Carbon dots - novel, green nanomaterials as components of high-performance photoinitiating systems dedicated to the development of hydrogel polymer materials in 3D VAT technology

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Introduction

Carbon dots currently represent a rising star among nanomaterials. Many researchers are undertaking the synthesis of these materials and new applications for carbon dots are being sought. In this research work, various types of carbon dots were synthesized using citric acid as a precursor. In addition, a procedure was used that effectively purified the synthesized materials. The next step was to study the effect of the synthesized carbon dots on the radical photopolymerization processes of the acrylic monomer. The use of carbon dots (CDs) as components of initiator systems for hydrogel production was also investigated.

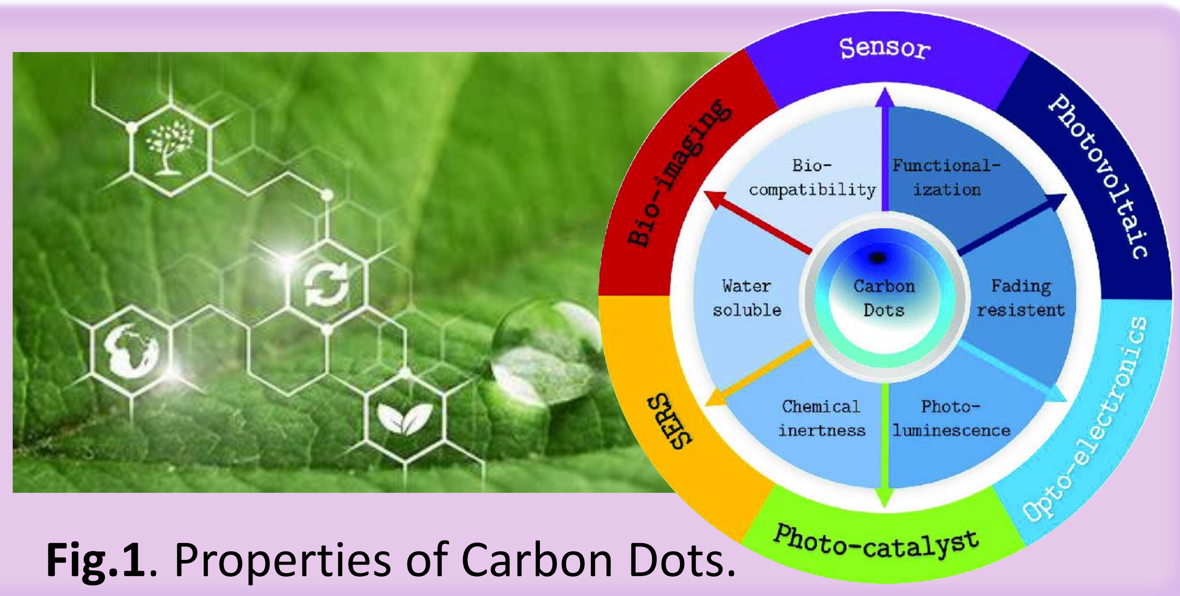

Fig.1. Properties of Carbon Dots.

