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Green heterogeneous catalyst for biodiesel synthesis

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Catalizzatore verde eterogeneo per la sintesi di biodiesel

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PAROLE CHIAVE
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Summary
The depletion of fossil fuel and global warming are major environmental concerns in recent decades and alternative sources of energy like solar, wind, hydro, biomass and even nuclear has been extensively studied by different scientists as potential solutions. However, one important problem associated with the running out of fossil fuel is normally overlooked i.e. the cease of chemical raw materials supply for plastics, medicine and other fine chemicals. Among all, biomass is the only hope that would harvest energy from sun with the cogeneration of important raw materials for our future. Also, due to its carbon neutrality, non toxicity, biodegradability and compatibility with the existing infrastructures for oil refinery and transportation system, biofuel has become a promising alternative as liquid transportation fuel.

Riassunto
L'esaurimento dei combustibili fossili e il riscaldamento globale sono i principali problemi ambientali degli ultimi decenni; numerosi scienziati stanno studiando fonti di energia alternative come possibili soluzioni (ad esempio energia solare, eolica, idroelettrica, a biomassa e persino nucleare). Tuttavia, un importante problema, associato con l'esaurimento dei combustibili fossili, viene normalmente trascurato e cioè porre fine alla richiesta di materie prime chimiche per la plastica, la medicina e altri prodotti della chimica nobile. Tra tutti, la biomassa è l'unica speranza per raccogliere energia dal sole con la co-generazione di importanti materie prime per il nostro futuro. Inoltre, i biocarburanti, grazie al loro carbonio neutro, non tossico, biodegradabile e compatibile con le infrastrutture esistenti per la raffinazione del petrolio e per il sistema di trasporto, sono diventati una promettente alternativa come combustibile liquido per i trasporti.

The main resistance for massive production of biofuel is the lack of huge sustainable biomass supply as the farming of terrestrial plant for biomass is too inefficient per area of land used, and normally causes competition for fertile land with food crops. In the light of this, development of non-edible and renewable biomass from aquatic life forms such as microalgae has drawn a lot of attention, and we believe it is one of the best solutions for the future biofuel. Microalgae such as dinoflagellates are commonly found in the salt water algal bloom, which means that if we can mimic the natural blooming mechanism in artificial cultivation, it will open up a way to generate a huge amount of algal biomass in a short time with essentially zero cost. It is because dinoflagellates carry out photosynthesis with assimilation of carbon dioxide to produce oils, polysaccharides and proteins. According to our analysis shown in table 1, the oil obtained from dinoflagellates is mainly composed of triglycerides containing C_{16} to C_{22} fatty acids side chain which is the most favourable molecular weight for the production of biodiesel. More importantly, as dinoflagellates do not release toxins, they actually help to purify the water when harvested, as they absorb the excess nitrates, phosphates and heavy metals ions from sewage. We believe that in the future sewage can be used as nutrient for the farming of microalgae based on artificial algal bloom to produce sustainable biomass for biodiesel production, and at the same time with the bonus of carbon dioxide fixation and water purification.

Table 1 - Fatty acid profile for oil obtained from Dinoflagellates

Fatty Acid	Formula	Weight %
Octanoic acid	C8:0	0.00
Decanoic acid	C10:0	0.00
Dodecanoic acid	C12:0	0.00
Myristic acid	C14:0	0.55
Pentadecanoic acid	C15:0	0.00
Palmitic acid	C16:0	18.89
Palmitoleic acid	C16:1n7	0.56
Heptadecanoic acid	C17:0	0.00
Stearic acid	C18:0	8.07
Oleic acid	C18:1n9	41.18
Linoleic acid	C18:2n6	13.02
α-linolenic acid	C18:3n3	5.88
Arachidic acid	C20:0	0.56
Eicosenoic acid	C20:1n9	8.06
Behenic acid	C22:0	0.28
Erucic acid	C22:1n9	0.00
Docosadienoic	C22:2	1.28
Tricosylic acid	C23:0	1.39
Lignoceric acid	C24:0	0.28

Apart from the generation of biomass, polluting nature of the existing biofuel manufacturing also hindered the development of biofuel. Conventional biodiesel synthesis involves the use of polluting non-renewable strong acid and base as homogeneous catalysts for the esterification of fatty acids and transesterification of triglycerides into fatty acid methyl esters as shown in figure 1. It normally adopts the energy intensive batch mode for large scale synthesis at elevated temperature which is energy inefficient and expensive to operate. Another problem for this kind of operation is the leaching of the strong acid or base into the final biodiesel which requires large amounts of fresh water to wash and hence generates a lot of sewage containing acid, base and oil. Advancement in catalysis for a greener biodiesel becomes crucial for the future development of biodiesel. One of our interests is to develop new long-lived and effective nanosized metal oxide heterogeneous catalysts for conversion of algal oil into biodiesel to minimize the environmental pollution. By controlled hydrolysis of various metal precursors followed by calcination, a series of nanosized metal oxide catalysts have been prepared as shown in figure 2. The catalytic conversion study of canola oil with

