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Nanoparticle applications in Algal-biorefinery for biofuel production

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ABSTRACT

Rapidly depleting fossil fuel resources and rising greenhouse gas emissions have accelerated the search for cost-effective renewable energy sources. Algal feedstock has long been touted as a potential source of several biofuels because of its renewable and sustainable features. However, despite ongoing efforts to develop low-cost technology and improve economic feasibility, biofuels derived from algae are still not yet commercially viable. Multifunctional nanoparticles (NPs) have been proposed as a strategy to enhance the prospect of commercializing algal-based biofuels. NPs synthesized by various routes can support different stages of algal biorefinery. Improvement of 20–30 % cell growth, 80–99 % harvesting efficiency, enhanced product extraction, and ~85–99 % conversion were achievable with NPs addition. This review provides a comprehensive outlook on the current and significant applications of NPs in the production of different algal-based biofuels such as biodiesel, bioethanol, biohydrogen, biogas, bioelectricity, and jet biofuel as well as in the implementation of algal biorefinery. The challenges, future trends, and the roadmap for further improvements in NP-assisted algal biofuels are also highlighted. Overall, this comprehensive review will help in understanding the recent advanced applications of nanoparticles in the production of algal biofuels.

1. Introduction

Fossil fuels have been the primary energy source since the industrial revolution. The Annual Energy Outlook 2021 has projected that the energy delivered across the end-use sectors in the US will increase by 25 % in 2050, and less than 20 quadrillions BTU will come from renewable energy [1]. Fossil fuels will continue to be the primary energy source [2], with the crude oil price estimated at $95/barrel in 2050 [1,3]. Despite the increasing number of countries pledging to meet the net zero GHG emissions target by 2050, very few have concrete and long-term strategies to meet this goal [4]. The G20 member countries, the world's largest and advanced economies are responsible for 80 % of global greenhouse gas (GHG) emissions. The development of mitigation strategies and alternative renewable fuels to counter the excessive appetite for fossil fuels has not only become increasingly critical, but also a moral obligation.

A total of 127.7 billion liters of biofuel are produced worldwide in 2014 [5] and 201 billion liters in 2020 [6]. To be more competitive, feedstock, product yield and quality, capital costs, logistics, and market acceptance, must be addressed [7,8]. Algal biofuels are promoted as the only cleaner fuel alternative, with a market share valued at $500 billion by 2050 [9]. Algae is environmentally-friendly and could reduce GHG emissions, with a positive economic impact if developed as an integrated

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List of abbreviations

Abbreviations

AC	Amorphous activated carbon
AC-nZVI	Aminoclay-nanoscale zerovalent iron
ACs	Aminoclays
AD	Anaerobic digestion
AFRA	Aviation fuel range alkanes
Ag	Silver
Al_2O_3	Aluminum oxide
APTES	(3-aminopropyl) triethoxysilane
Au	Gold
B	Boron
BEA	Beta zeolite
BMP	Biochemical methane potential
BP	Biophotolysis
BTU	British thermal units
$Ca(OCH_3)_2$	Calcium methoxide
Ca^{2+}	Cationic calcium
CaMgO	Calcium Magnesium Oxide
CaO	Calcium oxide
CD	Current density
CdS	Cadmium sulfide
CdSe	Cadmium selenide
CeAC	Cerium aminoclay
CeO_2	Cerium oxide
CF	Carbon felt
CH_3^-	Methoxide anions
CH_4	Methane
CNF	Carbon nanofiber
CNT	Carbon nanotube
Co	Cobalt
CO_2	Carbon dioxide
$CoCl_2$	Cobalt chloride
CPAM	Cationic polyacrylamide
Cr_2O_3	Chromium oxide
CTAB	Cetrimonium bromide
CuO	Copper oxide
DF	Dark fermentation
$DP-H_2$	Direct photolysis
EDLVO	Extended Derjaguin-Landau-Verwey-Overbeek
EIA	Energy Information Administration
FAME	Fatty acid methyl esters
Fe^0	Zero-valent iron
Fe_2O_3	Ferric oxide
Fe_3O_4	Ferrimagnetic magnetite
FFAs	Free fatty acids
GHG	Greenhouse gas
GM	Genetically modified
GO	Graphene oxide
GP	Graphite paste
GR	Fullerene, graphene
H_2	Hydrogen
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulfide
$H_3PW_{12}O_{40}$	Phosphotungstic acid
HED	High energy density HED
HG	Hybrid graphene
HUSY zeolite acid	Hierarchical H-style ultra-stable Y zeolite
IONPs	Bare iron-oxide NPs
$IP-H_2$	Indirect photolysis
LCA	Life cycle analysis
LHHW	Langmuir–Hinshelwood–Hougen–Watson
Li	Lithium
LSPR	Localized surface plasmon resonances
MA-MFC	Microalgal-assisted MFC
MFCs	Microbial fuel cells
MgO	Magnesium oxide
$MgSO_4$	Magnesium sulphate
MJ	Mega Joule
MnO_2	Manganese Oxide
MNPs	Magnetic nanoparticles
Mo	Molybdenum
MPa	Mega Pascal
NADH	Nicotinamide adenine dinucleotide
Nb_2O_5	Niobium oxide
NER	Net Energy Ratio
NFs	Nanofibers
NH_3	Ammonia
$(NH_4)_6Mo_7O_{24}$	Ammonium heptamolybdate
NHOC	Net heat of combustion
Ni	Nickel
$NiCl_2$	Nickel chloride
$NiFe_2O_4$	Nickel ferrite
NPs	Nanoparticles
NTs	Nanotubes
NWs	Nanowires
O_2	Oxygen
O^{-2}	Anionic oxygen
O_2^-/HOO●	Superoxide anion/free radicals
ORP	Oxidation-reduction potential
ORR	Oxygen reduction reaction
PBRs	Photobioreactors
PD	Power density
PDDA	Poly (diallyldimethylammonium chloride
PEG	Polyethylene glycol
PEI	Polyethylenimine
PEM	Proton exchange membrane
PES	Polyethersulfone
PF	Photo-fermentation
PNS	Non-sulfur photosynthetic bacteria
PP	Polypyrrole
Pt	Platinum
Pt/CC	Platinum coated carbon cloth
Pt–Ru/RGO	Reduced graphene oxide-supported platinum-ruthenium
PUFAs	Polyunsaturated fatty acids
QCHED	Quadricyclane High energy density
RGO	Reduced graphene oxide
Rh	Rhodium
ROL	*Rhizopus oryzae* lipase
ROS	Reactive oxygen species
SBA	Santa Barbara Amorphous
SFAs	Saturated fatty acid
SG	Sulfonated graphene
SGO	Sulfonated graphene oxide
SiC	Silicon carbide
SiO_2	Silicon dioxide
SO_3H	Sulfonic acid
SO_4/ZrO_2	Acidic sulfated zirconia
SrO	Strontium oxide
$SrTiO_3$	Strontium titanate
TAG	Triacylglycerol
TBD	Triazabicyclodecene
TIEs	Total input energies
TiO_2	Titanium oxide
VFAs	Volatile fatty acids
VS	Volatile solid
WO_3/ZrO_2	Tungstated zirconia
$Y_3Fe_5O_{12}$	Yttrium iron-oxide

ZnO	Zinc oxide	ZrO_2	Zirconium dioxide
ZnS	Zinc sulfide	ZSM5	Zeolite Socony Mobiles Number 5

biorefinery [10,11]. To achieve sustainability and economic feasibility, major obstacles in the upstream (algal strain selection, nutrient, and reactor optimization, supply of carbon dioxide, source of illumination) and downstream (harvesting, pretreatment, extraction, and conversion) processes have to be overcome [12,13].

The production cost of algal-based biodiesel at $2.76/L is still significantly higher than normal diesel at $0.6–1.22/L [14]. Based on techno-economic and life cycle analysis (LCA), the only option to scale up output is to utilize the biomass in an integrated biorefinery setup where every valuable product is extracted and valorized [15]. In addition to producing biofuels, algal biorefineries could also produce syngas, bio-oil, and valuable chemicals [16–22]. The key bottleneck can be solved by employing cost-effective, and scalable separation techniques [15]. Incorporating advances in nanotechnology, together with green chemistry and process engineering, opens the avenue for a more process-efficient and cost-effective industry [23–28]. Nanoparticles (NPs) could facilitate many processes to overcome critical challenges especially in the use of NPs in micronutrient supplementation [29], light backscattering [30], lipid synthesis enhancement [31], separation [2], flocculation [32], and catalysis [25].

Despite numerous studies conducted in the realm of algal biofuel and algal biorefinery based on NPs, the key question is whether this research domain has been thoroughly explored. Obvious gaps persist in the use of NPs to improve microalgal biofuel production and the feasibility of microalgal biorefinery. Specific areas of concern include production costs, energy consumption, product losses, and overall performance of microalgal biorefinery processes, as well as its environmental implications [33].

The novelty of the current review is in providing an outlook on recent advances in NPs applications in algal-based biofuel production such as biodiesel, bioethanol, biomethane, biogas, bioelectricity, and jet biofuel. Different aspects of improvement, including NPs-assisted algal cultivation, harvesting, extraction, and conversion, are discussed. The challenges and future directions of NPs engineering in a biorefinery with techno-economic analyses are highlighted. The updated information on the application of nanotechnology in algal biofuel production and algal biorefinery, and the expected outcomes from its implementation could provide base-line knowledge for more innovative research, development and commercialization.

2. Initiatives to develop algal biofuels

There are about 200,000–800,000 microalgal species that exist in nature, but only a few have been characterized and explored for research and commercial purposes [34]. Microalgae are single or multicellular, photosynthetically driven microorganisms that could live in harsh or mild environments, float in freshwater, seawater, or wastewater, and under sunlight or artificial light. Microalgae convert CO_2 to O_2 and produce sugar, lipids, and protein through photosynthetic respiration [35]. Microalgae production does not require fertile land, a large amount of fresh water, pesticides, or herbicides [36]. Closed photobioreactors and open raceway ponds are the two common ways of cultivation, requiring specific design for optimal algal growth [11].

Microalgae is the best third-generation feedstock for biofuel production because of its high and continuous growth, as well as the ability to grow on marine or wastewater while being integrated into CO_2 fixation [37]. Fig. 1 shows different types of algal biofuels and conversion methods [38]. Although the entire production chain, including culture selection [39,40] cultivation [2], harvesting and drying [41], pretreatment and extraction of biomass [17,42,43] and conversion to biofuels [2] has been extensively discussed, several limitations must be overcome to realize its commercialization. These challenges include:

- Environmental and economic issues of cultivation.
- Harvesting and dewatering of the biomass account for 20–30 % of the overall production costs. Cell-compatible, non-toxic, recyclable, and eco-friendly processes should be explored.
- Lipid extraction depends on species, cell wall characteristic, and the nature of lipids. Strategies should be developed to minimize the energy and time for product development.
- The high cost of conversion to final products must be reduced.
- Policies for practical implementation, and commercialization, particularly in developing countries, must be tackled.

Several companies in the USA, Europe, and other regions of the world, with a current share of about 78, 13, and 9 % of the global biofuel production capacity, respectively, have ventured into producing algal fuels on a commercial scale [44]. Companies such as Solazyme, Algenol, and Sapphire Energy have invested with a promise of producing millions of gallons of fuel in a short time [45]. Among the strategies is placing photobioreactors near CO_2 emissions sources for carbon capture [46]. Genetically-modified (GM) microalgae with improved characteristics and cellular metabolism could achieve enhanced lipid accumulation or specific valuable products and high CO_2 fixation. The GM microalgae, however, requires heavy investment to minimize the risk of contamination into the ecosystems [47]. The application of NPs is therefore a feasible route to improve the growth rate, cell metabolism, and productivity of algal-based biofuels.

3. Nanoparticle applications

Nanotechnology makes use of small particles (<100 nm) with nanostructures, which include nanotubes (NTs), nanofibers (NFs), nanowires (NWs), and nanoparticles (NPs) [48]. NPs represent a three-dimensional particle with a large surface area per unit volume but may or may not possess size-dependent features [27]. These give unique properties such as strong stability, ease of size and shape modification, tunable surface characteristics towards hydrophobicity or hydrophilicity, as well as being eco-friendly [27,49]. The synthesis of NPs via physical [50], chemical [51], and biological [52] routes have been explored. The biosynthesis method has big potential for further development [53]. NPs have found wide applications, including in bioenergy sector [54], with the production reaching about 58,000 tonnes in 2020, and the total market value is estimated to grow to $125 billion by 2025 [4].

