ADDITIVE-FREE PHOTOCHEMICAL UPCYCLING OF BIO-BASED (MICRO)PLASTICS INTO VALUE ADDED CHEMICALS

Athanasia KOTSARIDOU[1*], Dimitrios A. GIANNAKOUDAKIS[1], Konstantinos TRIANTAFYLLIDIS[1]
[1]*Aristotle University of Thessaloniki, Department of Chemistry, Thessaloniki, Greece*
** e-mail corresponding: nancykotsa7@gmail.com*

Significance and Relevance

Our approach targets to the development of sustainable methods for biobased (micro)plastics upcycling with the smallest environmental footprint, through additive-free heterogeneous photocatalysis, enabling the conversion of plastic waste into value-added chemicals. This work demonstrates as proof of concept for low-cost, energy-efficient, easy to operate, and environmentally friendly strategy to the controlled breakdown of specific bonds in polymers, as for instance C-C bonds in the cased of bio-based polylactic acid (PLA). The predominately desired compounds are lactic acid and pyruvic acid, although some additional compounds are also welcome. The key parts of the processes are on the one hand to optimize crucial experimental parameters (like solvent, temperature, duration, nature of the light irradiation etc.) and on the other to design and develop advanced nano-photocatalysts of specific physicochemical features. Regarding the novel photocatalytic nanostructured materials, they should be designed to have a high specific surface area, large pores volume, and an abundance of surface functional groups, especially acid ones, since they are expecting to ultimately improve the overall photocatalytic efficiency.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization and Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Poster

Introduction and Motivations

Plastic waste ending up in landfills or released into the natural environment due to insufficient recycling and reuse technologies poses serious threats to ecosystems and human health. Bio-based, biodegradable plastics like PLA have been proposed as a solution, and their demand is expected to soar, with global annual production projected to triple in 2 years. Although PLA is assumed as a promising alternative to traditional petroleum-based plastics, its degradation remains significantly slower than desired[1]. Meanwhile, PLA nature bio-decomposition releases predominately CO_2 and H_2O, resulting in carbon emissions. Hence, it is an urgent need for novel and efficient catalytic recycling method that can convert PLA into value-added chemicals. Photocatalysis offers a green and sustainable approach addressing this challenge, providing an advantage over conventional plastic recycling, which often involves high energy input, toxic solvents and strong acidic or basic conditions[1]. To trigger the potential of a targeted photocatalytic PLA upcycling, we synthesized novel nanomaterials based on our previously experience[2,3].

Materials and Methods

Herein, we test a wide range of commercial and novel home-made nano-photocatalysts including TiO_2 P25 and P90 nanoparticles, synthesized titanate nanotubes, metal-doped titanium oxide nanoparticles and nanotubes (Mn, Pt, Cu), zinc oxide nanoparticles, bulky and nanosized defected graphitic carbon nitride (g-C_3N_4), carbon quantum dots etc. The materials were synthesized using different protocols including hydrothermal, ultra-slow precipitation, and calcination methods, while they were previously characterized via various techniques (XRD, SEM, N_2-sorption, DR UV-Vis, TA) to determine their physicochemical properties. Photocatalytic tests of PLA upcycling were performed in different solvents with emphasis on using the “greenest” ones, namely water, acetonitrile or mixtures of them. Various other parameters were explored with the most vital to be the catalyst/plastic ratio (1/10), nature of irradiate light of specific wavelengths (UV-A (375 nm), violet (427 nm), royal blue (425 nm), green (525 nm) and their combinations.

Results and Discussion

Among the various tested materials, some synthesized materials showed capable to initiate the photocatalytic PLA conversion. In the case of water as solvent and only by the heat provided by the