Carbon dots synthesis

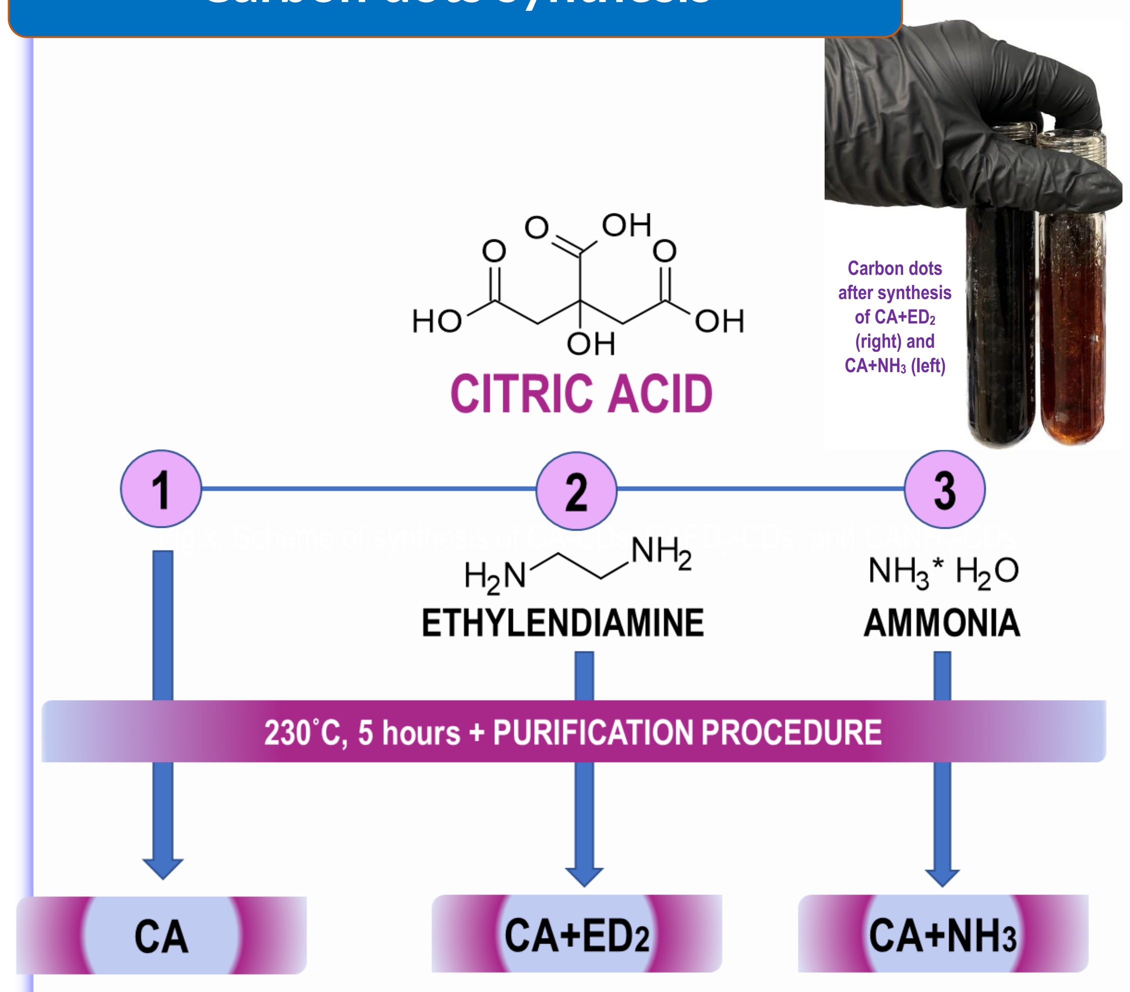

Fig.1. Scheme of synthesis of different kinds of carbon dots.

