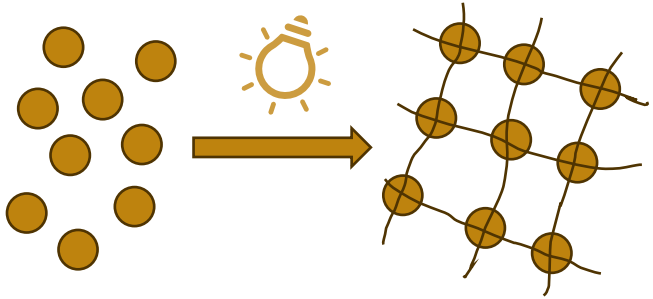
Natural Photoinitiators for 3D Printed Water-driven Actuators

D. Zhu
Research School of Chemistry
Australian National University
Canberra, Australia
February 20th, 2024

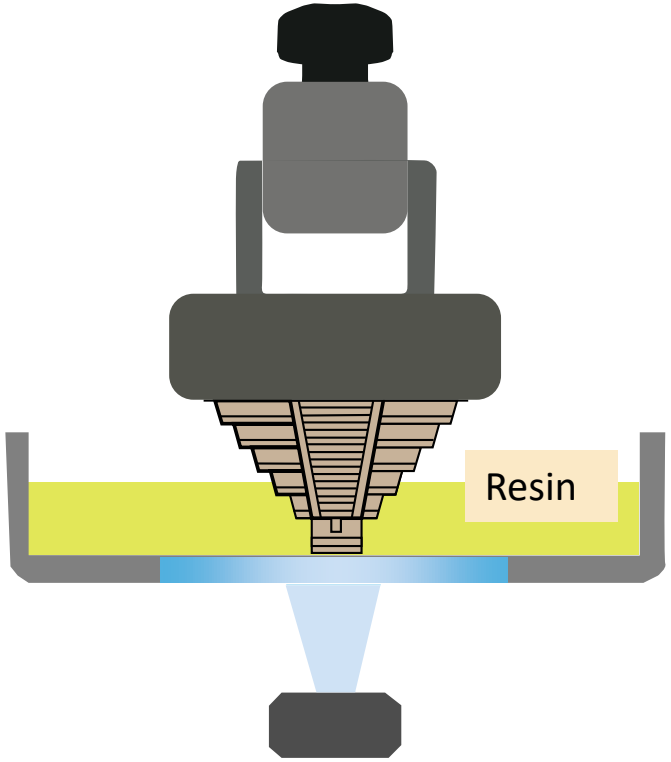
Australian National University

Light-based 3D Printing



Features

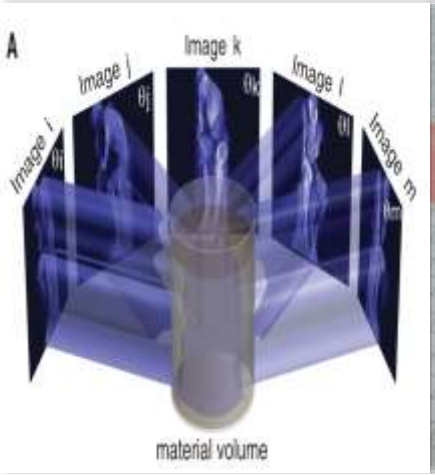
- High resolution
- High printing accuracy
- Low cost
- Low initial vat volume

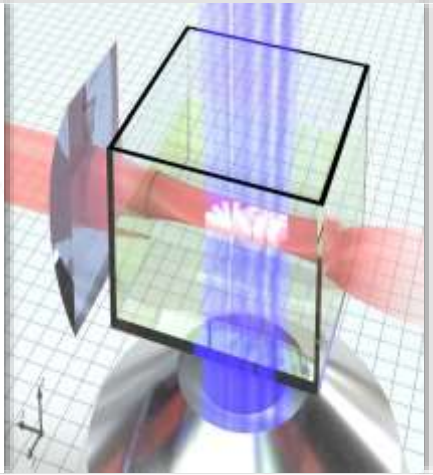


Irradiation at 405 nm

Nat. Commun. ***2022, 13 (1), 5875.***

Advances and shortcomings





Commercial photoinitiators:

