

SUPPLEMENTARY INFORMATION

Highly efficient carbon dot–based photoinitiating systems for 3D-VAT printing

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Fig.S26. s-SNOM amplitude data taken simultaneously with the data in Figure 17 in the main text, with incident illumination at 1490 cm⁻¹. The data was demodulated at the 3rd harmonic of the AFM tapping frequency to reduce the influence of background effects, and the data has been normalised to the maximum recorded value.

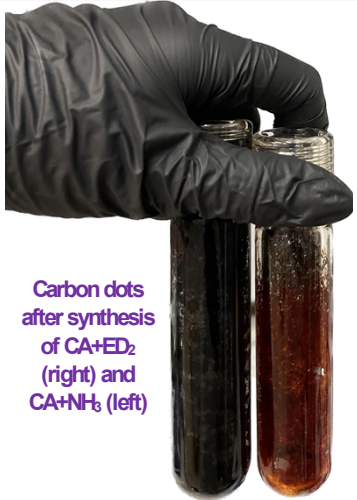
Fig.S27. A 3D hydrogel material made by free-radical photopolymerization of an HEA/water mixture (1/1 wt. %) in the presence of a ternary photoinitiating system based on CA-NH₃-CDs(0.2 wt. %) and IOD (2 wt. %).

Fig.S28. A printout made by photopolymerization of a HDDA/PEGDA/WATER (40/40/20 wt%) mixture in the presence of N-phenylglycine (2 wt%).

Bibliography

Synthesis of Carbon Dots

Table S1. One-pot "bottom-up" synthesis of carbon dots

Carbon dots	Reagents	Reaction terms	
CA-CDs	citric acid	230°C, 5h	
CA-ED ₂ -CDs	citric acid + ethylenediamine		
CA-NH ₃ -CDs	citric acid + ammonia		

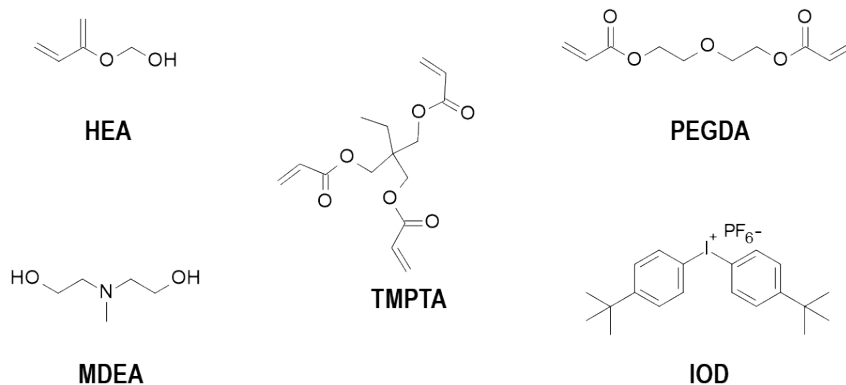


Fig.S1. Structures of the monomers used for photopolymerization measurements and other additives.

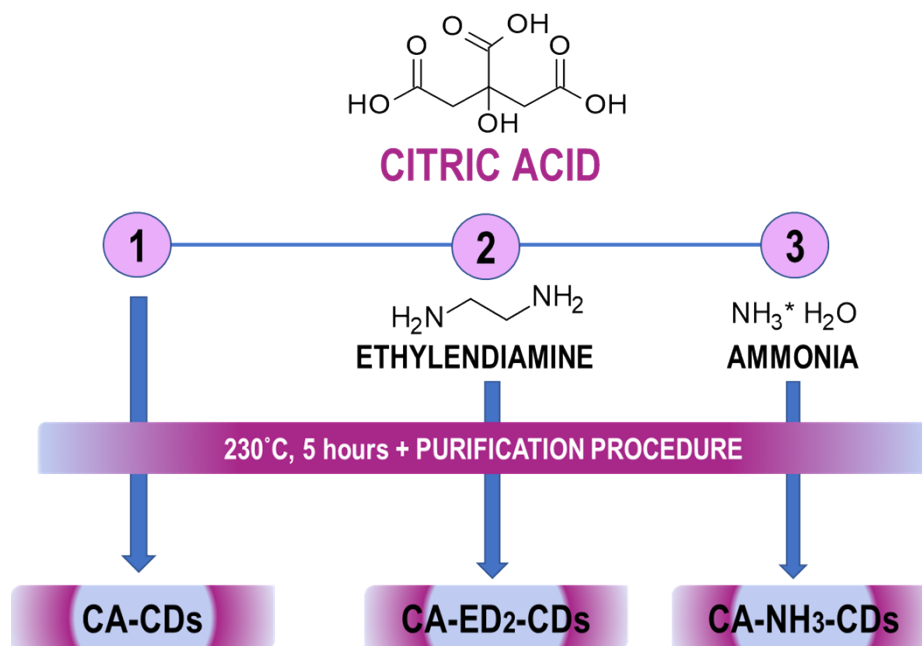


Fig.S2. Scheme of synthesis of CA-CDs, CA-ED₂-CDs, and CA-NH₃-CDs.

Purification of synthesis materials

During the synthesis of carbon dots by hydrothermal methods, fluorophores can be formed. In a previous article¹ it was shown that purification of carbon dots is an extremely important research step. In view of the fact that the purification procedure using the phalcons with a 10,000 kDa membrane presented in the paper was effective in the present study was also applied.