Carbon Dots Purification Procedure

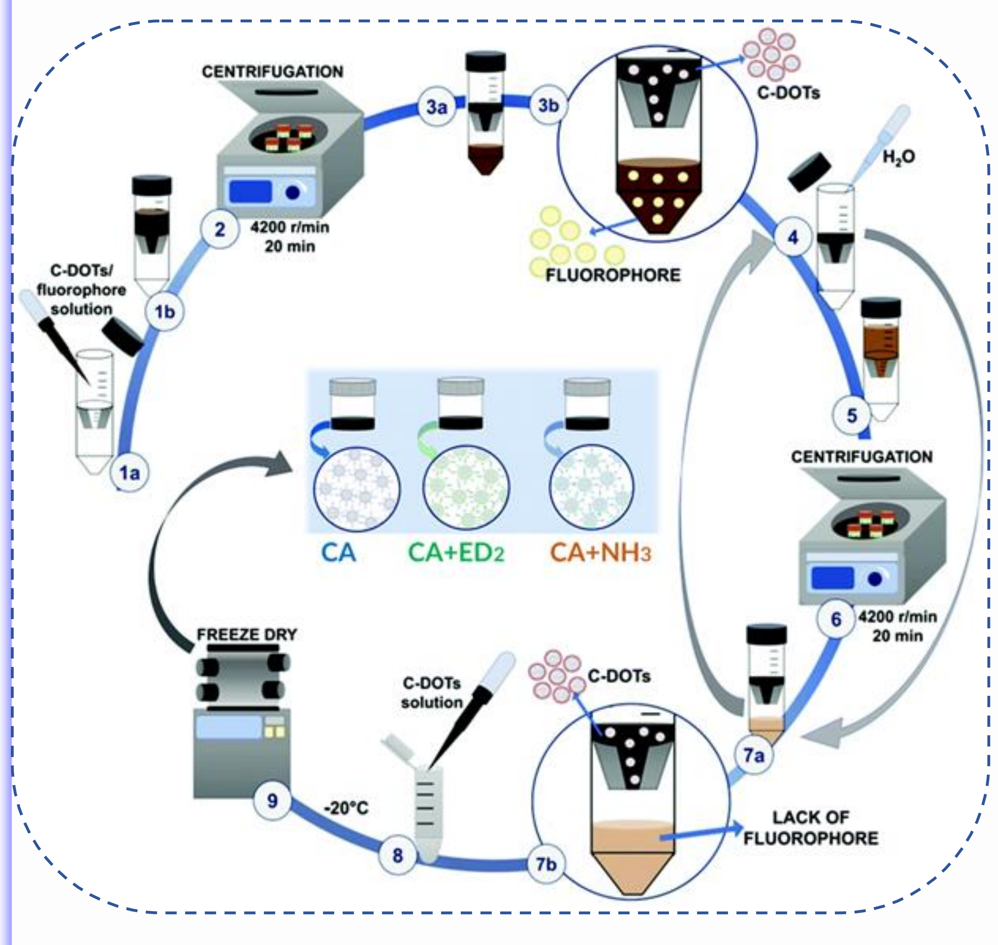

Fig.2. Purification procedure of carbon dots.

Carbon dot purification procedure. The process for carbon dot purification was carried out according to the following steps: (1) carbon dot/fluorophore solution was placed in Vivaspin®20 centrifugal concentrators, 10 000 MWCO (Sartorius, Germany); (2) the product was centrifuged at a rotation speed of 4200 rpm for 20 minutes; (3) as a result of the centrifugation process, a solution containing carbon dots, the remaining fluorophore and other impurities retained over the membrane, while the low-molecular weight fluorophore fraction passed through it; (4) the fluorophore layer was transferred to another container and distilled water was poured into the concentrator to rinse off the solution from the above membrane; (5) a vial refilled with distilled water was then centrifuged; (6) the filtrate content was analysed again; (7) (a and b) stages 4, 5, 6, 7a, and 7b were repeated until no fluorophore was visible in the filtrate solution; (8) the layer containing pure carbon dots was transferred to a separate pot, frozen and lyophilized.

Spectroscopic properties of carbon dots

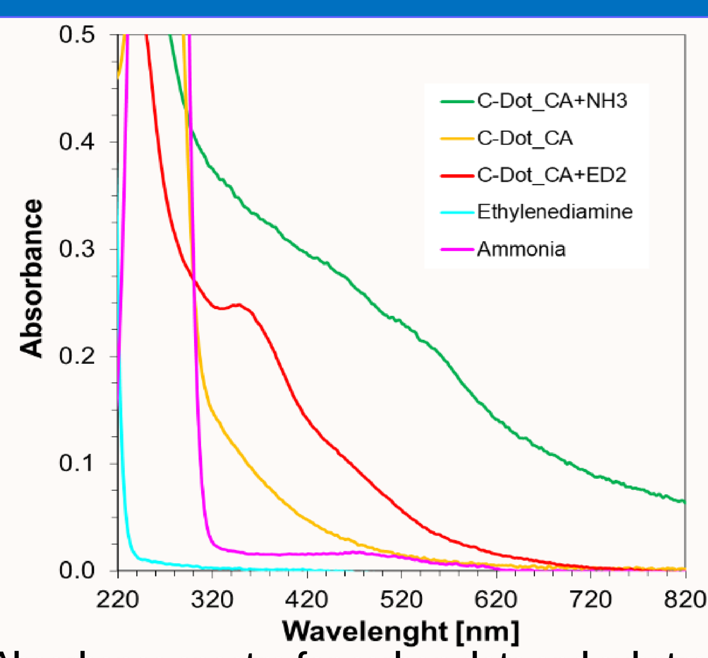

Fig.3. Absorbance spectra for carbon dots and substrates used for synthesis.