Environmental concerns
Health concerns

Volumetric 3D printing

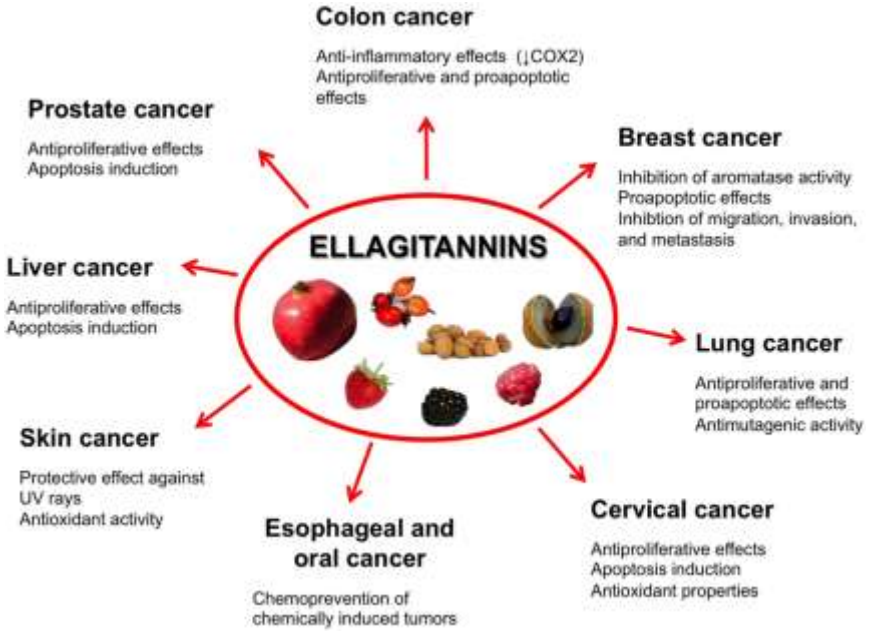
Multi-light 3D printing

Multi-color 3D printing

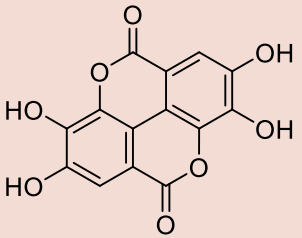
How to resolve?

Science **2019**, *363* (6431), 1075-1079.
Nat. Photonics **2022**, *16* (11), 784-791.
Adv. Funct. Mater. **2022**, *32* (28), 2112329.