NPs can be incorporated from algal cultivation to biofuel application in engines, attributable to their recyclability, stability, high storage capacity, and adsorption efficiency. The enhancement in catalytic performance, and biofuel yield, ultimately confers economic benefits [25,37]. Magnetic NPs (MNPs), NFs, and NTs as nanocatalysts could improve metabolic reactions [55], enhance anaerobic consortia activity and electron transfer, and reduce the effect of inhibitory chemicals [24]. Magnetite and maghemite are the most common NPs for bioenergy applications because of their magnetic characteristics, allowing reusability and easy recovery.

4. Nanoparticle-assisted algal biofuels

4.1. Biodiesel

Biodiesel based on Fatty acid methyl ester (FAME), is the most explored microalgal biofuel due to its renewability, high lubricity, and

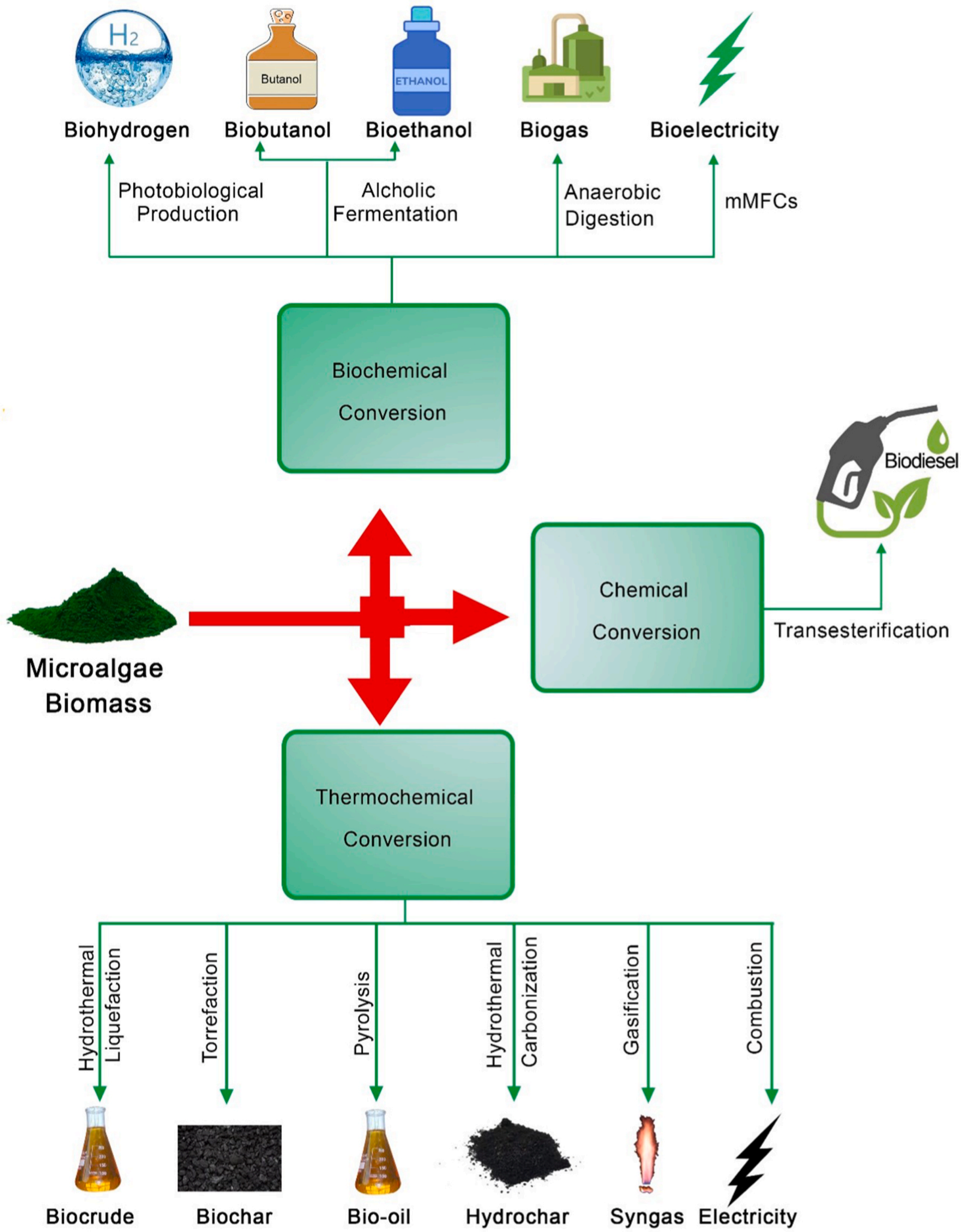

Fig. 1. Different types of algal biofuels and conversion methods (Modified from Ref. [38]. Under CCBY license).

sulfur-free and toxic-free properties [56]. Algal biofuel does not face the fuel-versus-food debate experienced by first-generation biofuels [57]. Microalgae have high lipid content (20–50 % dry cell weight) [58] and the triglycerides can be transformed into biofuels via transesterification, micro-emulsification, and pyrolysis (thermal cracking) [59]. Transesterification produces biodiesel commercially from various feedstocks [60], using homogeneous, heterogeneous, and magnetic catalysts [61]. Hydrochloric or sulfuric acids as homogeneous catalysts for esterification and transesterification processes, may require wastewater neutralization and catalyst recycling, and the high cost of corrosion-resistant equipment become the main concerns [62]. Conversely, heterogeneous nanocatalysts are gaining attention due to their potential for cost-effectiveness and recyclability [63].

Nanocatalysts with high specific surface area and activity exhibit both homogeneous (high activity) and heterogeneous (easy recovery) properties and could increase conversion efficiency, and the products are more environmentally-friendly [37,64]. The activity/selectivity depends on the metal type, content, size, shape, porosity, and acid-base properties, which can be controlled by modifying the physical characteristics [65]. The operating parameters that affect the transesterification process include temperature, time, catalyst type and dosage, alcohol/oil ratio, stirring rate, and the oil feedstock [66]. Metal oxide nanocatalysts [67,68], nanohydrotalcites [69,70], nanozeolites [71,72], and magnetic nanocatalysts [73–75] are efficient catalysts due to their high yield and selectivity [63].

Nanocatalysts can be categorized into acid, base, and bi-functional nanocatalysts. Acid nanocatalysts catalyze esterification and trans-esterification processes [76]. They may have lower activity but greater tolerance towards polar contaminants such as water and free fatty acids (FFAs). Acid nanocatalysts include zirconia [77], HUSY zeolite acid [78], and acidic sulfated zirconia (SO_4/ZrO_2) [79]. Nanodiamond, carbon nanotube (CNT), carbon nanofiber (CNF), fullerene, graphene (Gr), and graphene derivatives such as graphene oxide (GO), reduced graphene oxide (rGO), sulfonated graphene (SG), sulfonated graphene oxide (SGO), and amorphous activated carbon (AC) have exhibited outstanding physical, chemical, and mechanical properties [80]. Functionalized carbon-based catalysts with phenolic (–OH) and acidic (–COOH and –SO_3H) groups are promising solid catalysts [81,82]. GO is highly effective in catalyzing the conversion of lipids to biodiesel from wet microalgae biomass, with 96 % conversion efficiency with increasing catalyst content over 1–5 % [83]. SGO used to catalyze the transesterification of lipids from *Chlorella pyrenoidosa* attains conversion efficiency to FAME of 84.6 % as compared to only 48.6 % with SG. Despite a lower SO_3H content of 0.44 mmol/g in SGO as compared to 1.69 mmol/g in SG, the SGO catalyst contains higher hydrophilic hydroxyl content, resulting in higher conversion efficiency of lipids. With higher SO_3H content as compared to 0.38 mmol/g in GO, SGO also exhibits higher conversion efficiency than GO (of 73.1 %), although both have similar hydroxyl content [84]. Table 1 shows different types of catalysts for microalgae oil-to-biodiesel conversion, which includes metal oxides, molecular-sieve zeolites A [85], SrO-carbon-dot NPs [86], and WO_3/ZrO_2 [87]. Niobium oxide (Nb_2O_5) utilized in sequential reaction for direct conversion of *Monoraphidium contortum* lipid without requiring lyophilization or lipid extraction, attains 94.27 % FAME yield [88].

Basic nanocatalysts (mostly solid) show both Lewis and Brønsted basic activity centers, allowing them to donate electrons (e^-) or accept protons (H^+). Basic nanocatalysts could accelerate reactions under mild conditions, but pure oil is required [65]. $CaMgO/Al_2O_3$ catalysts exhibit the highest FAME yield of 85.3 % at 60 °C, 3 h, and up to 10 % loading (based on the weight of oil) in the transesterification of *N. oculata* oil [89]. Nano-$Ca(OCH_3)_2$ is an efficient solid catalyst with 99 % biodiesel yield from *Nannochloropsis* [90], while CaO nanocatalyst from waste eggshell has a yield of 92.03 % [91]. Pure MgO and CaO cannot achieve conversion in the transesterification of *N. oculata* oil, whereas the CaO/Al_2O_3 exhibits a biodiesel yield of 97.5 % and a methanol/lipid molar ratio of 30. Both basic site density and strength are shown to be important for high biodiesel yield [92].

A nano-CaO catalyst synthesized from waste eggshell for direct transesterification of *Chlorella pyrenoidosa* has attained 93.44 % FAME using 2.06 % wt./wt. catalyst at 60 °C and 3 h, with the catalyst being stable and reusable over six cycles [93]. When supercritical methanol-extracted *Chlorella vulgaris* CCAP lipids are treated with water and CaO/TiO_2 nanocatalyst, the overall FAME yield increases by 28.1 %,

Table 1
Performances of Nanocatalysts and catalytic conditions in microalgal-based biodiesel conversion.

Nanocatalysts		Microalgae species	Reaction conditions	Conversion efficiency (wt. %)	References
Type	Dosage		Time (h); temperature. (°C); pressure		
HBeta[a]	2 wt % of oil + methanol	*Nannochlorop[b]is gaditana*	4; 155; autoclave	25 (FAME)	[350]
HZSM-5[b]	2 wt % of oil + methanol		4; 155; autoclave	2 (FAME)	
Ni/HBeta	10 wt %	Microalgae oil	8; 260; 40 bar	100 (diesel-range alkanes)	[351]
			8; 260; 40 bar		
Ni/HZSM-5	10 wt %			100 (diesel-range alkanes)	
Nb_2O_5	10 wt %	*Monoraphidium contortum*	1; 200; –	94.27 (FAME)	[88]
Molecular sieve zeolite A	4.5 g catalyst/1 g algae	*Nannochloropsis oculata*	19; 60; atmospheric	~17	[85]
Graphene oxide	5 wt %	*Chlorella pyrenoidosa*	0.67; 90; –	95.1 (FAME)	[83]
Sulfonated graphene oxide	5 wt % of reaction mixture (1 g biomass)	*Chlorella pyrenoidosa*	0.67; 90; –	84.6 (lipid)	[84]
WO_3/ZrO_2	15 % wt./oil wt.	*Scenedesmus obliquus*	3; 100; -	94.58 (biodiesel)	[87]
SrO-carbon-dot NPs	0.3 g/g dried biomass	*Chlorella vulgaris*	0.042; 59.85; –	97 (FAME)	[86]
Al_2O_3/CaMgO	10 wt % of oil	*Nannochloropsis oculata*	3; 60; –	85.3 (FAME)	[89]
CaO	3 wt %	*Nannochloropsis* sp.	3; 80; –	99.0 (biodiesel)	[90]
80 wt% CaO/Al_2O_3	2 wt % of oil	*Nannochloropsis oculata*	4; 50; –	97.5 (biodiesel)	[92]
CaO	1.39 w/w %	*Chlorella vulgaris*	3; 70; –	92.03 (biodiesel)	[296]
CaO	2.06 % wt./wt. of reaction mixture	*Chlorella pyrenoidosa*	3; 60; –	93.44 (FAME)	[93]
CaO/TiO_2	200 mg/0.3 g biomass	*Chlorella vulgaris*	1; 260; 9.0–10.0 MPa	28.1 % (FAME)	[94]
CaO	3 mg/mL	*Chlorella vulgaris*	4; 80; –	~67 (FAME)	[352]
$SrTiO_3$	0.3 g/0.5 g dry cell weight	*Chlorella vulgaris*	1; 270; 9–10 MPa	16.65 (FAME)	[98]
MgO/ZSM-5	3 wt %	*Spirulina platensis*	1; 75; –	92.1 % (biodiesel)	[97]
Polye[c]hylene Glycol encapsulated $ZnOMn^{2+}$	3.5 % (w/w)	*Nannochloropsis oculata*	4; 60; –	87.5 (biodiesel)	[99]
TBD[c]-Fe_3O_4 @SiO_2	32.5 mg	*Chlorella vulgaris*	2; 65; –	97.1 (FAME)	[62]
Mg–Zr	10 wt % of dried biomass	*Nannochloropsis* sp.	4; 65; –	28 (FAME)	[96]
Fe_2O_3	1 % (w/w)	*Neochloris oleoabundans* UTEX 1185	6; 65; –	86.0 biodiesel)	[74]
Zn–Mg-ferrite magnetic NPs	0.12 g/g biomass	*Spirulina* sp.	1; 320; –	37.1 (bio crude oil)	[73]
Cellulase/lipase immobilized magnetic NPs	2 g	*Chlorella salina*	60; 45; –	93.56 (FAM[c])	[100]
Lipase-alkyl-gr[b]fted Fe_3O_4@ SiO_2	1203.11[a]U/g	*Chlorella vulgaris* ESP-31	48; 40; –	97.3 wt (oil)	[353]
RO Lipase/MNP-AP-GA	8.6 mg	*Chlorella vulgaris*	24; 45; –	69.8 wt (oil)	[101]