Morphological properties of carbon dots

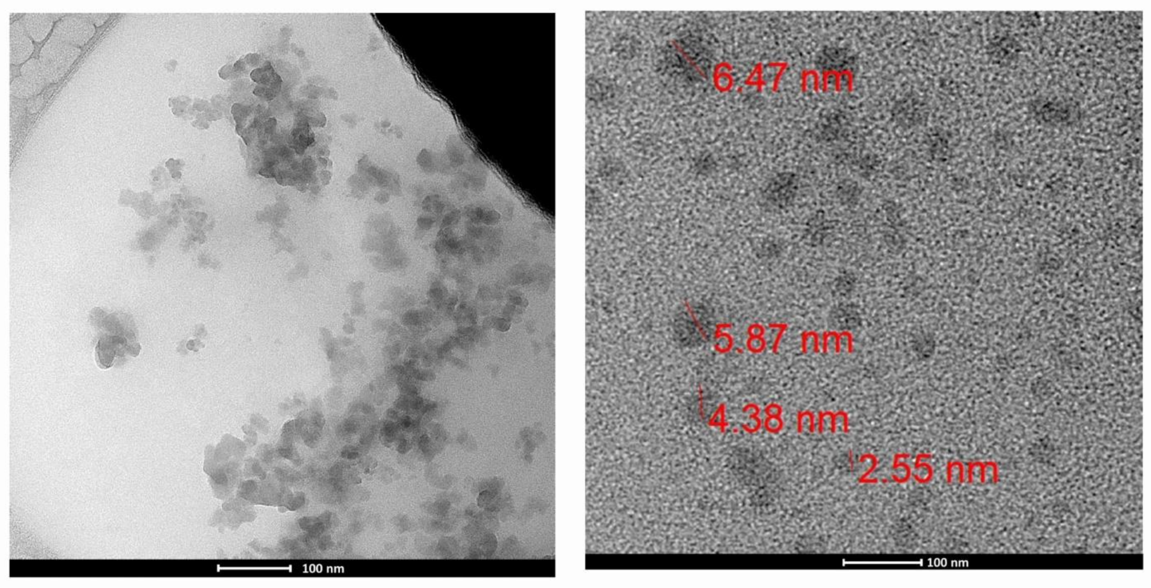

Fig.3. TEM image of (a) CA+ED$_2$ and (b) CA+NH$_3$ Carbon Dots.