Nature: an alternative source of safe photoinitiators

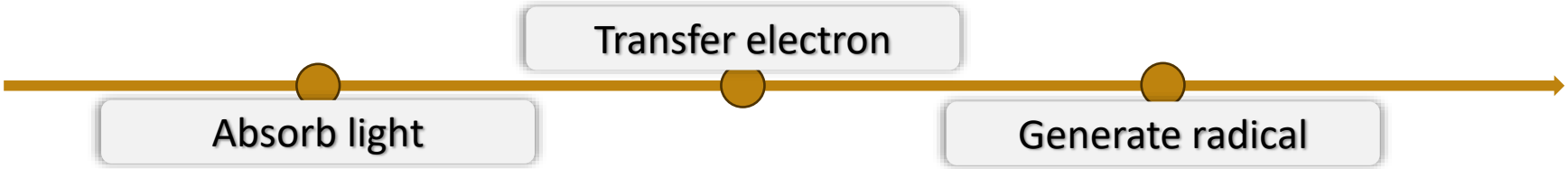


Pomegranate

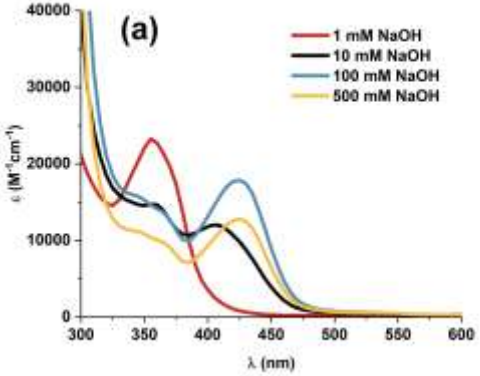


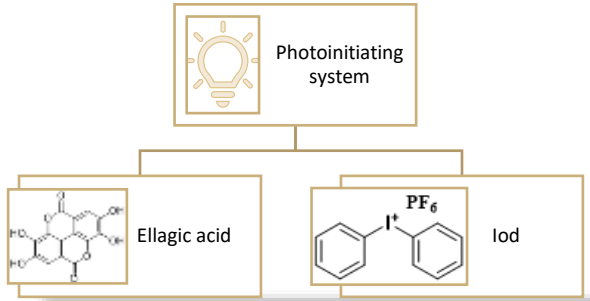
Ellagic acid

Photoinitiation mechanism



Photoinitiation mechanism



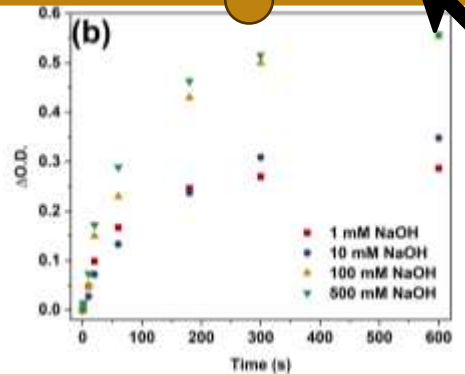


- Electron transfer occurs within photoinitiating system
- Alkali affects electron transfer rate

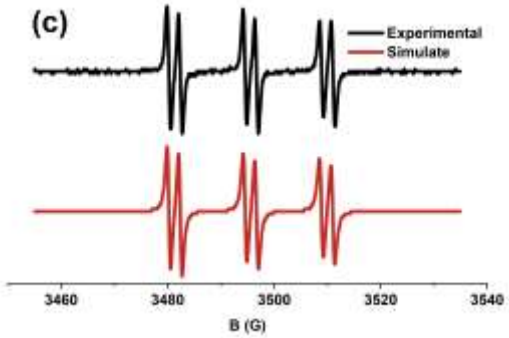
Transfer electron

Absorb light

- Ellagic acid absorbs light at 405 nm
- Alkali affects light absorption property
- Ellagic acid is excited



Electron paramagnetic resonance-spin trapping (EPR-ST)



Generate radical

- Phenyl radical was generated to initiate polymerization

Phenyl radical

Photoinitiation mechanism:

$$Ellagic\ acid \xrightarrow{hv} Ellagic\ acid^*$$

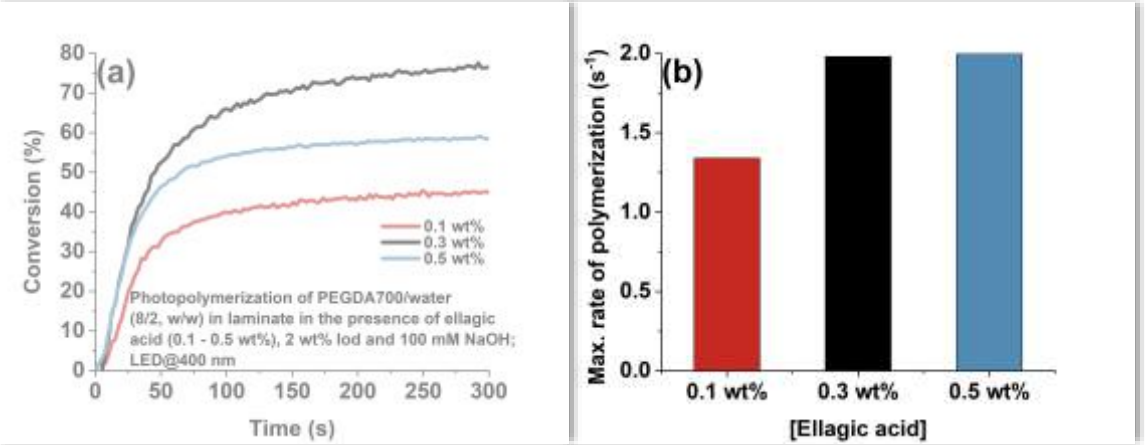
$$Ellagic\ acid^* + Iod\ (Ph_2I^+) \rightarrow\rightarrow Ellagic\ acid^{*\cdot} + PhI + Ph^\cdot$$

