.; Wang, C., Biomimetic synthesis of calcium carbonate under phenylalanine: Control of polymorph and morphology. *Mater. Sci. Eng. C* **2020**, 114, 111019.
70. Yang, C.; Yang, X.; Zhao, T.; Liu, F., An indirect CO₂ utilization for the crystallization control of CaCO₃ using alkylcarbonate. *J. CO₂ Util.* **2021**, 45, 101448.
71. Bekyarova, E.; Ni, Y.; Malarkey, E. B.; Montana, V.; McWilliams, J. L.; Haddon, R. C.; Parpura, V., Applications of carbon nanotubes in biotechnology and biomedicine. *J. Biomed. Nanotech.* **2005**, 1, (1), 3–17.
72. Patolsky, F.; Weizmann, Y.; Willner, I., Long-range electrical contacting of redox enzymes by SWCNT connectors. *Angew. Chem. Int.* **2004**, 116, (16), 2165–2169.
73. Ding, J.; Zhang, H.; Jia, F.; Qin, W.; Du, D., Assembly of carbon nanotubes on a nanoporous gold electrode for acetylcholinesterase biosensor design. *Sens. Actuators B Chem.* **2014**, 199, 284–290.
74. Zhang, Y.; Kang, T.-F.; Wan, Y.-W.; Chen, S.-Y., Gold nanoparticles-carbon nanotubes modified sensor for electrochemical determination of organophosphate pesticides. *Microchim. Acta* **2009**, 165, (3-4), 307–311.
75. Liang, Z.; Lao, R.; Wang, J.; Liu, Y.; Wang, L.; Huang, Q.; Song, S.; Li, G.; Fan, C., Solubilization of single-walled carbon nanotubes with single-stranded DNA generated from asymmetric PCR. *Int. J. Mol. Sci.* **2007**, 8, (7), 705–713.
76. Yu, S.; Cao, X.; Yu, M., Electrochemical immunoassay based on gold nanoparticles and reduced graphene oxide functionalized carbon ionic liquid electrode. *Microchem. J.* **2012**, 103, 125–130.
77. Han, J.; Ma, J.; Ma, Z., One-step synthesis of graphene oxide–thionine–Au nanocomposites and its application for electrochemical immunosensing. *Biosens. Bioelectron.* **2013**, 47, 243–247.
78. Kumar, S.; Kumar, S.; Srivastava, S.; Yadav, B. K.; Lee, S. H.; Sharma, J. G.; Doval, D. C.; Malhotra, B. D., Reduced graphene oxide modified smart conducting paper for cancer biosensor. *Biosens. Bioelectron.* **2015**, 73, 114–122.
79. Kang, B.; Li, J.; Chang, S.; Dai, M.; Ren, C.; Dai, Y.; Chen, D., Subcellular tracking of drug release from carbon nanotube vehicles in living cells. *Small* **2012**, 8, (5), 777–782.
80. Ji, Z.; Lin, G.; Lu, Q.; Meng, L.; Shen, X.; Dong, L.; Fu, C.; Zhang, X., Targeted therapy of SMMC-7721 liver cancer in vitro and in vivo with carbon nanotubes based drug delivery system. *J. Colloid Interface Sci.* **2012**, 365, (1), 143–149.
81. Taghavi, S.; Nia, A. H.; Abnous, K.; Ramezani, M., Polyethylenimine-functionalized carbon nanotubes tagged with AS1411 aptamer for combination gene and drug delivery into human gastric cancer cells. *Int. J. Pharm.* **2017**, 516, (1-2), 301–312.