Photopolymerization Processes of Carbon Dots

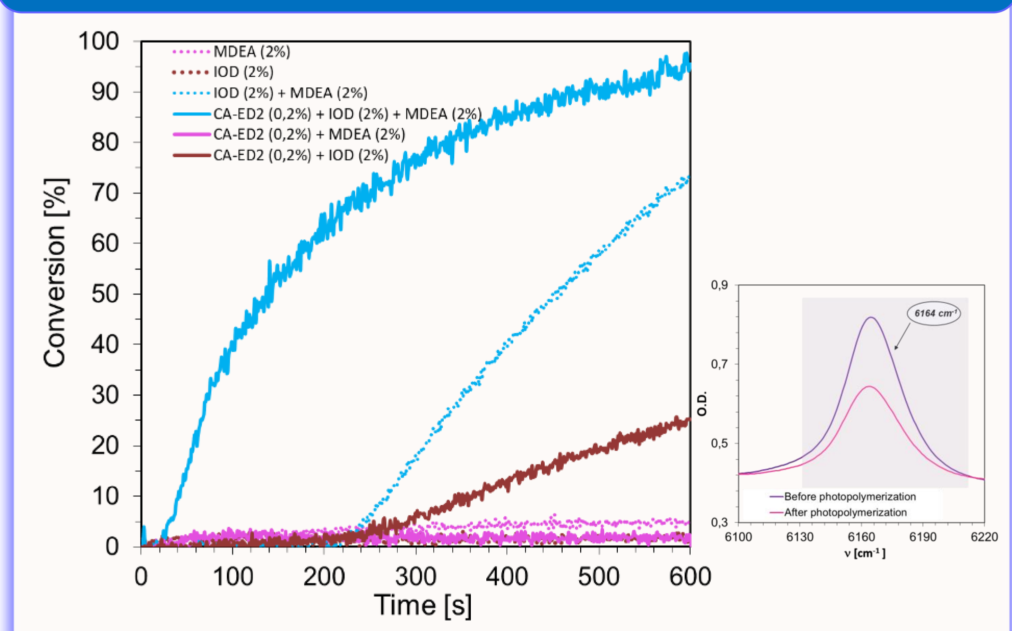

Fig.4. Free-radical photopolymerization during the manufacturing of hydrogels, initiated by photoinitiating systems based on IOD (2.0 wt%), MDEA(1.5 wt%) and CA+ED$_2$ (0.2 wt%) (continuous line), together with appropriate references (dotted line).

Measurments kinetic photopolymerization processes

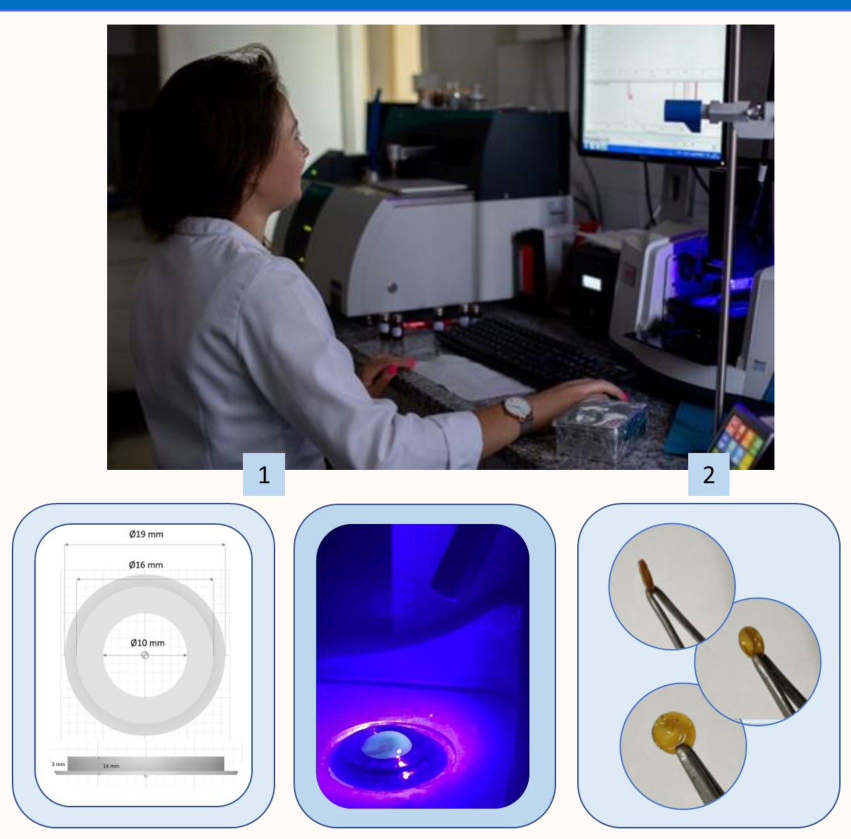

Fig.5. (1) Ring designed to carry out photopolymerization processes (2) and the resulting hydrogel material after photopolymerization of the initiator system containing synthesized carbon dots.