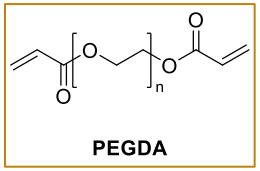
$$Ph^\cdot + M \rightarrow M^\cdot$$

$$M^\cdot + M \rightarrow P^\cdot_{n-1}$$

$$P^\cdot_{n-1} + M \rightarrow P^\cdot_n$$

Ellagic acid concentration effect



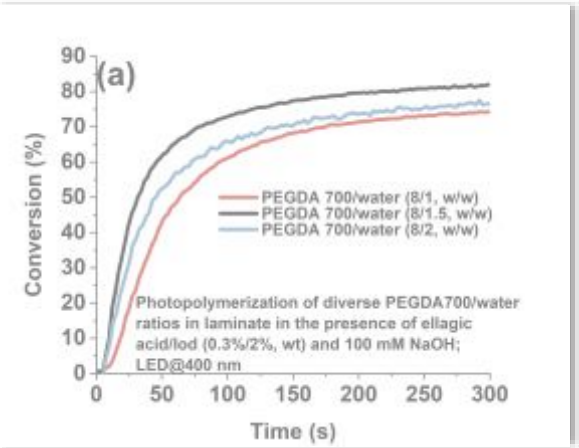


- Water-soluble

[Ellagic acid]

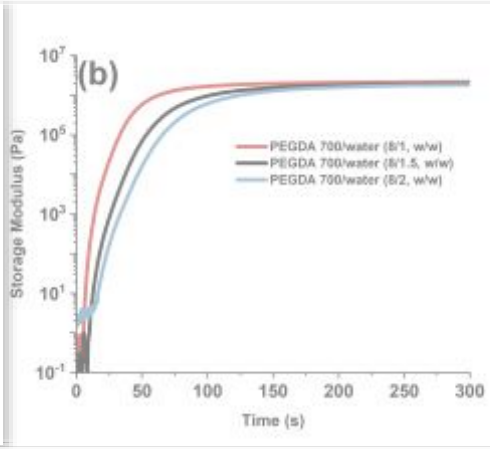
Concentration of ellagic acid affect:
- functional group conversion
- maximum rate of polymerization

Water content effect



Layer-by-layer 3D printing

Shear strength



Photopolymerization

Water affects:
- dissolution of ellagic acid
- amount of PEGDA

Shear strengths

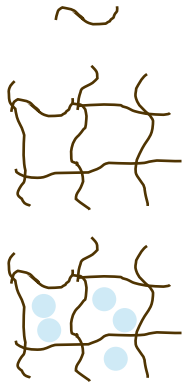
- PEGDA/water (8/1 w/w): rapid increase of shear strength