(–): Not available.
[a] Hierarchical beta zeolites.
[b] Hierarchical ZSM-5 zeolites.
[c] Triazabicyclodecene.

hydrocarbon by 2.5 times, and oxygenates by 3.8 times, as compared to control. The subcritical water could disrupt the cell wall of the biomass and facilitate the transfer of oil to the catalyst surface. Furthermore, intermediates have been formed on the catalyst surface, to accelerate the formation of FAME and other oxygenates [94].

Lipid transesterification using methanol and CaO nanocatalyst, as described by the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model, suggests that the reactants are adsorbed on the catalyst surface, then react to form products at the surface, and finally, the products are desorbed from the surface, following elementary kinetics. The transesterification reaction is a result of the reaction of anionic oxygen (O^{-2}) on the CaO surface. Electronegative cationic calcium (Ca^{2+}) is a relatively weak acid and the oxygen atom of CaO exhibits a strong basic property and serves as the basic site on the surface of CaO NPs. This allows a proton to be removed from the organic molecule to initiate the base-catalyzed reaction [95]. The first step in the transesterification reaction is the extraction of a proton (H^+) from methanol to form methoxide anions (CH_3^-), which attacks the triglyceride's carbonyl carbon (-COO), forming an alkoxycarbonyl intermediate. In the second step, the alkoxylcarbonyl intermediate is split into FAME and mono/di-glyceride anion [93].

The heterogeneous basic catalyst Mg–Zr converts *Nannochloropsis* sp. biomass directly to produce 28 % FAME at 10 wt. % catalysts (based on dry biomass) [96]. Triazabicyclodecene (TBD)-Fe_3O_4@silica NPs used in integrated harvesting and non-FFA oil transesterification of *Chlorella vulgaris* achieves 97.1 % FAME [62]. Other types of nanocatalysts for lipid-to-FAME transesterification include MgO/ZSM-5 [97], photochemically-synthetized $SrTiO_3$ [98], and polyethylene glycol (PEG) encapsulated $ZnOMn^{2+}$ [99].

Magnetic nanocatalysts (MNPs) with biocatalysts have been applied to produce biodiesel at a laboratory scale. MNPs may be the key route in industrial biodiesel production to reduce energy consumption, process costs, and waste generation. Oil extraction and direct conversion through inter-esterification of wet *Chlorella salina* oil to biodiesel have been investigated using cellulase and lipase immobilized on MNPs, with the catalytic property maintained over ten cycles [100]. *Rhizopus oryzae* lipase (ROL) loaded on Fe_3O_4 MNPs functionalized with 3-aminopropyl triethylenesilane, and 3-aminopropyl triethylenesilane-glutaraldehyde have boosted the biodiesel production from *Chlorella vulgaris*. The ROL/3-aminopropyl triethylenesilane-glutaraldehyde especially shows 69.8 % conversion, and the covalent bonding considerably reduces catalyst waste. After five cycles, the conversion rate is twice that of ROL/3-aminopropyl triethylenesilane and three times that of ROL/MNP [101]. Despite huge potential, the use of MNPs in biodiesel production has advantages and disadvantages depending on the operating parameters (temperature, time, catalyst load, and methanol/oil ratio), but ease of production and purification, catalyst reuse, and low waste generation remain the main challenges [63].

4.2. Bioethanol

Bioethanol could lead to improved engine performance, cleaner combustion, and greater biodegradability [102]. The feedstocks include sugarcane, corn, wheat, or barley (first-generation biofuel, mostly food-based), lignocellulosic biomass (second-generation) [103], and macroalgal biomass (third-generation) [104]. Corn is the dominant feedstock in the USA, while sugarcane is the main feedstock in Brazil [105]. Bioethanol from the fermentation of microalgal sugars [106] are attained from *Mycrocystis aeruginosa* [107], *Desmodesmus* sp. [108], *Chlorella minutissima* [109], *Nannochloropsis gaditana* [110], *Scenedesmus* sp. [111], *Chlorella* sp. [112], and *Chlorella vulgaris* [106], which are rich in carbohydrates. The main processes are pretreatment, enzymatic hydrolysis, fermentation, and ethanol purification [113]. These make microalgal-based production not currently commercially viable. The feedstock must be broken down to extract cellulose and hemicellulose, and contamination must be reduced during cultivation [103,113]. In the pretreatment stage, inhibitors such as phenolic compounds, carboxylic acids, and furans could disturb the metabolism of *Saccharomyces cerevisiae* and reduce the yield [114].

Immobilization of enzymes could address the problems of inhibitors [115], as the nano-immobilized enzymes have a higher surface-to-volume ratio [116]. Conversion of sugarcane leaves to ethanol is improved by immobilizing cellulase on MnO_2 NPs, with high stability as the enzyme retains 75 and 60 % binding efficiency and catalytic activity, respectively after five cycles. NPs provide a large surface for cellulase to bind to the active sites to increase conversion efficiency [117]. Cellulase immobilized on Fe_3O_4@SiO_2-GO nanocomposite has 80 % of the initial activity retained after eight cycles of reuse. The two distinct features of this nanocomposite are the high magnetic responses and specific surface area [118]. Immobilized β-galactosidase on SiO_2 NPs and co-immobilized cultures of *Saccharomyces cerevisiae* and *Kluyveromyces marxianus* for whey hydrolysis in a single-stage batch process produce 63.9 g/L bioethanol yield [119]. During hydrolysis, the immobilized β-galactosidase can be reused up to fifteen times without deterioration in activity. *Saccharomyces cerevisiae* immobilized in calcium alginate beads have the bioethanol yield increased by 100 %, whilst the yield is only 88 % with suspended cells [120].

Nanocomposites such as RGO-supported Pt–Ru (i.e., Pt–Ru/RGO) NPs promote the enhancement of biomass yield of *Chlorococcum minutum* and conver sugars into ethanol via dark fermentation using *Saccharomyces cerevisiae*.Tris-acetate phosphate medium containing1 mg/L of Pt–Ru/RGO NPs attain higher total chlorophyll (8.26 mg/L) and wet biomass (14.0 g/L) as compared to untreated cultures. Adding Pt–Ru/RGO NPs at 0.5 or 1 mg/L to the media enhances ethanol production from *C. minutum* to 32.6 and 31.2 g/L at 72 h, respectively. The use of Pt–Ru/RGO NPs improves biomass and ethanol production by stimulating, most likely, the electron transport in photosynthesis [121]. The Ni@ZnO@ZnS photo-nanocatalyst for bioethanol production and water treatment using *Spirulina platensis* achieves 96 % conversion efficiency with 0.4 L bioethanol/kg of dry photo-nanocatalyst [122]. Further studies are needed on NPs-assisted microalgal-bioethanol to realize commercial production.

4.3. Biohydrogen

Hydrogen (H_2) is a zero-carbon, high-density energy carrier with a calorific value of ~122 kJ/g and a heating efficacy of ~2.75 times that of hydrocarbon fuels [123]. It is clean as H_2 combustion produces only water. Different techniques to produce H_2 include coal and biomass gasification, natural gas reforming, water electrolysis, photobiological production, photoelectrolysis, high-temperature decomposition, and bacterial fermentation [124]. Fermentation is a better option than the thermochemical route as they are eco-friendly and cost-effective [20]. Microalgae is a viable source to produce H_2 [52,125] via biophotolysis (BP), photo-fermentation (PF), and dark fermentation (DF) [20, 125–128]. BP involves photoautotrophic cyanobacteria and microalgae, which split the water molecules, utilizing light to produce H_2 and O_2. There are two photolysis routes via BP: direct (DP-H_2) and indirect (IP–H_2). In the DP-H_2 route, H_2 is produced in anaerobic conditions through photosynthesis utilizing sunlight. The IP-H_2 route involves a photosynthetic route during the first stage with carbon fixation for cellular metabolism, producing electrons from nicotinamide adenine dinucleotide (NADH). In the second stage, the oxygen-sensitive hydrogenase enzyme is activated under anaerobic conditions while simultaneously generating H_2 using electrons provided by fermentation [129].

For PF-H_2 generation, microalgal biomass is utilized in the presence of light where the non-sulfur photosynthetic bacteria (PNS) such as *Rhodobacter* sp., *Clostridium* sp., *Rhodobacter sulfidophilus*, *Rhodopseudomonas palustris,* etc. exhibit robust activities [130]. The presence of key enzymes such as hydrogenase and nitrogenases involved in simultaneous nitrogen fixation as well as hydrogen evolution allows H_2 production during PF-H_2 [126]. During DF-H_2, different organic biomass can be utilized as a feedstock [131] where the DF-H_2 microbes utilize the substrates to biosynthesize pyruvate, which enters the acidogenic glycolytic pathway to produce H_2 [132]. It is a high-rate process that produces up to 4H_2 moles per mole of glucose [133]. However, as the H_2 concentration increases, there is a formation of reducing substrates such as acetone, ethanol, butanol, lactate, or alanine due to a metabolic shift, which could lower the H_2 productivity [26].

Each route has its own advantages and disadvantages, with various factors influencing the yield [128,131,134]. The major barriers to commercial-scale operations are the low H_2 yield and the high production cost [111,135]. Improving pretreatment and optimal process parameters could enhance bioavailability of simple sugars, and H_2 productivity. Genetic engineering and synthetic biology also significantly improve H_2 yield [20,128,132,136] but these are cost and labor-intensive, and time-consuming. The development of a new, simple, and cost-effective strategy is pertinent to attain greater hydrogen production rate [26].

NP applications could improve H_2 yield and rate [30,137,138]. Iron (Fe) [139], nickel (Ni) [127], and titanium oxide (TiO_2) NPs [140] elevate hydrogenase activity in PF-H_2. The addition of Fe NPs has led to increased microalgal biomass and photosynthetic pigments, which in turn increases H_2 generation [30]. With 200 mg/L zero-valent iron (Fe^0) NPs addition during dark fermentation, H_2 generation increases 6.5 times, with the specific H_2 yield of 20.25 mL/g volatile solids [138]. This is attributed to the fact that Fe^0 is a reductive agent that can quickly react with the oxidants within the broth to lower the oxidation-reduction potential (ORP), making the environment more favorable for H_2 producers [141]. The Fe^0 NPs could be ionized into ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions. Fe^{2+} stimulates the expression of functional genes such as hydrogenases and dehydrogenases [142], and ferredoxins and other hydrogenases, which are active during the H_2-producing metabolism, utilizing Fe^{2+} as critical ions [142].

