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Tri-functionality of Fe_3O_4-embedded carbon microparticles in microalgae harvesting

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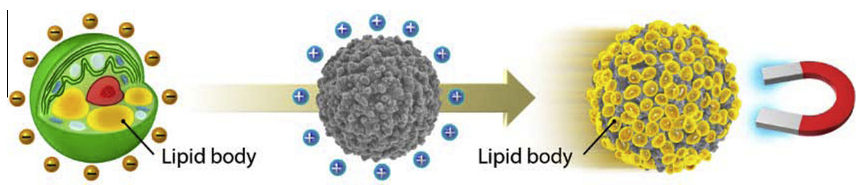
HIGHLIGHTS

- Fe_3O_4-embedded carbon microparticle was synthesized via spray pyrolysis in one-step.
- Carbon microparticles were designed to be cationic, magnetic and lipophilic.
- Tri-functional microparticles could separate microalgae with 99% efficiency.
- Tri-functional microparticles could adsorb lipid bodies extracted from microalgae.

GRAPHICAL ABSTRACT



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ABSTRACT

Microalgae have received significant attention as promising resources for biodiesel. However, the downstream processes for the production of biodiesel, which range from cultivation, harvesting, dewatering, and lipid extraction to oil upgrading, are economically impracticable and can be improved. Therefore, efficient microalgal harvesting and integrated technologies are required to realize microalgae-based biodiesel. Herein, tri-functional (cationic, magnetic, and lipophilic) carbon microparticles filled with magnetite (Fe_3O_4) are synthesized through one-step aerosol spray pyrolysis and applied in microalgal harvesting and serial microalgal lipid entrapment. Carbon microparticles are tri-functional in the following respects: (i) the cationic carbon microparticles facilitate flocculation with anionic microalgae due to electrostatic attractions; (ii) the magnetic properties of the carbon microparticles, owing to embedded magnetites, enable the separation of microalgal flocs from low concentration cultures ($\sim$2 g L^{-1}) with a separation efficiency of 99%; and (iii) the lipophilicity enables the recovery of lipid droplets extracted from oleaginous microalgae. Microalgal lipids are directly separated through adsorption onto magnetic carbon microparticles from concentrated microalgal slurries after harvesting. The tri-functionality may facilitate the integrated use of magnetic carbon microparticles in microalgal biorefineries and the tri-functional microparticles could potentially be applied in various areas such as biomedicine, catalysis, magnetism, energy materials, and environmental remediation.

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1. Introduction

The need for magnetic nano/microparticles has increased recently owing to their remarkable functionality and potential viability in a variety of fields ranging from catalysis, anode materials for Li-ion batteries, magnetic fluids, environmental remediation, and magnetic storage media to medical diagnosis, drug delivery, and biotechnology [1–4]. Magnetic particles possess innate magnetism and unique chemical properties depending on their composition, size, and morphology [5,6]. In particular, they are easily attracted by an external magnetic field and can be utilized in the separation of desirable or unsolicited materials in liquid suspensions. Here, magnetic particles are utilized to separate microalgae from a dilute culture medium and recover microalgal lipids after microalgal harvesting.

Microalgae have garnered vast attention as a potential biofuel resource because they have great advantages such as higher oil yields, lesser land requirements, adaptability, a wide range of final products, and CO_2 capture abilities [7–10]. To obtain microalgal biomass, microalgal harvesting from open ponds or photobioreactors is a prerequisite in microalgal biorefineries. A variety of harvesting methods including centrifugation, flocculation, filtration, sedimentation, and floatation have been suggested and utilized, but harvesting remains the bottleneck and significantly increases the process cost [11,12]. Magnetophoretic harvesting has recently been reported as a more efficient method, as it has a high harvesting efficiency, low environmental toxicity, scalable throughput, and relatively low operational costs [13–16]. In this regard, one important issue in magnetophoretic harvesting is the synthesis of magnetic particles with certain properties and desired structures. Synthetic methods towards magnetic flocculants should be simple, green, and inexpensive. The reuse of magnetic particles or iron resources may enhance economic feasibility. The surface charge is also essential to attract negatively charged microalgae [17,18]. Furthermore, magnetic particles that could be comprehensively applied in multiple downstream steps are preferable to minimize production costs, but integrated approaches have rarely been attempted in microalgal biorefineries [19]. For example, intracellular lipids from microalgae are required in order to produce microalgal biodiesel. Currently, the processes used to obtain intracellular lipids involve complicated steps such as microalgal harvesting, drying, cell disruption, and lipid extraction with hazardous solvents or expensive supercritical fluids [20]. Accordingly, magnetic particles may alleviate such tedious procedures in the selective recovery of lipid bodies as well as microalgae.