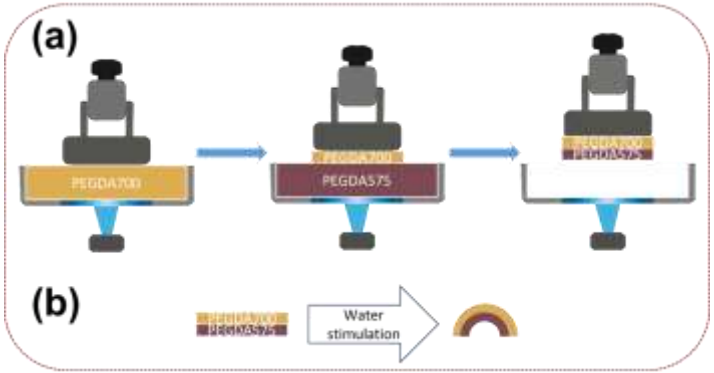
Bilayer hydrogel

Chain length

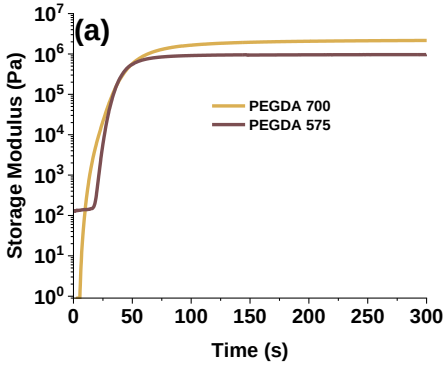
Mesh size

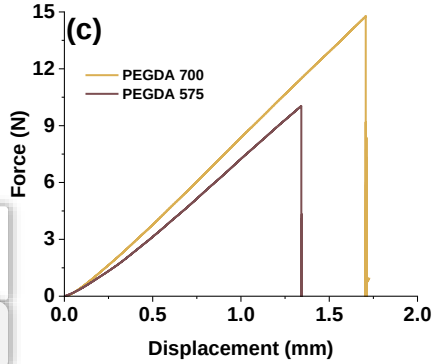
Swelling capacity





Development of multi-material resins for actuator





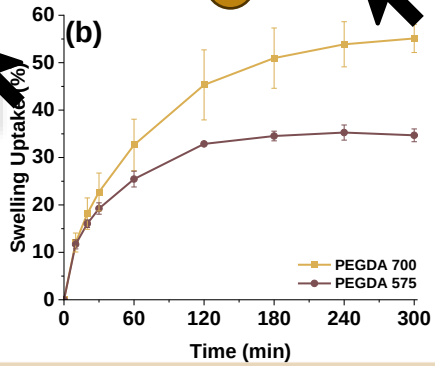
- Longer chain PEDGA affords more water uptake

Swelling kinetics

Actuator

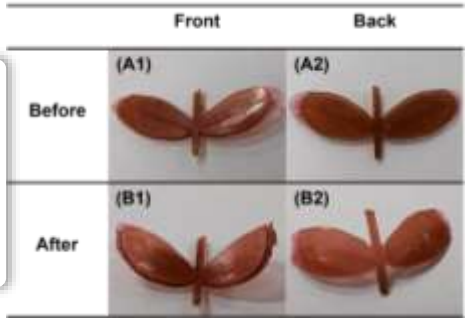
Shear strength

- Similar shear strength

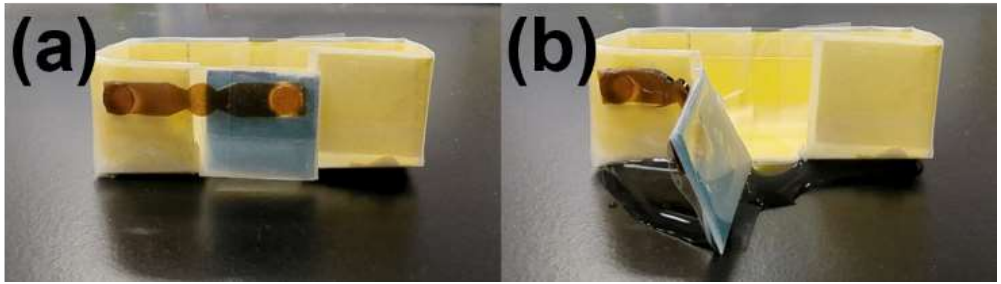


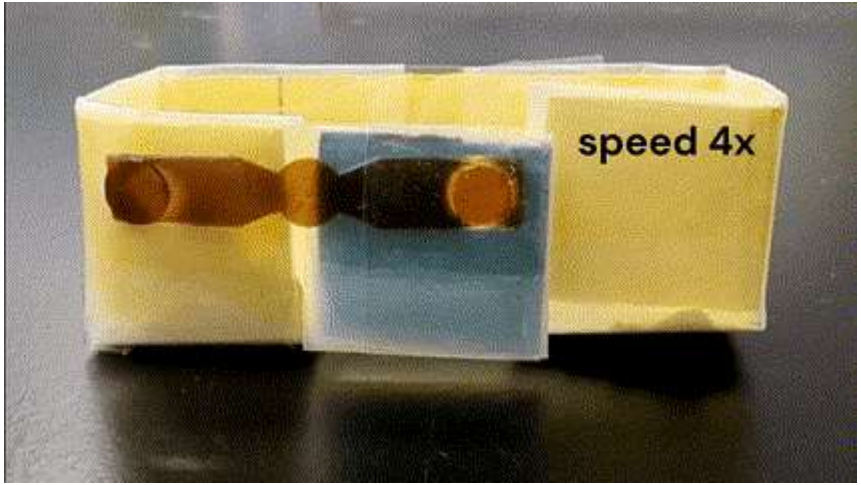
Bending test

- More water uptake cause more shape transformation
- PEGDA 700: more displacement before fracture



Smart switch





ACKNOWLEDGEMENT

Prof. Pu Xiao

Prof. Michelle Coote

Prof. Yun Liu

Prof. Mark Humphrey

Group members

Australian National University

Australian Government

Australian Research Council

Australian National University