Methods of photopolymerization processes

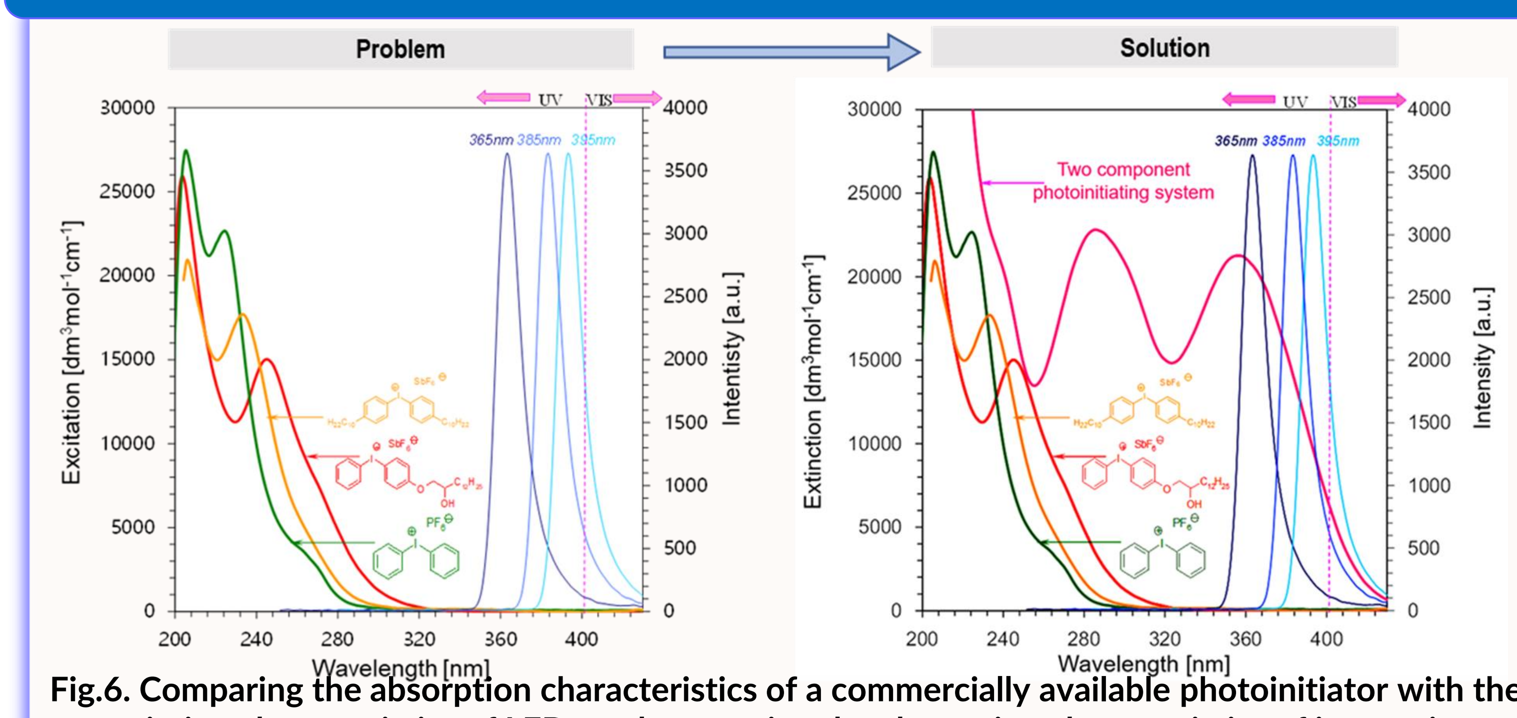

Fig.6. Comparing the absorption characteristics of a commercially available photoinitiator with the emission characteristics of LEDs and comparing the absorption characteristics of innovative initiating systems and a commercially available photoinitiator with the emission characteristics of UV-LEDs.