To impart essential functionalities on magnetic particles for comprehensive utilization in microalgal biorefineries, functionalization with appropriate polymeric or inorganic materials is carried out following the synthesis of the core magnetic particles [14,21–25]. A cationic surface charge is typically favorable, owing to the interactions with negatively charged microorganisms. As such, cationic polyelectrolytes, cationic polymers, and aminosilanes have been used as coating materials [15,21–23]. On the other hand, fatty acids have also been applied to form hydrophobic or lipophilic surfaces for the recovery of oil and hydrocarbon pollutants [24,25].

Here, we report the integrated usage of magnetic particles in microalgal downstream processes, specifically microalgal harvesting and lipid extraction. Towards that end, magnetic particles were designed to be tri-functional (cationic, magnetic, and lipophilic) carbonaceous particles filled with Fe_3O_4 via aerosol spray pyrolysis. Cationic magnetic particles with lipophilic and hydrophobic properties are rarely reported because most cationic functionalizing agents are hydrophilic. However, this synthetic approach enabled the one-step preparation of tri-functional carbon microparticles filled with nano-magnetites (Fe_3O_4) by the strategic optimization of the polyvinylpyrrolidone (PVP) to iron nitrate mass ratio. During spray pyrolysis, PVP was converted to a cationic and lipophilic coating layer by virtue of the unique characteristics of this synthetic method, namely the short residence time, as PVP not was completely burned. The utility of tri-functional carbon microparticles filled with nano-magnetites was demonstrated by their application in microalgal harvesting and successive microalgal lipid entrapment.

2. Materials and methods

2.1. Preparation of magnetic carbon microparticles

Four types of magnetic microparticles were prepared via ultrasonic spray pyrolysis, which was previously described in the literature [26]. Iron nitrate nonahydrate (Sigma–Aldrich, ⩾98%) and polyvinylpyrrolidone (PVP, Sigma–Aldrich, Average mol. wt.: 40,000) were dissolved in distilled water for the preparation of the precursor solution. The concentration of iron nitrate nonahydrate was fixed at 0.15 mol L^{-1} and the mass ratios of PVP to iron nitrate nonahydrate were controlled at 0, 0.33, 0.66, and 0.8. The aerosol droplets containing the aforementioned precursor solution were atomized by an ultrasonic nebulizer operated at 1.7 MHz and were carried into an electric tubular furnace by the flow (4 L min^{-1}) of the reducing gas (5% H_2/95% Ar). The temperature of the tubular furnace was adjusted to 800 °C. The length and inner diameter of the quartz reactor were 1200 and 29 mm, respectively. A thimble filter was used to collect the synthesized magnetic microparticles.

2.2. Characterization

The phase compositions of the prepared magnetic microparticles were confirmed by X-ray diffraction (XRD, Rigaku, D/MAX-2500 RC) with Cu Kα irradiation (λ = 1.5406 Å). The surface morphologies of the magnetic particles were observed by field emission scanning electron microscopy (FE-SEM, FEI, Magellan 400). High resolution transmission electron microscopy (TEM) was conducted on an FEI Titan G2 TEM (KARA) at an accelerating voltage of 300 kV. Elemental distribution images of nano-magnetite (Fe_3O_4) filled carbon microspheres were acquired by TEM equipped with energy-dispersive X-ray spectroscopy (EDS). The TEM sample was prepared by dropping the particle suspension in anhydrous ethanol onto a lacey carbon TEM grid. The zeta potential data of the prepared magnetic particles were obtained using a zetasizer (Malvern, Nano ZS90). The dispersion medium of magnetic particles was distilled water adjusted pH 7 at 25 °C. The magnetic properties were measured at room temperature using a vibrating sample magnetometer (VSM, Lake Shore Cryotronics, Model 7300). X-ray photoelectron spectroscopy (XPS, Thermo VG scientific, Sigma Probe) with a monochromatic Al Kα X-ray source was used to investigate the compositional and chemical state of the magnetic particles. All XPS spectra were calibrated using the C 1s peak at 284.5 eV as the internal reference. The peak fitting was conducted using Thermo Scientific Avantage software. The 'Smart' and 'Gaussian–Lorentzian mix' were chosen as the curve-fitting options for the background and line shape. The FT-IR spectra of PVP and magnetic microspheres were obtained using Fourier transform-infrared spectroscopy (FT-IR, Bruker Optics, IFS66V/S).

2.3. Lipophilic test of nano-magnetite (Fe_3O_4) filled carbon microspheres

The lipophilicity of the particles was evaluated through their interactions with oleic acid. Approximately 5 mg of either the bare