LEDs (max 50 °C), PLA microplastics (size range: 500-1000 μm) was found being very photo-stable, while the commercial benchmark TiO_2 P25 showed a very limited PLA conversion under UV-A light without the addition of any additive. Our developed titania oxide/hydroxide nanoparticles prepared by ultrasound-assisted ultra-slow precipitation (Ti-US) demonstrated a 72% higher PLA conversion comparing to P25. Additionally, the novel Ti-US, aside from producing valuable lactic and formic acid, contributed also to the production of acetic acid, thus increasing the range of chemicals generated through the photocatalytic upcycling of PLA. This nano-architectured material has a surface area above 400 m^2/g and the pores volume exceed 0.5 cm^3/g. In addition, it possesses a significant volume of micropores (~0.08 cm^3/g). Ultimately important are also the nanoparticles' (NPs) morphological, structural, and surface chemical features. The rough external "sponge-like" surface of the NPs has a high density of SFGs, predominately acidic, with the surface pH to be found equal to 3.0. The acid surface environment is anticipated to play a key role on interacting with the PLA particles and acting as a "bridge" for the transfer of the photo-induced charges (e^-/h^+), initiating polymer's C-C cleavage without the need any acidic additive.

Even though the presented conversions are not assumed very high, these results indicate that further optimization of the process (maybe even addition of some environmental-friendly additives like molecular oxygen) and above all materials/composites further development could improve the yield of the sustainable photocatalytic plastic up-cycling. This fact can be supported by the best results obtained from a multi-doped titanate nanotubes composite (TiNTNbs-gC_3N_4CuPt). Pure titanate nanotubes or graphitic carbon nitride barely reached a 10% PLA conversion separately, while addition of Pt or Cu to the nanotubes did not impact positively the PLA conversion. On the contrary, the TiNTbs nanocomposite with g-C_3N_4, co-doped with Pt and Cu (TiNTbs/gC3N4CuPt) showed a very promising PLA conversion of almost 20 %.

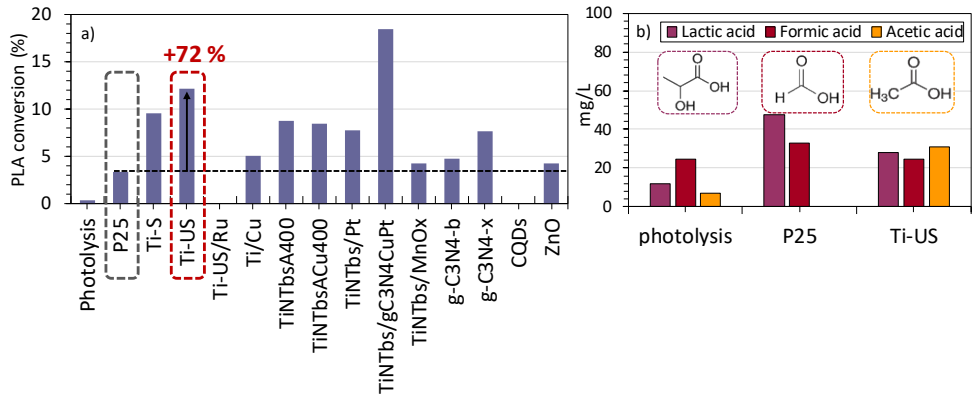

Figure 1. Photocatalytic upcycling of PLA with synthesized nanomaterials a) PLA conversion, b) products of PLA photodegradation (Experiment conditions: 15 mL solution of PLA/H_20 1% w/v, 1 g/L catalyst, 375 nm, 50 °C, 400 rpm, 96 h).

References

1. T. Uekert,Kasap H., E. Reisner. Photoreforming of Nonrecyclable Plastic Waste over a Carbon Nitride/Nickel Phosphide Catalyst. Journal of the American Chemical Society 2019, 141 (38), 15201–15210.
2. D. A. Giannakoudakis, K.Vikrant, A. P.LaGrow, D. Lisovytskiy, K. H.Kim, T. J.Bandosz, & J. Carlos Colmenares. (2021). Scrolled titanate nanosheet composites with reduced graphite oxide for photocatalytic and adsorptive removal of toxic vapors. Chemical Engineering Journal, 415(December 2020), 128907. https://doi.org/10.1016/j.cej.2021.128907
3. D. A. Giannakoudakis et. al., 2021. Boosting the Photoactivity of Grafted Titania: Ultrasound-Driven Synthesis of a Multi-Phase Heterogeneous Nano-Architected Photocatalyst. Advanced Functional Materials, 31(1).

Acknowledgements

"This project is carried out within the framework of the National Recovery and Resilience Plan Greece 2.0, funded by the European Union – NextGenerationEU (Implementation body: HFRI, Project No.: 015949)."