

PHOTOCATALYTIC AND BIODEGRADABLE BIOPLASTIC EXTRACTION FROM STEMS AND LEAVES OF VARIOUS PLANTS

Musurmonov Abror Alisherovich

Choriyev Jahongir Olimjon o'g'li

Denau Institute of Entrepreneurship and Pedagogy Biology student

Ubaydullayeva Shohista Hidoyatillo qizi

Termiz Institute of Agrotechnologies and innovative Development Quarantine
direction of plants and agricultural products student

Abstract: Large numbers of leaves fall on the earth each autumn. The current treatments of dead leaves mainly involve completely destroying the biocomponents, which causes considerable energy consumption and environmental issues. It remains a challenge to convert waste leaves into useful materials without breaking down their biocomponents. Here, we turn red maple dead leaves into an active three-component multifunctional material by exploiting the role of whewellite biomineral for binding lignin and cellulose. Owing to its intense optical absorption spanning the full solar spectrum and the heterogeneous architecture for effective charge separation, films of this material show high performance in solar water evaporation, photocatalytic hydrogen production, and photocatalytic degradation of antibiotics. Furthermore, it also acts as a bioplastic with high mechanical strength, high-temperature tolerance, and biodegradable features. These findings pave the way for the efficient utilization of waste biomass and innovations of advanced materials.

Key words: Biocomponents, biodegradatin, biomineral, lignin-cellulose, solar water evaporation, photocatalytic.

Introduction

The world has 4.1 billion hectares of tree coverage, which accounts for 31% of the total land area. The global number of trees is approximately 3 trillion, and they make great contributions to carbon sequestration, timber stocks, water and air quality control, etc. The leaves constitute one of the most important components of a tree, and they serve as the primary sites of photosynthesis to produce food for the whole tree and play an important role in transpiration via stomata. Given that large numbers of leaves fall off trees over time¹, it is unfortunate the majority of them ultimately decay naturally into fertilizers, and this process emits greenhouse gases (CO₂, CH₄, and N₂O) into the atmosphere (Fig. 1). In addition to this natural process, waste dead leaves have been mainly treated via incineration, landfilling, and composting; whereas incineration emits

large amounts of CO₂ and noxious gases/particulates, landfilling generates CH₄ and refractory leachate, and composting requires a long time. In recent years, breakthroughs in the structural reconstruction of wood have been made by Hu and coworkers. For example, they demonstrated that wood can be converted into a bioplastic by lignin regeneration and a moldable lightweight 3D structural material via rapid water shock². In contrast to wood, which is of great value and mainly contains lignocellulose, dead leaves are waste with considerable biominerals that provide great challenges for utilization. Recently, the carbonization of dead leaves was explored as a means to produce carbon materials used as adsorbents for dyes and heavy metals and electrodes for supercapacitors and batteries. However, this process consumes high amounts of energy because the biostructures of the leaves are completely destroyed. Therefore, it is urgent to explore strategies for turning waste leaves into useful materials while retaining their biocomponents. While the organic lignocellulose of leaves has received great attention, calcium oxalate monohydrate (whewellite), a biomineral used for structural support and calcium storage, is frequently neglected during biomass utilization⁴. The formation of whewellite sequesters calcium away from the cytoplasm, where the concentration of ionic calcium remains at the micromolar level. As the leaves age, whewellite accumulates and generally constitutes from 1% to 80% of the dry weights of leaves. This has stimulated us to pay special attention to the whewellite biomineral for turning dead leaves into useful materials. In this work, we exploited whewellite as a strong binder for lignin and cellulose via extensive chemical bonding and hydrogen bonding, leading to the invention of an active multifunctional material (AMM) from the dead leaves. Furthermore, the optical, thermal, mechanical, and biodegradable properties of the AMM film enable its high performance in solar water evaporation, photocatalytic hydrogen production, photocatalytic degradation of antibiotics and as a high-temperature-resistant bioplastic (Fig. 1). The production of AMM from dead leaves and its wide applications will play important roles in addressing critical energy and environmental issues⁵.



Figure-1. Schematic illustration of technologies for treating dead leaves. Comparison of the approach developed in this work with traditional technologies.