Under PF-H_2, *Chlamydomonas reinhardtii* CC124 produces 45.2 % more H_2 with an average of 0.61 mL/L/h, higher than the control. The presence of SiO_2 NPs improves the *C. reinhardtii* CC124 cell growth, with a 23 % increase in chlorophyll, due to the improvements in light distribution [137]. The application of nickel ferrite ($NiFe_2O_4$) NPs induces fungal cellulase production for subsequent H_2 production during DF. Rice straw is hydrolyzed using cellulase enzyme catalyzed by $NiFe_2O_4$ NPs, to sugar hydrolysate. By utilizing *Bacillus subtilis* PF-1, a total of ~1820 mL H_2/L is produced via DF-H_2 [143]. Highly-efficient microalgal H_2 production makes use of a novel supercritical water gasification and chemical looping [144], but more integrated approaches must be developed using microbial consortium and two-stage systems [10,21].

4.4. Biogas

Anaerobic digestion (AD) is a sustainable process for producing methane-rich biogas [145] by converting organic matter through hydrolysis, acidogenesis, acetogenesis, and methanogenesis [146]. During hydrolysis, hydrolytic bacteria break down carbohydrates, lipids, and proteins into monomers. In the acidogenesis phase, the monomers are converted by fermentative bacteria, into volatile fatty acids (VFAs). With acetogenic bacteria during acetogenesis, the VFAs are converted to acetic acid, H_2, and CO_2. Methanogenic bacteria convert acetic acid and H_2 into methane (CH_4) and CO_2 in the final phase [147]. The composition of biogas is affected by the type of biomass, precursors, additives, and conversion method. Biogas is typically composed of CH_4 at 50–75 %, and CO_2 at 25–45 %, in addition to small amounts of N_2, H_2, H_2S, NH_3, and other volatile organic carbons, with an average calorific value of 21–24 MJ/m^3 [148].

Microalgal-based biogas production has great economic potential, especially if developed in a biorefinery [10,149,150]. Carbohydrates, lipids, and proteins of microalgal biomass can be processed with other organic wastes in AD [151]. The constituents of algal cell walls such as biopolymers, cellulose, and hemicellulose provide some resistance and could hamper AD processes. The intermolecular and intramolecular hydrogen bonding has made dissolving cellulose in typical solvents difficult, which limits the hydrolysis stage. The selection of enzymatic, chemical (acid or alkali), physical (microwave, shear force, or ultrasound), and thermal [152] pretreatment methods must be economical, with positive energy balance [153].

NPs can improve the solubility of feedstock, chemical modification of organic matter, and the release of biopolymeric components such as protein and carbohydrates [154,155]. Co, Ni, and Fe are essential micronutrients for many reactions, including those involving VFAs for the production of biogas, and the lysis of cells [156]. A high cumulative biogas yield may be achieved by combining pretreatment with NPs, leading to early dissolution of the algal cell wall and faster impact on microbial activities. Addition of 100 mg/L Fe_3O_4 NPs to organic waste in an AD for 60 days at 37 °C increase the biogas yield by 180 % and methane by 234 %, where Fe^{2+} disintegrates the organic materials and improves the production of biogas [157].

The use of Ni, Co, Fe_3O_4, and MgO NPs reduces the rigid cell wall of microalgal biomass and improves the bioenergy yield [158]. Microwave (MW) pretreatment coupled with Fe_3O_4 NPs enhances the dissolution of *Enteromorpha* cell walls, resulting in the highest yields of biogas, and H_2 (51.5 % v/v). At 10 mg/L Fe_3O_4 NPs, the cell wall disintegration is much improved, resulting in a 28 % increase in biogas yield [154]. The application of Ni, Co, and Fe_3O_4 NPs, in combination with autoclave, microwave, and ultrasonic pretreatment methods suggests that the synergistic effects of microwave and NPs significantly increase the biogas output [159].

The NPs could serve as electron donors or acceptors, and enhance the enzymic activities during biogas production [160]. The presence of Fe, Ni, and Co NPs successfully enhances the generation of methanogens in the digester sludge [161] and is required for anaerobic bacterial enzymic activities [162]. The Fe_2O_3 NPs as electron transfer conduits to methanogens enhance biogas generation of granular sludge during the AD treatment of beet sugar industrial wastewater [163]. At 30 mg/L of α-Fe_2O_3 NPs treatments of *Chlorella pyrenoidosa*, the biochemical methane potential (BMP) test demonstrates a 25.14 % increase in the biogas yield (605 mL/g VS_{fed}) and 22.4 % increase in methane content [149]. The micronutrients $NiCl_2$, Fe_2O_3, $(NH_4)_6Mo_7O_{24}$, $CoCl_2$, and their NPs affect biogas production from cattle waste slurry. All the NPs are shown to have a greater impact on the biogas than the micronutrients, but the $NiCl_2$ micronutrient and Ni NPs result in the highest biogas productivity [164]. With the introduction of Ni NPs, the rigid cell walls of *Chlorella vulgaris* are dissolved before bacterial disintegration [165]. More research is needed to find ways to overcome the inhibition caused by the presence of NPs in the ADs, especially on the methane-producing archaea in the microbial communities.

4.5. Microbial Fuel Cells

Microbial fuel cells (MFCs) could produce clean bioelectricity through a biocatalytic reaction by electroactive bacteria or yeast [166]. O_2-generating bioactive microalgae or microalgal-assisted MFC (MA-MFC) is a viable source of higher power output in comparison to regular MFC [167]. As shown in Fig. 2, the typical MA-MFC consists of an anode, a cathode, and an electric conductor that allows electrons to flow through a proton exchange membrane (PEM) for the transfer of protons [168]. The four basic processes of the MA-MFC are photosynthesis, electron transport to the anode, organic matter anodic oxidation by electrochemically active bacteria, and cathodic reduction of oxygen [169]. Generally, MA-MFCs can be configured in a single chamber, double chamber, dual chamber, and algal sediment [170]. A single chamber is the simplest configuration allowing microalgae to generate electricity within only one chamber [171]. Microalgae could typically be grown in the MA-MFC's anodic or cathodic chambers and utilized as

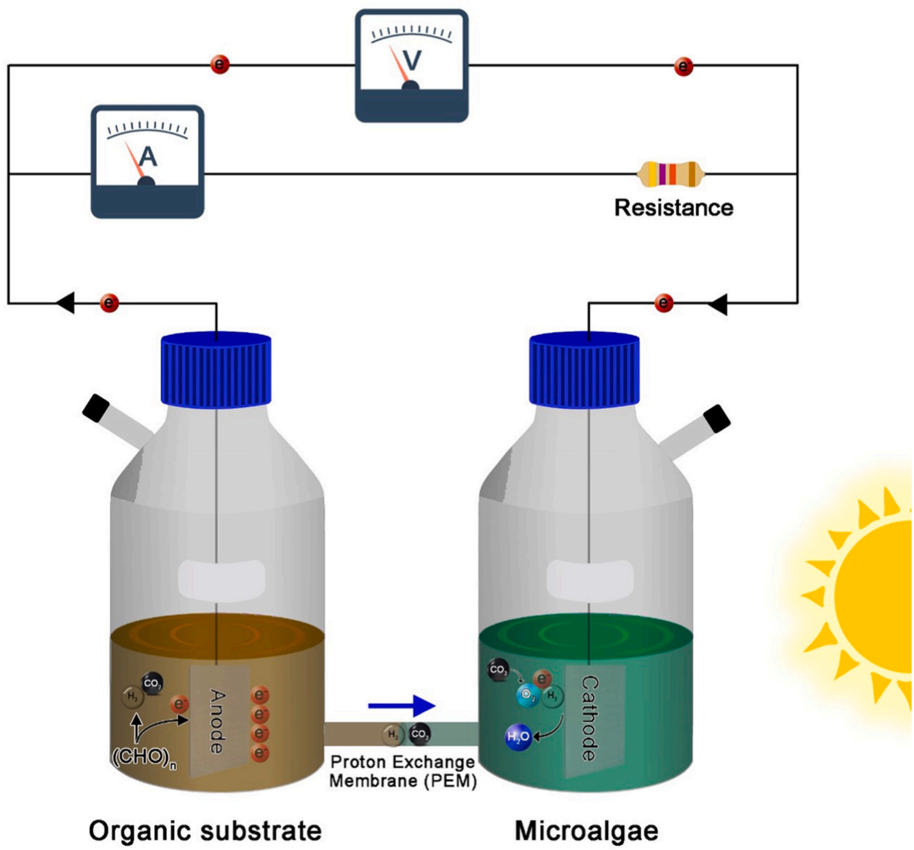

Fig. 2. Typical microalgae-assisted microbial fuel cell (MA-MFC).

bio-oxygenators to receive electrons in the cathodic chamber [172,173].

Chlorella vulgaris [172–174], *Chlorella pyrenoidosa* [175,176], *Scenedesmus obliquus* [177,178], *Oscillatoria* sp. [179], *Dunaliella tertiolecta* [180], *Spirulina* platensis [181], and mixed microalgae [182,183] have been utilized in the MA-MFCs. Factors such as temperature, pH, chlorophyll content, algal cell density, dissolved oxygen content, electrolyte materials, porosity, surface area, stability, as well as durability of the anode and cathode affect the overall energy output [27,170]. Lower costs, high-valued biomass, high CO_2 sequestration, high reaction rate, moderate operational conditions, and resistance to hazardous materials make MA-MFCs efficient and sustainable. However, there are still major limitations that hinder commercial application [184]. The materials of the MFC components must be carefully considered to avoid heat losses, which could limit the practicality of the MFC [185]. The fabrication of MFC utilizing nanomaterials has revolutionized the development of components, especially in the modification of cathode and anode to enhance performance, power density (PD), electron conductivity, thermal stability, oxygen reduction reaction (ORR) rate, anti-corrosion property, and cost [186,187]. Metallic NPs (such as Pt, Au, Ag, Pd, and Cu), metal-oxides (such as MnO_2, ZnO, CeO_2, TiO_2, Al_2O_3, and SiO_2), quantum dots (such as CdSe, ZnS, CdS) [185,188,189], graphene [190] and CNT [189] have been explored in MFC application.

Integration of CNT-Au-Pt nanocomposite in Osmium redox polymer and *Gluconabacter oxydans* DSM 2343 into carbon felt (CF) electrode achieve a maximum PD of 32.1 mW/m^2 and current density (CD) of 1.03 A/m^2 [189]. In *Shewanella putrefaciens* CN32 MFC, a developed 3D structured porous NiO/Gr nanocomposite anode exhibits a strong electrocatalytic capacity and achieves a maximum PD of 3.632 W/m^2 [191]. A dual chamber MFC equipped with TiO_2, or hybrid graphene (HG) modified cathodes to modify the graphite paste (GP) bare electrode has been developed using a green method. The MFC performance with the modified cathodes attains lower charge transfer resistance (R_{ct}), hence achieving a maximum PD of 80 mW/m^2 for GP-TiO_2 and 220 mW/m^2 for GP-HG, as compared to 30 mW/m^2 for the pristine GP electrode [192]. Polyethersulfone (PES) nanocomposites containing various Fe_3O_4 NPs have been utilized as PEM in MFC, achieving a maximum PD of 9.59 ± 1.18 mW/m^2 and CD of 38.38 ± 4.73 mA/m^2 at 20 wt. % NPs [193].

Oxygen mass transfer resistance, improper ion transfer, and elevated over potential may have a negative impact on the ORR at the cathode of MA-MFCs [194]. The cathodic ORR can be improved by catalysts developed and utilized during the cathode fabrication of the MA-MFCs. Platinum (Pt) is commonly used on the electrode surface of the chemical FCs as an efficient ORR catalyst [195]. However, Pt is costly and may exert toxic effect and inhibit algal growth [196]. Effective catalysts that can replace Pt to enhance ORR include transition metals along with their alloys, and metallic oxide NPs, as it poses high charge density [172, 197–199]. The $CuO/MnO_2/Fe_3O_4$, in combination with activated graphite (composite cathode) and Pt-coated carbon cloth (Pt/CC) cathodes provide the highest PD and CD, as well as algal growth of *Chlorella vulgaris* and electrocatalytic activity. In contrast, the Pt/CC electrode alone has failed and inhibited algal growth, while the composite cathode results in a PD of 6 W/m^2, a CD of 25 A/m^2, and a specific algal growth rate of 0.256/d [195].