82. Cheng, G.; Li, B., Nanoparticle-based photodynamic therapy: New trends in wound healing applications. *Mater. Today Adv.* **2020**, *6*, 100049.
83. Yuan, X.; Zhang, X.; Sun, L.; Wei, Y.; Wei, X., Cellular toxicity and immunological effects of carbon-based nanomaterials. *Part. Fibre Toxicol.* **2019**, *16*, (1), 1–27.
84. Wu, C.; Khang, S.-J.; Keener, T. C.; Lee, S.-K., A model for dry sodium bicarbonate duct injection flue gas desulfurization. *Adv. Environ. Res.* **2004**, *8*, (3-4), 655–666.
85. Adeva-Andany, M. M.; Fernández-Fernández, C.; Mouriño-Bayolo, D.; Castro-Quintela, E.; Domínguez-Montero, A., Sodium bicarbonate therapy in patients with metabolic acidosis. *Sci. World J.* **2014**, 2014.
86. Pinheiro, V. B.; Baxmann, A. C.; Tiselius, H.-G.; Heilberg, I. P., The effect of sodium bicarbonate upon urinary citrate excretion in calcium stone formers. *Urology* **2013**, *82*, (1), 33–37.
87. Myneni, S. R., Effect of baking soda in dentifrices on plaque removal. *J. Am. Dent. Assoc.* **2017**, *148*, (11), S4–S9.
88. Zambon, J.; Mather, M.; Gonzales, Y., A microbiological and clinical study of the safety and efficacy of baking-soda dentifrices. *Compend. Contin. Educ. Dent.* **1996**, *17*, (19), S39–44.
89. Tanzer, J.; Grant, L.; McMahan, T., Bicarbonate-based dental powder, fluoride, and saccharin inhibition of dental caries associated with *Streptococcus mutans* infection of rats. *J. Dent. Res.* **1988**, *67*, (6), 969–972.
90. Legier-Vargas, K.; Mundorff-Shrestha, S.; Featherstone, J.; Gwinner, L., Effects of sodium bicarbonate dentifrices on the levels of cariogenic bacteria in human saliva. *Caries Res.* **1995**, *29*, (2), 143–147.
91. Zhao, J.; Liu, S.; Li, B.; Yang, H.; Fan, C.; Cui, W., Stable acid-responsive electrospun biodegradable fibers as drug carriers and cell scaffolds. *Macromol. Biosci.* **2013**, *13*, (7), 885–892.
92. Memarian, P.; Sartor, F.; Bernardo, E.; Elsayed, H.; Ercan, B.; Delogu, L. G.; Zavan, B.; Isola, M., Osteogenic properties of 3D-printed silica-carbon-calcite composite scaffolds: Novel approach for personalized bone tissue regeneration. *Int. J. Mol. Sci.* **2021**, *22*, (2), 475.
93. Savelyeva, M. S.; Abalymov, A. A.; Lyubun, G. P.; Vidyasheva, I. V.; Yashchenok, A. M.; Douglas, T. E.; Gorin, D. A.; Parakhonskiy, B. V., Vaterite coatings on electrospun polymeric fibers for biomedical applications. *J. Biomed. Mater. Res. A* **2017**, *105*, (1), 94–103.
94. Kumar, G. S.; Giriya, E.; Thamizhavel, A.; Yokogawa, Y.; Kalkura, S. N., Synthesis and characterization of bioactive hydroxyapatite–calcite nanocomposite for biomedical applications. *J. Colloid Interface Sci.* **2010**, *349*, (1), 56–62.
95. Li, X.; Yang, X.; Liu, X.; He, W.; Huang, Q.; Li, S.; Feng, Q., Calcium carbonate nanoparticles promote osteogenesis compared to adipogenesis in human bone-marrow mesenchymal stem cells. *Prog. Nat. Sci. Mater. Int.* **2018**, *28*, (5), 598–608.
96. Åhlén, M.; Cheung, O.; Strømme, M., Amorphous mesoporous magnesium carbonate as a functional support for UV-blocking semiconductor nanoparticles for cosmetic applications. *ACS Omega* **2019**, *4*, (2), 4429–4436.
97. Yamasaki, Y.; Yoshida, Y.; Okazaki, M.; Shimazu, A.; Uchida, T.; Kubo, T.; Akagawa, Y.; Hamada, Y.; Takahashi, J.; Matsuura, N., Synthesis of functionally graded MgCO₃ apatite accelerating osteoblast adhesion. *J. Biomed. Mater. Res.* **2002**, *62*, (1), 99–105.

98. Sweeney, S.; Grandolfo, D.; Ruenraroengsak, P.; Tetley, T. D., Functional consequences for primary human alveolar macrophages following treatment with long, but not short, multiwalled carbon nanotubes. *Int. J. Nanomed.* **2015**, *10*, 3115.
99. Magrez, A.; Kasas, S.; Salicio, V.; Pasquier, N.; Seo, J. W.; Celio, M.; Catsicas, S.; Schwaller, B.; Forró, L., Cellular toxicity of carbon-based nanomaterials. *Nano Lett.* **2006**, *6*, (6), 1121–1125.
100. Sayes, C. M.; Liang, F.; Hudson, J. L.; Mendez, J.; Guo, W.; Beach, J. M.; Moore, V. C.; Doyle, C. D.; West, J. L.; Billups, W. E., Functionalization density dependence of single-walled carbon nanotubes cytotoxicity in vitro. *Toxicol. Lett.* **2006**, *161*, (2), 135–142.
101. Kagan, V.; Tyurina, Y.; Tyurin, V.; Konduru, N.; Potapovich, A.; Osipov, A.; Kisin, E.; Schwegler-Berry, D.; Mercer, R.; Castranova, V., Direct and indirect effects of single walled carbon nanotubes on RAW 264.7 macrophages: role of iron. *Toxicol. Lett.* **2006**, *165*, (1), 88–100.
102. d'Amora, M.; Liendo, F.; Deorsola, F. A.; Bensaid, S.; Giordani, S., Toxicological profile of calcium carbonate nanoparticles for industrial applications. *Colloids Surf. B Biointerfaces* **2020**, *190*, 110947.
103. Yang, W.; Yao, C.; Cui, Z.; Luo, D.; Lee, I. S.; Yao, J.; Chen, C.; Kong, X., Poly(acrylic acid)-regulated synthesis of rod-like calcium carbonate nanoparticles for inducing the osteogenic differentiation of MC3T3-E1 cells. *Int. J. Mol. Sci.* **2016**, *17*, (5).
104. Hanafy, N.; El-Kemary, M.; Loporatti, S., Optimizing CaCO₃ matrix might allow to raise their potential use in biomedical application. *J. Nanosci. Curr. Res* **2018**, *3*, (124), 2572–0813.1000124.
105. Horie, M.; Nishio, K.; Kato, H.; Endoh, S.; Fujita, K.; Nakamura, A.; Kinugasa, S.; Hagihara, Y.; Yoshida, Y.; Iwahashi, H., Evaluation of cellular influences caused by calcium carbonate nanoparticles. *Chem. Biol. Interact.* **2014**, *210*, 64–76.

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