Results and Discussion

Synthesis and characterization of AMM. As illustrated in Fig. 2, AMM film, which appears black with a high mechanical flexibility and an adjustable thickness (Supplementary Fig. 1), was prepared from the dead leaves of red maple trees with a deep eutectic solvent (DES) composed of choline chloride and oxalic acid dihydrate. Additional information on the synthesis of materials and procedures used in the study are present in the Methods section. In this process, lignin was in-situ regenerated and cellulose was defibrillated. In addition, most of the hemicellulose, pigments, and mineral elements were removed. The yield of AMM calculated by the dry weight was 57.7%, and lignin, cellulose, and whewellite were the main components. X-ray diffraction (XRD) patterns (Fig. 2) demonstrated the presence of whewellite in both the AMM and the original leaf, together with lignocellulose, for which broad peaks were located at $10-55^\circ$. There were no other crystal impurities (minerals). In addition, the reduced crystallinity of the lignocellulose after DES treatment provided evidence for deconstruction of the dead leaves⁷. Moreover, in the Fourier transform infrared (FT-IR) spectra (Fig. 2), the signals at 1312 and 1615 cm^{-1} for C = O stretching vibrations of the whewellite were enhanced after the DES treatment, while the signal at 1728 cm^{-1} resulting from C = O stretching vibrations of the acetyl groups and carboxylic acids of hemicellulose was weakened. In addition, the characteristic vibrations for the aromatic skeleton of lignin at 1460 and 1512 cm^{-1} , as well as the C-OH and C-O-C stretching vibrations for cellulose at 1030, 1052, and 1157 cm^{-1} were clearly resolved. Furthermore, X-ray photoelectron spectra indicated C, O, and Ca as the main constituent elements of the AMM and increased C = O, O-C-O, and C-OH groups after the DES treatment. These oxygen-containing groups were responsible for the formation of an extensive hydrogen bonding network. The transmission electron microscopy (TEM) image reveals the coexistence of lignin flakes, cellulose nanofibrils, and whewellite nanoparticles in the AMM. The high-resolution TEM image and energy dispersive spectroscopy (EDS) elemental maps further demonstrated that whewellite nanoparticles were embedded in lignocellulose with intimate contacts⁹. AMM as the evaporator, photocatalyst, and bioplastic Solar water evaporation is an attractive technology for water purification, steam sterilization, and electricity generation due to its high energy efficiency and low environmental impact.

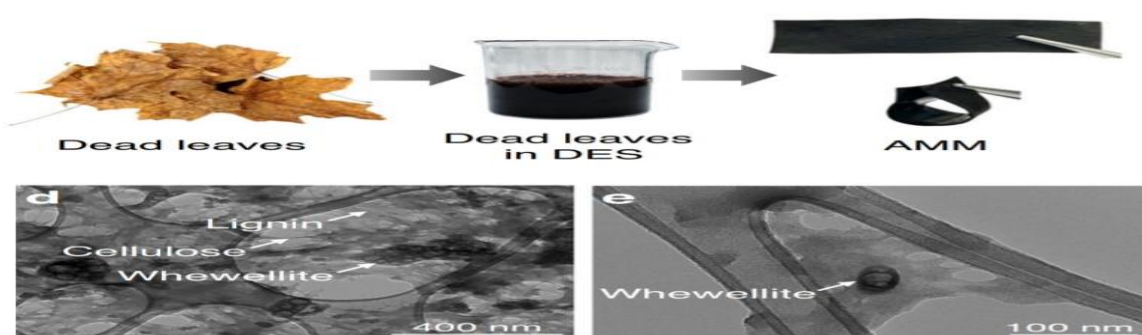


Figure-2. a Visual illustration of the conversion from red maple dead leaves to AMM with deep eutectic solvent (DES) and TEM images of AMM.