Superoxide anion/free radicals (O_2^-/HOO•), hydrogen peroxide (H_2O_2), and other reactive oxygen species (ROS) produced by algal photosynthesis can be electron acceptors for power generation [200]. However, most cathode materials do not efficiently adsorb ROS, and high power density supercapacitors with high charge/discharge rates and long cycle lifetimes are used to alter the cathode of MA-MFCs [201]. A significant level of electrochemical activity has been reported using ZnO–NiO modified rGO for ORR in the MA-MFC cathode. The MA-MFC PD of 31.92 and 20.18 mW/m^2, respectively, are obtained utilizing petaline and spongy ZnO–NiO@rGO. The improved electrochemical performance is partially attributed to the increased ROS adsorption capacity of ZnO–NiO@rGO cathodes [202]. Silver NP on activated carbon composite (Ag NPs@AC) is a new catalyst for cathodic reaction, which could attain the potential of 1000 mV, and a maximum PD of 22.5 W/m^2 in MFC based on *Spirulina platensis* biomass as facile feed for the microorganisms in seawater [203]. The major challenge that could decrease the efficiency of the MA-MFC is the limited digestibility of microalgal cell walls. Further research is required to determine the potential of the NPs on the MA-MFCs, assess their leaching to the solution over time, and evaluate the long-term performance at a larger scale. Substantial research has focused on improving the electrode material capacitance [204] and the specific surface area [205]. However, the interactions between algae and the cathode are not well understood.

4.6. Jet biofuel

Between 2005 and 2010, the total consumption of jet fuel is in the range of 5–6 million barrels/day, with an average cost of $320/t in 2004, and $1005/t in 2011. The US Energy Information Administration (EIA) estimates that the jet fuel cost will increase to $2.82/gallon in the next 30 years. This could result in 3.1 billion tons of GHG emission by 2050, compared to 0.78 billion tons in 2015 [206]. Jet biofuel therefore has a high potential to reduce dependence on fossil fuels and CO_2 emissions. Based on the American Society for Testing and Materials, compatibility and thermal oxidation stability, combustion characteristics, low freezing point and low-temperature fluidity, fuel volatility, and metering are important considerations for jet biofuel [207]. The future feedstocks include microalgae, and genetically-modified organisms and non-biological feedstocks (CO_2, renewable electricity, and water). Microalgae have exhibited higher yield of jet fuel at 91 t/ha/year, followed by oil palm at 19.2 t/ha/year [206]. Marine microalgal species such as *Schizochytrium* sp, *Nannochloropsis* sp, *Botryococcus braunii*, *Nitzschia* sp., and *Neochloris oleoabundans* can technically be advantageous for effective jet biofuel production as compared to other oil crops due to abundant amounts of triacylglycerol (TAG). However, the production is not yet commercially viable due to the high operation cost [208].

Typically, jet fuel consists of olefins, iso-paraffins, aromatic components, n-paraffins, and naphthenes. Cyclic components and the aromatics can be formed via wood catalytic liquefaction and pyrolysis. For bio-oil, the phenolic compounds can be hydro-deoxygenated and split into cyclic and aromatic compounds. For algal and vegetable oils, the fatty acids and their esters could produce naphtha fractions, >C9 hydrocarbons, diesel, and kerosene (C9–C14). These fatty acids and oils can be separately hydrocracked, deoxygenated, and hydroisomerized to form hydrocarbons in the range of jet fuel [209]. The factors influencing product characteristics from hydroprocessing of fatty acids, and their esters using various catalysts include reaction conditions, feedstock type, and catalyst properties. To produce jet fuels through hydroconversion process, bifunctional catalysts with both metal and acid functions are necessary. The metal function assists with hydrogenation/dehydrogenation and hydroconversion, while the acidity is essential for cracking and isomerization [210]. To reduce the jet fuel production cost, the metal type and particle size, reducibility of the metal, acidity of the catalyst, high selectivity, and lifetime cycle of the catalysts, must be optimal. Morphologically, mesoporous or nanosized catalyst are more advantageous [211]. The addition of MNPs to liquid fuels has a catalytic effect resulting in enhanced burning rate, shorter ignition delay, and lower emissions [212].

Metal catalysts supported on SiO_2/SO_4, 18Ni–Mo supported catalyst, 9 bimetal and trioic acid supported on SBA-15 catalyst (SBA = Santa Barbara Amorphous), 6Co–Mo metal impregnated natural zeolite, 19 ZSM5 zeolite (zeolite Socony Mobiles Number 5), 20 zeolite-Al_2O_3 composites supported NiMo catalyst have all been reported for the catalytic hydrocracking of vegetable oil to produce bio-gasoline and jet biofuel [213,214]. A two-step method uses 1 wt. % Pt/Al_2O_3 in the first step to produce long-chain hydrocarbons from palm oil, and the second step uses bulk and nanosized Pt supported on ZSM-5 and Beta on the first-step product where the nanosized catalysts exhibits better performance. The composition of 1 wt. % Pt/Al_2O_3, followed by 1 wt% Pt/nano-Beta zeolite enhance the yield of jet fuel (54.8 wt %) with iso/n-paraffin (I/N) ratio of 7 [215]. To improve mass transfer properties in acidic zeolites, 10 wt. % Ni is loaded on nanosheet ZSM-5 for oleic acid hydroconversion at 250 °C under 10 bar hydrogen to yield the aviation fuel range alkanes (AFRA) at 51 % with 97 % carbon balance [216]. The reaction with Ni supported on $H_3PW_{12}O_{40}$/nanosized hydroxyapatite in a single step at 360 °C under 30 bar hydrogen has resulted in product yields from Jatropha and palm oil exceeding 80 wt. % [217]. The addition of nano-sized Al or B to produce nanofluids or gelled fuels may be effective to increase the high energy density (HED) of jet fuel, which determines the flight range, load, and performance of the aircraft [218]. The addition of 25 wt. % of nano Al or nano-B in synthetic HED (HD-1) or quadricyclane HED (QC HED) fuels achieves a high density of 1.1–1.25 g/cm^3 and high volumetric net heat of combustion (NHOC) of 42.8–62.9 MJ/L, with shortened ignition delay, reduced fuel oxygen demand, and increased combustion efficiency [219].

Jet fuel with high iso-alkane content and strong acidity can be produced by loading $H_3PW_{12}O_{40}$ (HPW) on a Ni (meso-Y)-based hierarchical zeolite. The catalytic conversion of microalgal biodiesel at 255 °C with an increase of 2 MPa hydrogen (63.1 %) has significantly increased iso-alkane (20.5 %), and arene at 11.1 % [220]. The co-production of jet biofuel and high-value PUFAs from *Schizochytrium* sp. has also been reported. After separation of PUFAs by short-path distillation after transesterification, the remaining saturated fatty acids (SFAs) are catalytically deoxygenated over Pt/γ-Al_2O_3, followed by hydrocracking over Pt/mesoporous BEA zeolite (Pt/mesoBEA) catalyst to attain 20.4 wt% of jet biofuel with 54.6 wt% of PUFA-enriched esters (purity: 87.7 %) [221], this could possibly improve the economics in a biorefinery setup. The hydrodeoxygenation of algal oil to jet fuel using Pt, Rh, and pre-sulfided NiMo catalysts could lead to high hydrocarbon yield (76.5 %) and possible energy-saving through heat supply [222]. The nanoparticle-assisted algal jet biofuel production however has not been comprehensively researched especially on the nanocatalyst selection and design for optimal performance.

5. Biosynthesized nanoparticles

Green biosynthesis of NPs is gaining attention as it is more eco-friendly [223]. Biosynthesis of the NPs from various biological sources has been comprehensively reviewed [223,224], utilizing biosystems such as bacteria [225], fungi [226], plant extracts [227,228] seaweeds [229,230], yeast [231,232] and marine algae [225,233]. NPs may be produced intracellularly or extracellularly and released into the reaction media and can be separated by physical methods [234]. Compounds in the media, with functional groups such as carbonyl, hydroxyl, alkaloids, terpenoids, phenolics, and amines, as well as proteins, pigments, starch, chitosan, and laurate, may act as reducing or capping agents to stimulate the formation of metallic NPs [235] and prevent NPs aggregation [236]. Nitrate reductase for example is found to play a role in the biosynthesis of the Ag NPs under specific conditions [237].

The ability of algae to collect metals and reduce metal ions makes it an excellent alternative route for the NPs biosynthesis or as nano-bio factories where dead and dried live biomass are used for the biosynthesis of metallic NPs. The synthesis can be at ambient temperature and pressure, normal pH value, and in a simple aqueous medium. The different methods for the biosynthesis of algal-based NPs include the utilization of live algal cells for NPs synthesis, algal cell lysis, followed by filtration and centrifugation, and NP harvesting from algal broth supernatants [238,239]. Table 2 summarizes the different species of algae used for the biosynthesis of different metallic NPs. Different shapes of the Ag NPs have been synthesized by algal species such as *Chlorococcum humicola, Nannochloropsis oculata, Euglena gracilis*, and

Table 2
Different types of nanoparticles biosynthesized by different species of algae (Modified from Refs. [239,240]. Under CCBY license).

Algae species	Nanoparticles type
Bifurcaria bifurcata	Copper(II) oxide (CuO NPs)
Galaxaura elongata	Gold NPs (Au NPs)
Sargassum plagiophyllum	Silver chloride (AgCl NPs)
Ulva fasciata	Zinc oxide (ZnO NPs)
Turbinaria conoides	Gold NPs (Au NPs)
Jania rubens	Ferrimagnetic magnetite (Fe_3O_4 NPs)
Portieria hornemannii	Silver (Ag NPs)
Acanthophora specifera	
Amphiroa fragilissima	
Oscillatoria limnetica	
Caulerpa racemosa	
Caulerpa serrulata	
Chlorella pyrenoidosa	
Chlorella vulgaris	
Chlorococcum humicola	

Scenedesmus sp [240]. The different factors affecting the biosynthesis of algal Ag NPs include biomass, extract or precursor concentration, pH, temperature, illumination, and reaction time [241].

The applications of biosynthesized NPs have a significant impact on the economic viability of algal-based products such as biomass and other bioactive compounds [25,31,242–244]. The harvesting efficiency has reached 97 % in *Chlorella lobophora* and *Chlorococcum oleofaciens*, with the utilization of biosynthesized Ag NPs [245]. A low concentration of biosynthesized ZnO NPs (50 mg/L) increases *C. vulgaris* biomass and lipid synthesis as compared to the control, with the SFAs and PUFAs levels increasing by ~16 % and ~59 %, respectively, while the unsaturated fatty acids declined by ~20 % [31]. The *C. vulgaris* biomass treated with increased Ag NP from 50 μg/g to 150 μg/g-biomass has the lipid extraction level increased from 8.44 % to 17.68 %, and the carbohydrates level enhanced to 13.8 % [234]. The primary site for the NPs interaction is the cell wall [246], and an increase in Ag NP concentrations makes more small-sized NPs readily available to make strong contact with the cell wall, adhere to and cover the surface to rapidly rupture the cell membrane by lysing the molecules in the cell wall to form "pits/holes" hence facilitating the release of intracellular molecules [247]. The fabrication of biogenic NPs from wastes and other forms of biomass will improve the overall microalgal biorefinery processes and is a major step towards the intensification of biofuel research.