3D printing of hydrogels

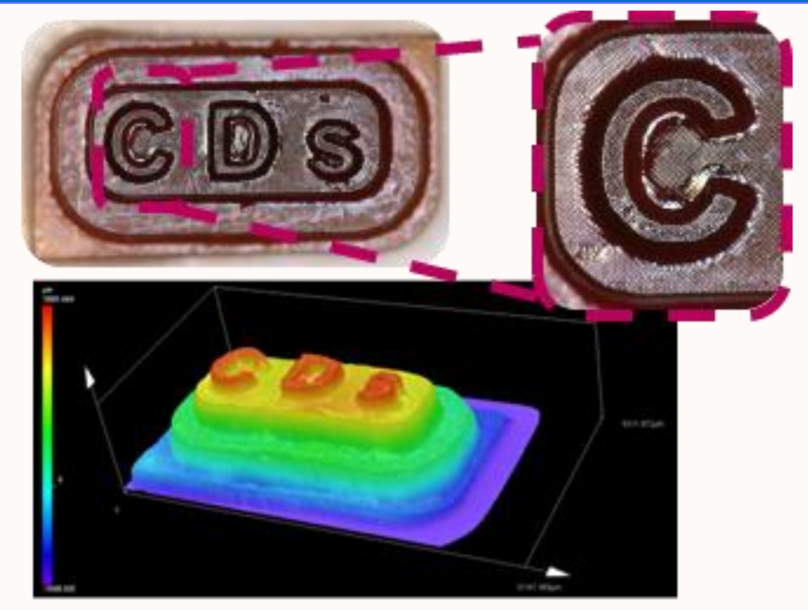

Fig.8. 3D hydrogel printout made by the free-radical photopolymerization of a HEA/water (1/1 wt%) mixture in the presence of a two-component photoinitiating system based on CA+ED$_2$ carbon dots (0.2 wt%), IOD (2 wt%) and MDEA (4 wt%). The printer used was a Lumen X.

Lumen X+ divides 3D models into stacks of horizontal layers as black-and-white image files. Using an industrial visible light projector, each image is projected onto a drop of liquid photo-curable composition on a vat of polydimethylsiloxane (PDMS).The illuminated areas react and solidify, and then the construction platform moves the cured layer up and out so that more of the photo-curable composition can be cured with the next image.

Different printouts with carbon dots initiating systems

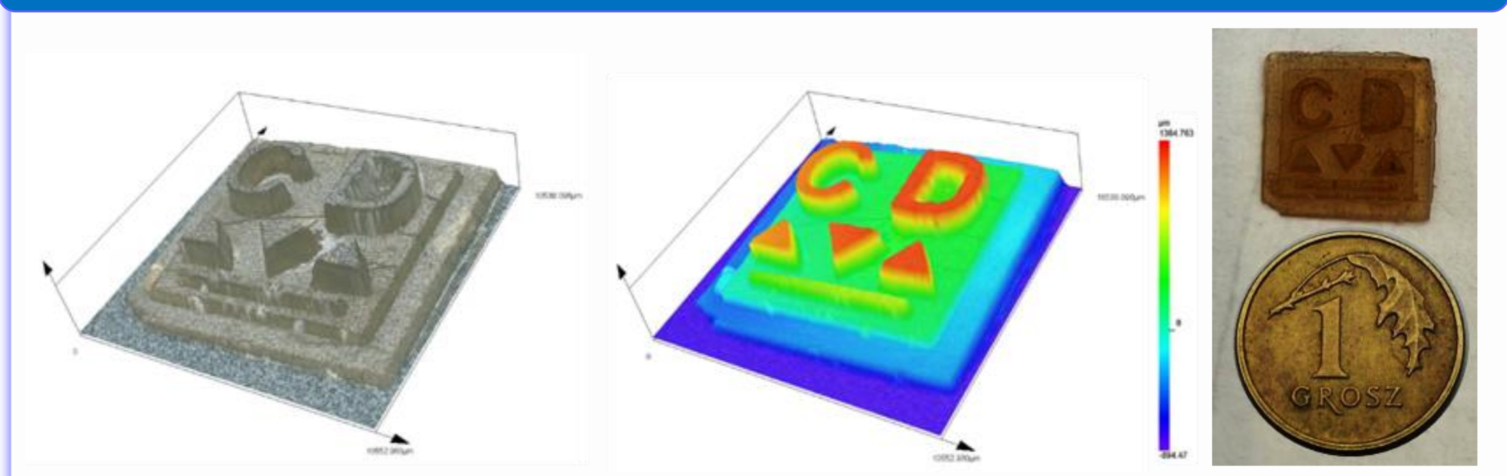

Fig.7. 3D printout made by the cationic photopolymerization of a TMPTA:PEGDA (1/1 wt%) monomers in the presence of a two-component photoinitiating system based on CA+ED$_2$ carbon dots (0.2 wt%) and IOD (2.0 wt%).

Innovation on invention

- The citric acid-based carbon dots obtained in the present study were investigated for their use as photosensitizers of iodonium salts and their applicability to the photochemical preparation of polymeric materials
- In the conducted radical photopolymerization studies using the synthesized carbon dots, their effective performance as photosensitizers of iodonium salts was demonstrated.
- The work also revealed the application of the developed initiator systems based on new types of carbon dots in 3D printing by DIW technique.

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