As a promising photothermal material, the AMM film was used for solar water evaporation, and it realized a high evaporation rate of $0.8 \text{ kg m}^{-2} \text{ h}^{-1}$ and an impressive solar-to-steam efficiency of 52.5% at ambient solar light intensity, which are among the highest values reported for state-of-the-art materials. This mainly resulted from the lignocellulose instead of the minerals and pigments light intensities. The photothermal effect is mainly caused by indirect nonradiative relaxation of electron-hole pairs, but if some photogenerated electrons and holes can be quickly captured by reactant molecules before recombination, photocatalytic reactions occur. Here, we conducted the photocatalytic hydrogen production reaction with a methanol-water mixture over the AMM film to demonstrate its catalytic capability for clean fuel generation. The use of methanol enabled favorable thermodynamics. As shown in the hydrogen production rate over the AMM film under simulated sunlight irradiation (1 kW m^{-2}) was as high as $12.4 \mu\text{mol h}^{-1} \text{ cm}^{-2}$, which was 4.2 times that over the original leaf. After filtering the UV light, the hydrogen production rate still reached $8.4 \mu\text{mol h}^{-1} \text{ cm}^{-2}$, marking an noble-metal-free and visible-light-responsive photocatalyst that outperformed dead leaves-derived pyrochar and hydrochar and realized an efficiency on the same order of magnitude as that of the prototypical water splitting photocatalyst, 1 wt% Pt/TiO₂ ($15.6 \mu\text{mol h}^{-1} \text{ cm}^{-2}$ and 0 under simulated sunlight and visible light, respectively). Compared to the AMM, the constituents lignin, cellulose, and whewellite¹¹, as well as the lignin-cellulose composite exhibited poorer photocatalytic efficiencies under simulated sunlight and visible light irradiation, implying that these three components might form heterostructures that allow effective separation of photogenerated electrons and holes. The trace pigments in the AMM made little contribution, as evidenced by the similar activity seen without them.

Methods and Materials

The leaves were thoroughly washed with pure water, laid out to dry at room temperature, and then ground into powders ($\leq 300 \mu\text{m}$). Three other types of dead

leaves, namely, those of the *Cercis canadensis*, *Quercus rubra*, and *Acer platanoides*, were collected and treated in the same manner. Choline chloride ($\geq 98\%$), oxalic acid dihydrate (98%), calcium oxalate monohydrate (99%), hydrochloric acid (36% solution), nitric acid (68- 70% solution), and hydrogen peroxide (30% solution) were purchased from Thermo Fisher Scientific. Sodium sulfate ($\geq 99\%$), sodium sulfite ($\geq 98\%$), sodium hydroxide ($\geq 97\%$), sodium chlorite (80%), sulfuric acid (95-98%), acetic acid ($\geq 99.7\%$), tetracycline (98.0-102.0%), methanol ($\geq 99.9\%$), chloroform ($\geq 99.8\%$), magnesium oxide (97%), chloroplatinic acid hexahydrate ($\geq 37.50\%$ Pt basis), zinc oxide (99.99%), titanium (IV) oxide (P25, $\geq 99.5\%$), tungsten (VI) oxide (<100 nm particle size), cerium (IV) oxide (99.95%), zirconium (IV) oxide (99%), gallium (III) oxide ($\geq 99.99\%$), molybdenum (IV) sulfide (99%), and tungsten (IV) sulfide (99%) were acquired from Sigma Aldrich. Synthesis of the AMM 69.8 g of choline chloride and 63.0 g of oxalic acid dihydrate (at a molar ratio of 1:1) were mixed and melted at 80 °C under stirring to form a transparent deep eutectic solvent. Red maple leaf powder (8.8 g) was added to the solvent and heated to 100 °C for 30 min, after which 13 mL of deionized water was introduced, and the mixture was held at 100 °C for another 2 h. Continuous magnetic stirring was employed during this process. After cooling to room temperature, the resulting solid material was collected by centrifugation, repeatedly washed with deionized water, and then dispersed in 150 mL of deionized water. The dispersion was ultrasonicated at 500 W for 30 min and subsequently centrifuged to give a black slurry. The black slurry was spread on a stainless steel plate to acquire the AMM after water evaporation at room temperature. The yield of AMM calculated by the dry weight was 57.7%. The dead leaves of *Cercis canadensis*, *Quercus rubra*, and *Acer platanoides* trees, as well as the leaf pulp and leaf veins of the red maple tree (separated by hand), were also used as raw materials with which to synthesize the AMM via the same method.