6. Nanoparticle-assisted algal biorefinery

The biorefinery set-up utilizing renewable resources aims to be a viable alternative to typical oil refinery with fossil fuels [248]. The use of microalgal biomass for the production of bioproducts within a biorefinery framework has yet to attain economic feasibility [15]. The typical algal biorefinery, as shown in Fig. 3, involves upstream and downstream processes [17,244,249–251]. The applications of nanotechnology could address some major challenges in achieving economic viability especially in providing solutions in biomass cultivation [252], biochemical compounds accumulation and enhancement [31,244],

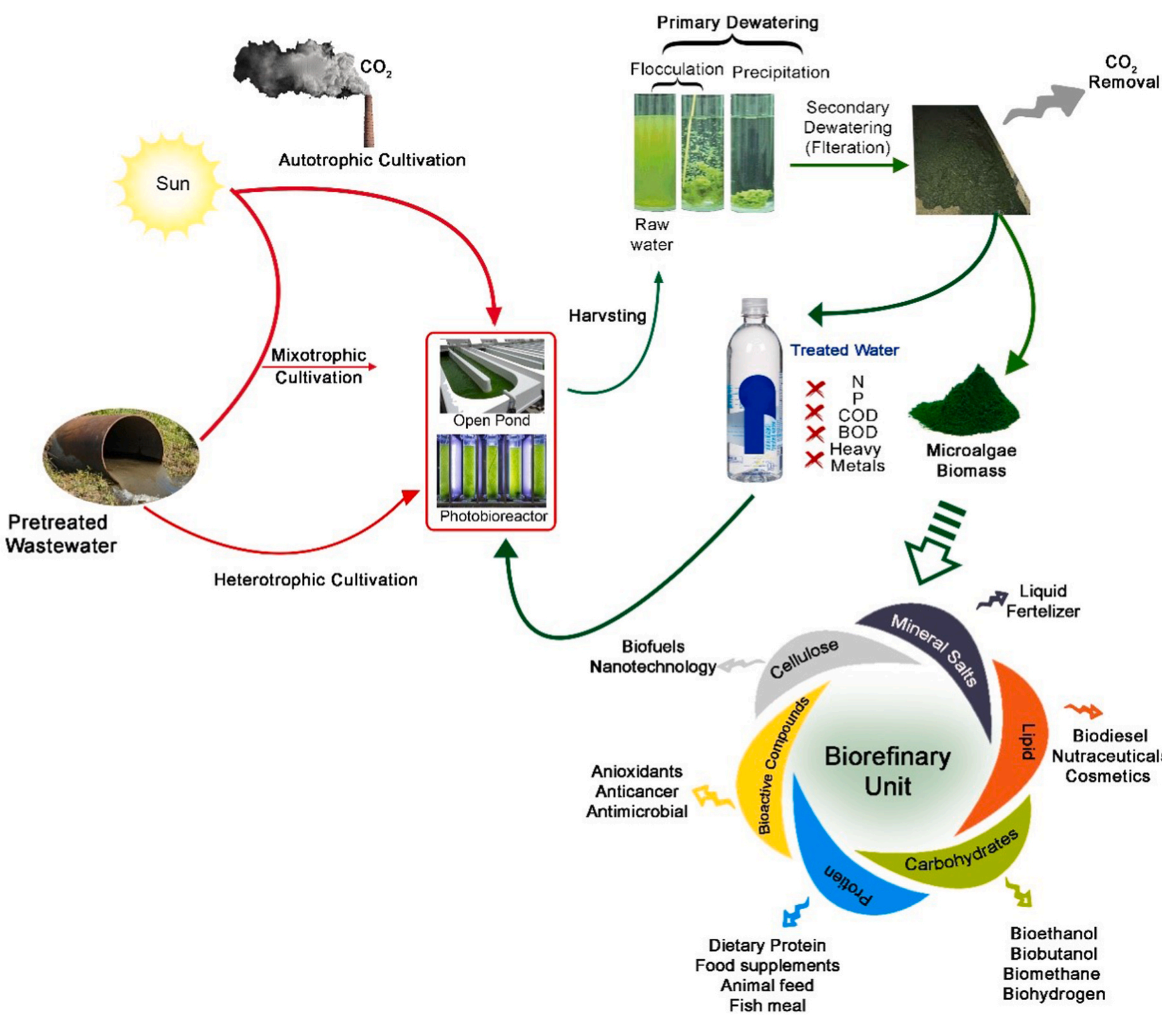

Fig. 3. Integration of wastewater and flue gas for algal biorefinery.

harvesting [253], cell wall disruption and extraction [254], and conversion process [96]. The major aim is to improve biomass production, lipid extraction efficiency, biofuel conversion, and the economics.

6.1. Cultivation

The cultivation of algae represents about 40 % of the overall cost of producing biofuels [255]. Algal cultivation requires optimal illumination, simple operating procedures, a low contamination rate, efficient mass transfer across the liquid-gas barrier, and a low-cost culturing system [11]. NPs have been used in either direct or indirect routes to induce cell growth and lipid accumulation" (as represented in Table 3). NPs can be incorporated directly into culture media to enhance photosynthetic cell growth and/or intracellular lipid accumulation without damaging the cells [23] or as inhibitors of co-existing fungal and microbial communities, which are the nutritional competitors [256]. Indirect, NPs can improve CO_2 capture, absorption efficiency in the cultivation media, and light transformation in the photobioreactors (PBRs) [257]. The effects of adding NPs to microalgal culture are shown in Fig. 4 [258]. The effects of the NPs are influenced by the physicochemical characteristics (such as types, sizes, geometries, dosages, oxidation state), algal species, and culture conditions [21,23,258,259].

Algal growth can be enhanced with the application of Fe_2O_3 [260], CeO_2 [261], TiO_2 [261], ZnO, MgO, Se, CuO [31,262], and α-Fe_2O_3NPs [29]. Different concentrations of cobalt Co NPs have been applied in the cultivation of *Platymonas subcordiforus*, *Chaetoceros curvisetus*, and *Skeletonema costatum* where no inhibition in *P. subcordiforus* growth is observed after 24 h of exposure, but growth is stimulated at 1 mg/L of Co NPs [263]. Higher cell densities of *C. reinhardtii* are reported at 0.1 and 1.0 g/L Cr_2O_3 NPs, after 72 h, and a marked decrease is observed at 10 g/L Cr_2O_3 NPs [264]. NPs induce the generation of ROS, which triggers the accumulation of intracellular lipids and carbohydrates [265]. The NPs of zero-valent Fe [266], TiO_2 [267], $MgSO_4$ [256,268], MgO [260], α-Fe_2O_3 [269], Fe_2O_3 [270], ZnO [271], SiC [272], and Ag [244] have all been utilized to enhance the lipid yield in algae. ZnO NPs and Ag NPs enhance the fraction of FAs and the ratio of SFAs/PUFAs [273,274]. The Ag NPs induce the highest total lipid content of *Scenedesmus* sp. (8.1 %) and *Thalassiosira* sp. (17.4 %) at 5 and 100 μg/L, respectively [275].

Several NPs are already proven to interact with plant cells by upregulating or downregulating specific genes [276]. NPs can interact with different enzymes involved in the algal metabolic pathway thereby altering the normal metabolic pathway of cells [277]. The enzyme AGPase (ADP-glucose pyrophosphorylase) essential for starch biosynthesis [278], acts as a bottleneck in microalgae lipid production (Fig. 5) [279]. AGPase enzyme catalyzes the conversion of glucose-1–phosphate to ADP-glucose - the precursor of starch biosynthesis Therefore, blocking

Table 3
Effects of direct or indirect uses of NPs on algal growth and lipid accumulation.

Uses	NPs			Microalgae	Impacts	References
	Types	Size (nm)	Concentration (mg/L)			
Direct	Fe_2O_3	<30	0–20	*Scenedesmus obliquus*	Increases (>10 % versus control) of growth rate after 7 days exposure	[260]
	$MgSO_4$	<100	1 g/L	*Chlorella vulgaris*	Significant improve the biomass yield	[268]
	ZnO	21.3–105	10	*Chlorella vulgaris*	Considerable increases in both biomass and growth rate	[31]
	CuO	24.4–118	50			
	MgO	12–34.7	50			
	Se	10–39	50			
	Silica	~74		*Chlorella vulgaris*	Cell growth is significantly increased when compared to the non-NPs condition.	[354]
	CeO_2	10–30	≤5	*Phaeodactylum tricornutum*	Increased growth rate (~10 %) compared with non-CeO_2 NPs control after 4 days exposure	[261]
	TiO_2	–	0.8	*Microcystis aeruginosa*	Enhanced (~50 % versus control) of growth rate after 11 days exposure	[355]
	ZnO	30	1 and 10	Chlorosarcinopsis sp. MAS04	Improved the cell density after 96 h exposure	[262]
	α-Fe_2O_3	20–40	0.1–5	*Chlorella vulgaris*	No significant difference was found in the growth rate compared to the control.	[29]
	ZnO	10–30	5–200	*Nannochloropsis oculata*	Improved polyunsaturated fatty acid content (PUFA[a]) and saturated fatty acids (SFAs)	[274]
	CuO	10–40	5–200			
	Fe_2O_3	20–40	5–200			
	Ag	20–50	0–50	*Nannochloropsis oculata*	Enhanced polyunsaturated fatty acid content (PUFAs) and saturated fatty acids (SFAs)	[273]
	AgNPs	6–10	5 μg/L 100 μg/L	*Scenedesmus* sp. *Thalassiosira* sp.	Increased the lipid production	[275]
	CNTs[a]	<2	5	*Scenedesmus obliquus*	Increased the lipid productivity by 8.9, 39.6, and 18.5 %, respectively. after 7 days exposure	[260]
	Fe_2O_3	<30	5			
	MgO	<50	40			
	α-Fe_2O_3	20	30	*Chlorella pyrenoidosa*	Enhanced the lipid accumulation and biomass production after 15 days cultivation	[269]
	ZnO	–	0.081	*Scenedesmus rubescens*	Increased the lipid content of cells	[271]
	SiC	–	150	*Scenedesmus* sp.	The lipid production significantly increased	[272]
	Fe_2O_3	<50	10	*Coelastrella terrestris*	Improved the lipid productivity	[270]
Indirect (Around PBRs)	Ag	50	10^{17} m^{-3}	*Chlamydomonas reinhardtii*	Increased (>30 % versus control) of growth rate	[284]
	Ag	10	–	*Chlorella vulgaris*	Enhanced microalgal pigment formation	[30]
	[a]u nanorods	30 length; 14 width	–			
	Ag–Au mixture	–				
	Au nanodisk	~90	Arrays; equipped PBRs	*Synechococcus elongatus*	Improved the growth rate (6.5 %)	[356]
	Spherical Ag	12	Embedded filters; equipped PBRs	*Chlamydomonas reinhardtii*	Biomass increased (25 % vs. control) after 10 days of incubation	[285]

(–): Not available.
[a] Carbon nanotube.

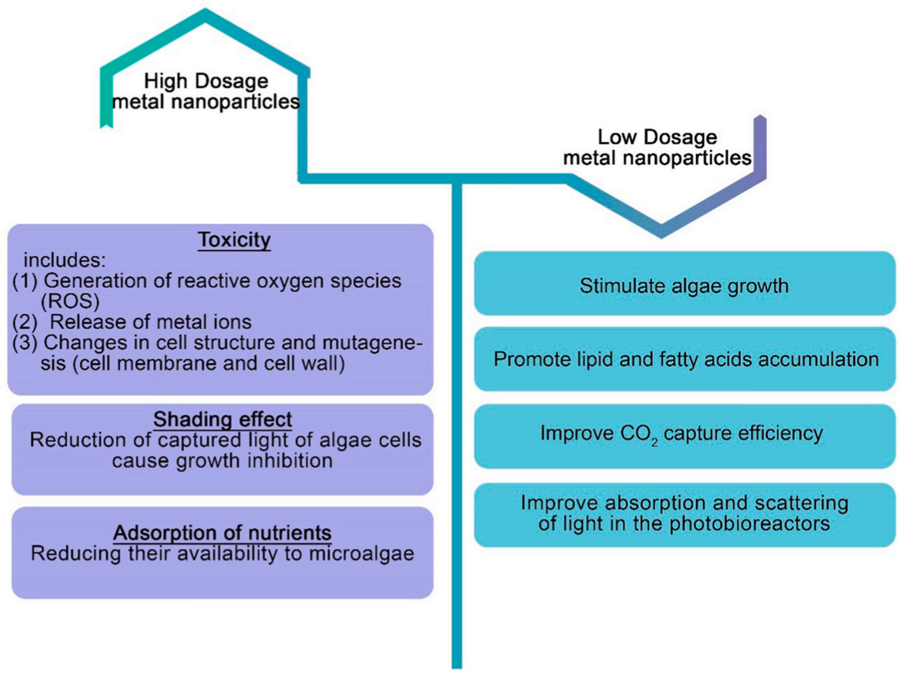

Fig. 4. Effects of nanoparticle addition on microalgal cultivation (Modified from Ref. [258]. With Copyright permission).