Figure 1 - Reactions involved in biodiesel production. Chemical reaction involved in the biodiesel synthesis require strong acid and base as catalyst. The transformation of viscous oil (triglyceride and free fatty acid) into thinner and lower boiling fatty acid enables it to be used by most of the internal combustion engine just with a minor modification

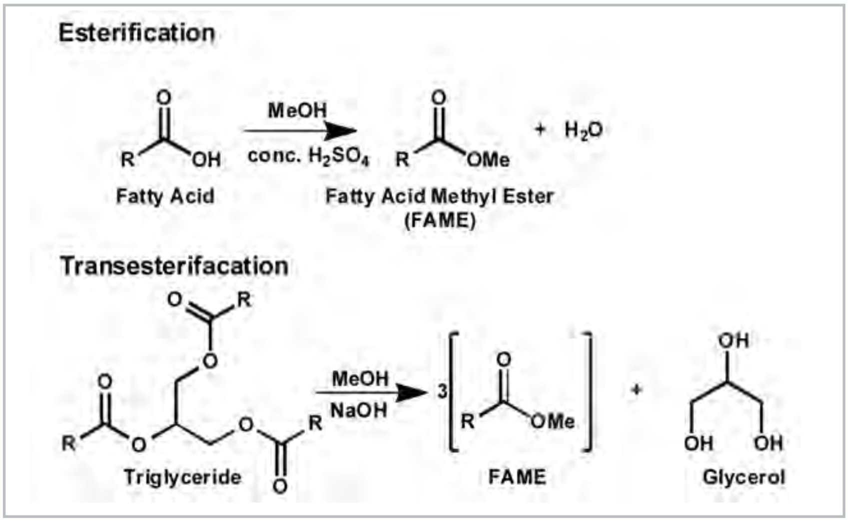
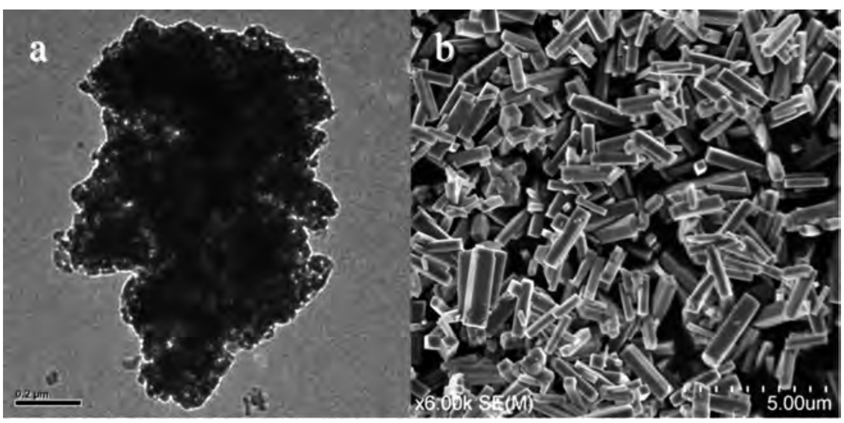


Figure 2 - a) TEM micrograph of Al_2O_3 coated MgO nanoparticles; b) SEM micrograph $CaTiO_3$ nanoblock



methanol using these catalysts shows that they are active catalysts for production of biodiesel at 100°C with conversion over 90%. The advantage of using heterogeneous catalysts is that it minimizes the metal ions leaching, which eliminates the need for washing the produced biodiesel. Biodiesel and valuable glycerol are now the only products that simplify the latter purification steps. Also, as the catalyst is phase-separated from the oil and biodiesel, continuous fixed-bed synthesis can be implemented for faster and easier large scale biodiesel synthesis. The study on continuous flow synthesis of biodiesel using these catalysts is now underway. The ultimate goal is to develop a synthetic protocol that enables a green and energy efficient biodiesel synthesis to promote the use biodiesel as alternative liquid fuel to replace fossil diesel.

In short, in order to make biofuel a practical solution for future transportation fuel, a holistic approach that tackles the problem from the production of biomass, to separation and extraction of useful raw materials, to chemical conversion to biodiesel, and finally to the purification of the biodiesel is critical. Therefore, we are now collaborating with a group of experts who are working on complementary areas including algae cultivation that mimics algal bloom, energy efficient separation and extraction of algal oil, and green biodiesel synthesis using heterogeneous catalysts in order to provide a one-stop solution for practical and economical algal biodiesel production.