Preparation of the control samples

The AMM without whewellite or other minerals (named lignin-cellulose) was obtained with a pretreatment procedure used to remove the metal salts from the leaf powders. Namely, 1 g of leaf powder was dispersed in 100 mL of 2 M hydrochloric acid and heated at 70 °C for 3.5 h. The resulting solid was thoroughly washed with deionized water until the pH reached 7 and then dried at 60 °C overnight. This solid, a substitute for the original leaf powders, was utilized to prepare the lignin-cellulose sample by following the same synthetic route described in the last section. The lignin sample was acquired by using sulfuric acid to treat the leaf powders. Namely, 1 g of leaf powder and 20 mL of a 72 wt% sulfuric acid solution were mixed and stirred at

room temperature for 2 h. Afterward, 750 mL of deionized water was introduced and boiled at 100 °C for 4 h. Finally, the solid was washed and dried at room temperature. The cellulose sample was prepared via two steps.



Figure-3. Biodegradability tests of the AMM and frequently used polyethylene plastics in soil

First, 1 g of the leaf powder was added to a 10 mL aqueous solution containing 0.4 M sodium sulfite and 2.5 M sodium hydroxide, which was then heated at 100 °C for 3 h. After repeated washing to remove the residual chemicals, the solid was dispersed in 10 mL of 30% hydrogen peroxide solution and boiled at 100 °C for 3 h until the color of the solid completely disappeared. The solid was then washed and dried at room temperature. The structures of these control samples were confirmed. In addition, two kinds of biochars, namely, hydrochar and pyrochar, were prepared for comparison with the AMM. The preparation methods were the same as those employed in a previous publication. Namely, the hydrochar was synthesized by stirring a suspension consisting of 7 g of leaf powder and 50 mL of deionized water for 2 h at room temperature, followed by hydrothermal treatment in a Teflon-lined stainless steel autoclave at 200 °C for 5 h. The resulting solid was washed with deionized water and dried at 60 °C overnight. In contrast, the pyrochar was prepared by pyrolyzing the leaf powders at 450 °C for 3 h under a 10 mL min⁻¹ argon gas flow. Electrochemical tests were carried out in a three-electrode cell in which a fluorine-doped tin oxide glass coated with sample, Pt, and a saturated calomel electrode acted as the working, counter, and reference electrodes, respectively. A 0.5 M sodium sulfate aqueous solution was used as the electrolyte. Mott-Schottky analyses were conducted at 1, 2, and 3 kHz in the dark, while the transient photocurrent response was acquired under visible light irradiation ($\lambda > 400$ nm, 0.85 kW m⁻²).

Mechanical tests

All film samples (except the original leaf) subjected to the mechanical tests were prepared by wet casting (immediately after synthesis) and subsequent drying at room temperature. The mechanical tests were conducted on a TA Instrument Q800 dynamic mechanical analyzer. The tensile properties of the samples were determined at room

temperature and at a constant speed of 3 N min⁻¹ until fracture. The effects of temperature on the tensile properties of the AMM were further investigated at 100 °C in the same manner. Dynamic mechanical analyses were carried out for the AMM and the original leaf in the temperature range of 30-190 °C with the frequency and amplitude set as 2 Hz and 5 μm (0.03% of the sample length), respectively. Biodegradability tests. To evaluate the biodegradabilities, thin films of the AMM and daily used polyethylene plastics (Ziplock bag, shopping bag, and plastic wrap) were buried in natural soil at a depth of 10 cm. The samples were monitored periodically to assess the biodegradation degrees.

Solar water evaporation

To test the solar water evaporation performance, an AMM film (1 g, 3 cm × 3 cm) was placed in a 100 mL beaker filled with 20 mL of deionized water and placed under simulated sunlight irradiation provided by a Newport 300 W xenon lamp equipped with an AM1.5 G filter. A Sartorius Entris analytical balance with a 0.1 mg accuracy was utilized to measure the evaporation rate in real time. An Omega HH11 digital thermometer was used to measure the surface temperature of the AMM film.

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