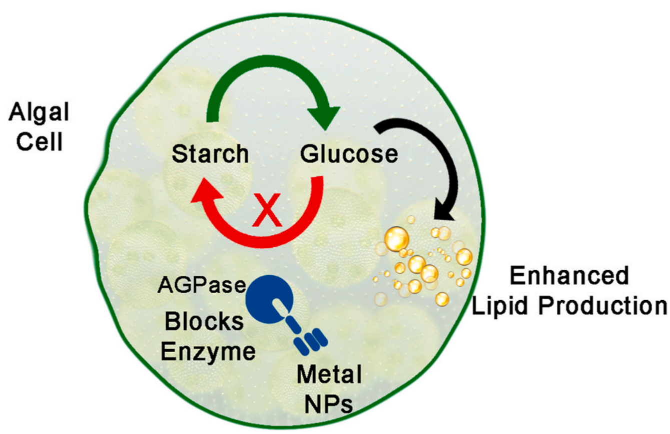

Fig. 5. A hypothetical model on blocking AGPase by engineered NPs to block starch synthesis pathway (Modified from Ref. [279]. Under CCBY license).

the starch synthesis pathway by inactivating AGPase [280], through the application of engineered NPs and biocatalyst could be an effective way to enhance lipid production in microalgae. Understanding in-depth molecular mechanisms of NPs–microalgae interactions leading to efficient enhancement of lipid production, will improve the productivity of biofuel production.

Precautions should be taken before introducing NPs during algal cultivation as NPs can be toxic, whereas most tested NPs for microalgae toxicity are metal oxides, such as TiO_2, ZnO, NiO, etc. The results indicated that applying more than 20 mg/L of NPs could have a negative impact on algal growth [281]. TiO_2 NPs may also adsorb nutrients such as P and Zn, reducing their availability to microalgae [282]. The overproduction of ROS is thought to be a major mechanism of the toxicity of NPs. In contrast, it leads to chemical reactions that cause 1) damage to cell structure, including loss of membrane fluidity and oxidation of unsaturated lipids, and 2) oxidizes lipids, proteins, and nucleic acids, by forming ROS causing cell structural alterations and mutagenesis. Therefore, screening of NPs is needed to evaluate the range of effective concentrations and their impact on enzymatic and microbial activity [258].

The metal NPs exposed strain (MNPS) in the nano metal-containing media has exhibited a higher growth rate, biomass cellular pigments, and lipid production than cultivation without the NPs [283]. Controlling the NPs incorporation within the bioreactor setup can influence the wavelength and the backscattering of light [23]. To overcome the limitation in the transport of light to the cells with high NPs, localized surface plasmon resonances (LSPR) with NPs outside of the closed PBRs can be used for the absorption and scattering of light [242]. Intense backscattering of the blue light from the Ag NP suspension elevates the growth of *Cyanothece* 51142 and *Chlamydomonas reinhardtii* by more than 30 % [284]. The spheroidal Ag and Au NPs, alone or in combination, surrounding the PBRs, enhance the growth of *Chlorella vulgaris* with increased light uptake [30]. Spherical AgNPs embedded within the flexible polymeric sheets could improve the distribution of blue light for algal absorption, resulting in a more than 25 % increase in dry biomass and a 35 % increase in photosynthetic pigments [285]. To improve mixing, nutrient availability, dissolved CO_2, and the efficiency of light exposure, nanobubble generators can be utilized [286,287]. Nanobubbles with a diameter of less than 100 nm have a larger surface-to-volume ratio, and a slower rise velocity allows more CO_2 to dissolve [288]. The chlorophyll and carotenoid contents in *N. oculata* and *C. vulgaris* cultures are significantly increased when the nanobubbles are supplied [289]. The nanobubbles technology has not yet been adequately explored for CO_2 fixation by the algal culture [290].

6.2. Harvesting

Microalgal harvesting is a critical bottleneck in algal biorefinery [291], and harvesting techniques such as centrifugation, immobilization, flotation, sedimentation, flocculation, filtration, electrophoresis, and magnetophoretic separation can be used [2,40]. However, there is no single universal technique that is suitable for all cases. The selection mainly depends on microalgal properties such as size, density, the value of the desired product, and the final market [292]. Conventional flocculants like $FeCl_3$ and alum are ineffective [292], with issues of toxicity and chemical recovery [293]. The NPs-based flocculation could be developed as a simple and low-cost harvesting technology in comparison with conventional flocculation, used in single (bare) or hybrid (composite) forms, coated with various cationic polymers, and chemicals [23,294]. Functionalized MNPs, aminoclay NPs, and multifunctional NPs are utilized to improve the harvesting efficiency as shown in Table 4 [250].

The MNPs such as Fe_3O_4 NPs have a high surface area, magnetic properties, and biocompatibility [295] and can be automated with high efficiency, scalable processing, and low contamination [294]. MNPs-microalgae interactions are still poorly understood, with some studies have shown that negatively charged MNPs may attract negatively charged microalgal cells [296,297], revealing potential pathways in microalgae harvesting. The conventional electrostatic concept fails to describe such behaviors and interactions between bare MNPs and microalgal cells. In contrast, the Extended Derjaguin-Landau-Verwey-Overbeek (EDLVO) theory could explain substrate adherence to the bacterial cell from a thermodynamic point of view, which is attributed to electrostatic, Lewis acid-base, and Lifshitz-van der Waals interactions caused by the heterogeneous functional groups on the microalgal cell wall membrane [298]. The bare iron-oxide NPs (IONPs) achieve more than 95 % efficiencies, attributable to the affinity of the microalgal cell wall with the NPs surfaces

Table 4
Microalgal harvesting using various nanomaterials.

Types of NPs	NPs			Microalgae		Performances			References
	Kind	Size (nm)	Concentration (g/L)	Species	Density (g/L)	Harvesting Efficiency (%)	Time (min)	Working pH	
Magnetic NPs	Bare Fe_3O_4	–	0.5	*Coelastrella* sp. UKM4 *Chlorella* sp.	1.27	94	4	Culture media	[301]
	Bare Fe_3O_4	–	0.15	*Chlam[a]domonas* sp. UKM6	1.27	82	4	Culture media	[301]
	Bare Fe_3O_4	13.1	10 g/g cell 0.5 g/g cell	*Chlorella vulgaris* *Scenedesmus ovalternus*	0.6 0.6	>95 >95	5 5	4 4	[299]
	$FeCl_2$ +$FeCl_3$	10–30	0.028 g/0.927 g cell	*Synechocystis* *Stigeoclonium* *Nanochloropsis* *Microytis*	–	94.7 94.8 98.1 98.7		–	[302]
	MNPs[a] ($FeCl_2$+$FeCl_3$)	~[b]0	0.33 g MNPs/g dry biomass	*Nannochloropsis maritima*	–	99.5	5	5–9	[303]
	[c]e	67.8–439.1	0.1 M	*Chlorella zofingiensis*	~0.95	98.3 ± 1.8	1	Culture media	[357]
	$Y_3Fe_5O_{12}$	<100	2.5	*Chlo[d]ella vulgaris*	–	>90	1	7.3	[300]
	Fe_3O_4@Arginine		0.2	*Chlorella* sp.	0.2	95	2[e]	8	[358]
	NiO	<50	0.075	*Chlorella vulgaris*	–	98.75			[253]
	PEI[b]-Fe_3O_4	247	[f].15	*Scenedesmus dimorphus*	0.8	>80	23	Culture media	[306]
	CPAM[c] -Fe_3O_4	–	0.12 0.025	*Chlorella ellipsoidea* *[g]otryococcus braunii*	0.7 1.8	96 95	<10 <10	7 7	[305]
	PDDA[d]-Fe_3O_4	65	0.1	*Chlorella* sp.	5[h]106 cells/mL	80	<10	–	[304]
Magnetic NPs	CTAB[e]-Fe_3O_4	–	0.46 g/g cell	*Chlorella* sp.	1.[i]–1.5	96.6	1	Culture media	[254]
	PP[f]-Fe_3O_4	50–100	0.02	*Chlorella protothec[j]ides*	1	99	3–5	10	[307]
	Silica-Fe_3O_4	141.8	–	*Chlorella pyrenoidosa*		83.7	180	–	[309]
	GO[g] -Fe_3O_4/PDDA	8.54	0.07	*Chlorella* sp. HQ	0.2	95.35	5	4–12	[304]
	APTES[h]-$BaFe_{12}O_{19}$	108	2.3[k]mg/mg cell	*Chlorella* sp. KR-1	1	99	2–3	6.5	[308]
Aminoclays NPs	MgAC[i]-Fe_3O_4	3.5–7.14	4.19–4.72	*Chlorella* sp. KR-1	2.0	>80	10	4	[314]
	MgAC-CeAC[j] mixture	20–1000	1	Mixed algae	0.2	100	60	7	[313]
	Humic acid/Mg-AC	–	2.5	*Chlorella* sp. KR-1	1.3	100	180	6.5	[311]
	Al-AC	30	0.6	*Chlorella* sp. KR-1	1.7	100	30	6–9	[311[c]
	AC-nZVI[k]	100	20	*Chlorell[d]* sp. KR-1	1.5	100	<3	9	[312]
Multifunctio[e]al NPs	ZrO_2	–	0.15	*Ch[f]orococcum* sp.	[g]	82.44	45	–	[31h]
	AC-TiO_2	0.6–10	3	*Chlorella* sp. KR-1	1.5	85	30	6.5	[3i9]
	TBD[l]-Fe[j]@Silica NPs	–	–	*[k]hlorella vulgaris*	–		1	Culture media	[62]

(–-): Not available.

[a] Magnetic nanoparticles.
[b] Polyethylenimine.
[c] Cationic polyacrylamide.
[d] Poly(diallyldimethylammonium chloride).
[e] Cetrimonium bromide.
[f] Polypyrrole.
[g] Graphene oxide.
[h] Octyltriethoxysilane/(3-aminopropyl) triethoxysilane.
[i] Aminoclay.
[j] Cerium aminoclay.
[k] Aminoclay-nanoscale zerovalent iron.
[l] Triazabicyclodecene.

[299]. The harvesting efficiency is similarly attained by the IONPs and Yttrium iron-oxide ($Y_3Fe_5O_{12}$) NPs [300], depending on the algal species [295]. An efficiency of 94 % is obtained when the IONPs are applied to *Chlorella* sp. UKM2 and *Coelastrella* sp. UKM4 cultures, while an efficiency of 82 % was obtained when applied to *Chlamydomonas* sp. UKM6 cultures [301]. The combination of $FeCl_2$ and $FeCl_3$ MNPs at a 1:4 ratio shows an efficiency of 94–99 % [302]. These MNPs can be reactivated and combined with ultrasonic treatment, but after five activations, the harvesting efficiencies are only 53–71.2 % [302]. At $FeCl_2$–$FeCl_3$ MNPs of 0.33 g/g dry biomass attained 99.5 % harvesting efficiency of *Nannochloropsis maritima* [303].

The MNPs are commonly coated with cationic polymers including polyethyleneimine (PEI), poly-(diallyl dimethylammonium chloride) (PDDA), cationic polyacrylamide (CPAM) [304–306] polypyrrole (PP) [307], cetrimonium bromide (CTAB) [254], and (3-aminopropyl) triethoxysilane (APTES) [308]. The flocculation efficiency of *Spirulina, Scenedesmus, Tetraedron, Chlorella*, and *Hematococcus* is 90 % when GO-Fe_3O_4 NPs are coated with the PDDA [304]. The magnetic core-shell SiO_2-coated NPs show 83.7 % harvesting efficiency for *Chlorella pyrenoidosa*, with a 4-fold higher lipid extraction [309]. The most common Aminoclays (ACs) used are Mg-AC [310,311], Fe-AC [310] Al-AC, Ca-AC [311], humic acid/Mg-AC [311], or Mg-AC-coated nZVI NPs [312]. The harvesting efficiency with the ACs is influenced by the microalgal species, operational conditions, and the structure as well as the dosage of the ACs [313,314]. The separation efficiency of the humic acid/Mg-AC in the form of the network-like precipitant formation reaches 100 % [311], and the Mg-AC/nZVI composites are applicable in a large-scale (24 L) system [312]. However, the zeta potentials of Mg-AC-Fe_3O_4 hybrid composites decrease at higher pH values, resulting in lower harvesting efficiency [314].

6.3. Cell-disruption and extraction

The techniques for cell disruption include mechanical (microwave, homogenizer, electric pulse field, sonication) and chemical (surfactant, enzymes, acid) methods [42]. These require high energy consumption and capital costs, with concerns about the target component deterioration [43]. Product purification using solvents is also energy-intensive [315]. Hence, the cell destruction and subsequent purification of high-value products may be the major bottleneck in algal biofuel production [17,23]. The NPs-assisted extraction could achieve no major alteration in the extracted lipid, with improved oil extraction efficiency. The metallic NPs generate ROS, which can perforate the cells, to enhance the bioproduct release [253]. The selection of the NPs, their compatibility, and their efficiency are dependent on the composition of the microalgal cell wall [25].

Multifunctional NPs can provide integrated harvesting and post-harvesting steps such as cell disruption, lipid extraction, and conversion of oils [250]. Metal-based NPs play an important role in *Chlorococcum* sp. biomass recovery due to the presence of positively charged ZrO_2 NPs, which effectively interact with the negatively charged cells to achieve an overall harvesting efficiency of 82.44 %, at a low dose of ZrO_2 of 15 mg/L [316]. AC-based NPs and particularly engineered NPs like Al-3-aminopropyltriethoxysilane (APTES) clay, Mg-APTES clay, and Ca-APTES clay are used to improve lipid extraction. The aminoclay NPs as harvesting agents are effective for the harvesting of oleaginous *Chlorella* sp. KR-1, with the oil extraction efficiency improved due to the destabilizing effect on the cells [317]. The cationic-charged aminoclay NPs assist in the weakening of the cell walls, decreasing the water layer within the cells, and making contact with the hydrophobic solvent to facilitate the release of intracellular oil [23]. Hydrogen peroxide promotes the Fenton-like reactions with the Fe-, Mn-, and Cu-based ACs, creating •OH free radicals on the surface of the microalgae to disrupt the cells and enhancing oil extraction [318].

Both flocculation and cell disruption can be achieved with AC-conjugated TiO_2 composites. The •OH radicals produced at the surface of the AC/TiO_2 composites destroy the microalgae surfaces and induce cell disruption. The addition of 3 g/L AC-conjugated TiO_2 composites increases the harvesting efficiency of *Chlorella* sp. KR-1 to 85 % and the cells are further disrupted by a simple 365 nm UV exposure for 3 h [319]. SiO_2-based NPs have a high potential for sequestration and selective separation of high-value chemicals in microalgae due to their structural porosity and large surface area [320]. The 1,5,7-triazabicyclo [4,4,0]dec-5-ene (TBD)-functionalized Fe_3O_4@SilicaNPs have been developed for harvesting *C. vulgaris* and catalyzing the transesterification reaction of the algal lipid [62]. The cultivation of microalgae with spherical NPs composed of calcium and silica results in a significant increase in cell growth with ease of harvesting [242]. Mesoporous silica nanocatalyst, SBA-15 loaded with Ti, elevates the FFAs by 10-fold with a higher water tolerance level [321]. The mesoporous structure of the NPs, similar to zeolite, could extract the lipids without cell decomposition [242]. The FFAs can be captured by the NPs having a mean particle diameter of 10 nm. Porous functionalized NPs effectively and specifically target the FFAs in the microalgal oil by entering the pores and subsequent absorption using primary amine groups to functionalize the pores [315]. After organic solvent washing, acid-esterification, and pH adjustment, the FFAs can be desorbed [322].

6.4. Enzymes immobilization

Immobilization of cells or enzymes to static support or carrier is effective for the sustained production of biofuels. The bound cells or enzymes can be reused for several cycles. Entrapment, adsorption, ionic and covalent bonding, cross-linking, and emulsions are among the common technique [323]. Biomass pre-processing may require an enzymatic hydrolysis step involving enzymes such as hemicellulases, β-glucosidases, and cellulases, for the conversion of cellulose to monomeric sugars [324,325]. However, conventional immobilization may cause deterioration of the enzyme-specific activities [326]. Immobilization of enzymes on nanomaterials could lead to an improvement in pH stability, regenerative capacity, thermal stability, increase in activity, and enzyme reusability [115]. NPs [327,328], NTs [329], GO nanocomposites [330], and nanofibers (NFs) [331] have been successfully used for enzyme immobilization.

Immobilization of lipase and cellulase on the MNPs, magnetic NFs, magnetic nanotubes (NTs), and silica have been studied [332–336]. Nanocomposites or hybrid nanomaterials are synthesized by coating the nanocores with an inorganic or organic layer, such as silica, and these nanocomposites allow for rapid grafting of various functional groups for optimal immobilization [337]. Enzyme immobilization on the Fe_3O_4 NPs and nanocomposites (Fe_3O_4/alginate) has significantly improved the activity and stability [338]. NFs as immobilizing nanomaterials are simple to handle and provide flexibility in the reactor design due to their durability and separability, ease of recovery of the non-MNPs, increased control of dispersion, and a decreased diffusion path [339]. Enzyme immobilization on nanomaterials can overcome the high cost of the saccharification process.

6.5. Conversion to biofuels

The processes involved in the conversion of algal biomass into biofuels are chemical conversion (transesterification for biodiesel production), thermochemical (hydrothermal processing, combustion, torrefaction, gasification, and pyrolysis), and biochemical (photo-fermentation, dark-fermentation, and anaerobic digestion) [340]. Each route has its advantages and disadvantages, hence a critical review of thermochemical and biochemical conversions of waste-grown algae has been compiled [341]. The thermochemical route from algal biomass has high efficiency, but the high energy and heating requirements may incur additional costs. The biochemical route makes use of nano/biocatalysis, which includes metal oxide [74], mesoporous [342], and carbon-based [343] nanocatalysts are more promising. Nano-encapsulation of cellulosic ethanol and lipase-catalyzed biodiesel production processes can be scaled up [100]. The NPs act as electron donors or acceptors and enhance the enzyme activity for biohydrogen and biogas production. The NPs as fuel additives improve the performance and combustion characteristics of biodiesel-powered engines with lower emissions [344].

7. Challenges and future outlook

World energy production has been over-dependent on fossil fuel that any switch to more sustainable options must consider a transition phase by utilizing the existing network and infrastructure developed for the fossil-fuel economy. Transport biofuels from liquid hydrocarbons can be produced with by-products such as H_2O and CO_2/CO [345], and renewable fuels such as biodiesel for diesel engines are actually the natural competitor to conventional diesel fuel [346]. Algal biorefinery to biofuels and high-value products using advanced technologies has the potential for scaling up while reducing the carbon footprint and mitigating the negative environmental impacts associated with fossil fuels. The major challenges for wide utilization of algal biofuels are" instead of The major challenges for wide utilization of algal biofuels are: energy consumption, high costs of cultivation, harvesting, de-watering, improving the biomass pretreatment, the scalability and selectivity of the extraction methods, and the efficiency of conversion processes to multiple products.

It is important to utilize Life cycle analysis (LCA) as a tool to evaluate environmental impact of algal-based biofuel, from raw material extraction, to its entire life cycle including the production, transportation, and utilization and during end-of-life disposal through analyses of energy consumption, GHGs emission, water usage, and wastes generation [347]. Other parameters may include plant capacity, feedstocks, chemicals (solvents and catalysts), labor, plant location, utilities, buildings, and taxes. Based on LCA, the Net Energy Ratio (NER), the ratio of total produced energy to consumed energy, for microalgal biodiesel is less than 2.5, as compared to about 5 for fossil diesel. Around 30–50 % of the total input energies (TIEs) in microalgal biodiesel production are consumed during cultivation, 5–10 % during transesterification, and the largest during oil extraction and dewatering. When using wet biomass (15–30 % w/w dry biomass weight), the input energy for dewatering can be low (1–10 % of the TIE), but the energy for the oil extraction is high (30–80 % of the TIE), as higher concentration of solvent may be used, requiring larger extraction reactor, more energy to heat the biomass, and more solvent to recycle with increased input energy for distillation column [348].

The adoption of nanotechnology within the algal biorefinery may be the way forward to improve qualitatively and quantitatively biofuel production and remove the limitations associated with feedstock availability, post-harvest biomass collection, and bioenergy generation [346]. Catalysts such as Li/ZnO–Fe_3O_4, Li/Fe_3O_4, nanocrystalline CaO, Sr–Al double oxides, $Ca(OCH_3)_2$, and nano-sulfated zirconia may attain high biodiesel yields (>99 %), but are expensive [347]. Using low-cost waste materials such as eggshells and mollusks to produce nano-catalysts could reduce the production costs. Nano-CaO from low-cost materials has exhibited high reusability, with high yield of biodiesel during transesterification of different oils [349]. The costs of feedstocks, plant capacity, location, and labor all have a major impact on the cost. Increasing plant capacity, and plant location with lower land costs, can greatly reduce the production costs, but without strong incentives from the government, biofuels from microalgae may not be able to replace fossil fuels. By considering the co-production of proteins, bioplastics, vitamins, and pigments, the cost of biodiesel production from microalgae can be reduced from 3.90 to 0.54 USD/L [348]. The LCA of algal biofuels using nanocatalysts has received limited attention especially to identify opportunities to reduce environmental impact of a nanocatalyst-based algal biofuel production by optimizing its design, materials, and production.

The challenges in the applications of NPs in algal biofuels production and algal biorefinery approach need to be addressed and can be summarized as follows.

- NPs can enhance lipid production in microalgae. There is a great need to understand the interaction mechanisms of NP-microalgae at the molecular level.
- NPs beyond certain levels can be toxic to microalgae, causing oxidative stress, agglomeration, and inconsistent nutrition availability. Therefore, NPs should be screened at different concentrations, shapes, and sizes to better asses the effects on microbial activity and to find the optimal process conditions.
- NPs should be assessed in terms of recyclability and reusability to mitigate the environmental impact and provide better resources sustainability.
- NPs are a promising candidate for improving the industrial growth of algal biofuels. However, there is still a need for efficient implementation in various aspects, including the design of modified nanocatalysts with varying combinations, types, scale-up parameters, reactor design, and the simplicity of operation under a variety of dynamic processing conditions.
- The impact of NPs, in case of not being separated, on biofuel combustion quality, gas emission, and engine performance must be evaluated, as the cost of separation could be the major barrier that may hinder commercialization effort.
- There is a need to develop a complete techno-economic and LCA of nanoparticles-aided algal biorefinery process for the co-production of multiple products and achieve economic feasibility.
- Since NPs application on microalgae is a relatively new research concept, policy-making and implementation of NPs will remain critical concerns for commercial production, particularly in developing countries. Therefore, management insights on the socio-economic impact and comprehensive policy with dynamic legislation on the entire production system are needed to attract investment and more importantly to meet the agenda of Global Sustainable Development Goals and mitigate climate change.

8. Conclusions

This review provides the state-of-the-art and current research status and bottlenecks in the application of nanoparticles in algal biofuel production and algal biorefinery. Great outcomes are achieved through the application of nano-additives at various stages of algal-biofuel production, which may represent a significant improvement towards the commercialization of algal biofuel. The unique physicochemical properties of NPs can improve the catalytic performance, yield, and subsequently economic feasibility. The deployment of NPs in biofuel production can reduce production costs by improving 20–30 % cell growth, 80–99 % harvesting efficiency, enhanced product extraction, and ~85–99 % conversion. Metal oxides, mesoporous, and carbon-based nanocatalyst applications could increase the conversion efficiency of lipids to biodiesel via the transesterification. Also, the use of nano-biocatalyst for bioethanol production has led to an improvement in enzyme activity and stability. Different types of NPs enhance the activity of various enzymes during biohydrogen and biogas synthesis, and improve the electrode material and the specific surface area, leading to a significant level of electrochemical performance during bioelectricity generation in algal-based MFC. The biosynthesized NPs improve the product yield but the effect on algal biofuel from the primary phase to the end product needs to be comprehensively addressed. NPs can aid different stages of algal biorefinery routes including the enhancement of growth, high-value products via nutritional alteration, inducing stress environments for induction of specific compounds, and application of backscattering light. MNPs with the potential for recycling can greatly improve the harvesting efficiency of biomass, and their incorporation during cell harvesting, disruption, extraction, and conversion can reduce overall production costs. It is pertinent to understand the long-term impact of NPs applications on the ecosystem and in vivo toxicity. The techno-economic and Life cycle analysis could identify the most energy-efficient, cost-effective, and high-yielding process route, in algal-based biofuel production are therefore critical to provide insights into the economic feasibility of NPs-based algal biofuels for pilot and large-scale implementation.

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Authors' contribution

HEAA: Conceptualization, Investigation, Writing - Original Draft, Funding acquisition; EAE, RMS, HAH: Investigation, Writing - Review & Editing; AE, SAM, KE: Writing - Review & Editing, Funding acquisition; MZHR: Writing - Review & Editing, Supervision, Project administration; MAA: Conceptualization, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

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.

Data availability

No data was used for the research described in the article.

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