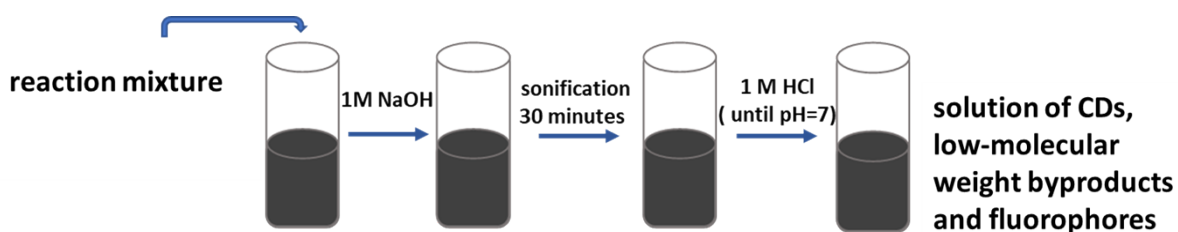


Fig.S3. Procedure for breaking agglomerates with NaOH solution

Spectroscopic characteristics of filtrates

The below graphs showed the high quality purification of the synthesized materials and the separation of fluorophores from valuable carbon dots used in further studies.

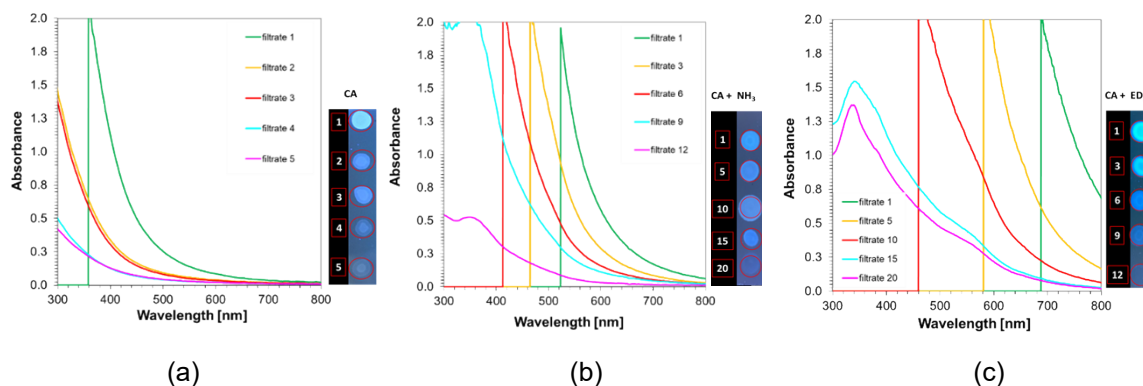


Fig. S4. The decrease in fluorescence due to leaching of the fluorophore from the solution and the resulting images of TLC plates with embedded solutions of the filtrates (a) CA-CDs, (b) CA-NH₃-CDs, (c) CA-ED₂-CDs

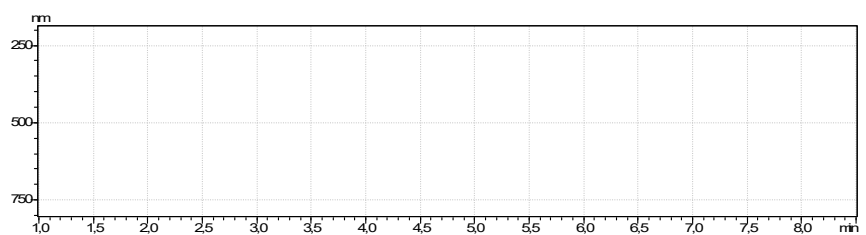
Commercial Carbon Dots (GQDs)

In addition to synthesized carbon dots, commercially available dots were used for the study. The commercially available dots were purchased from Sigma Aldrich. The form in which the mentioned materials appeared was a solid powder of brown color.

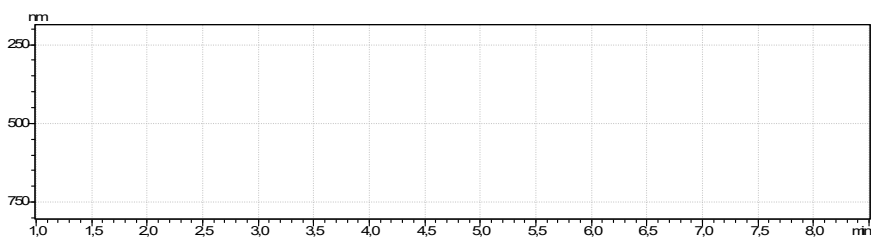


Fig.S5. Powdered carbon dot materials from Sigma Aldrich.

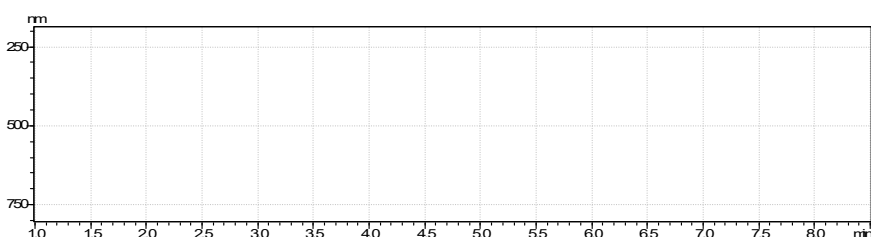
Analysis using the LC-DAD-MS system



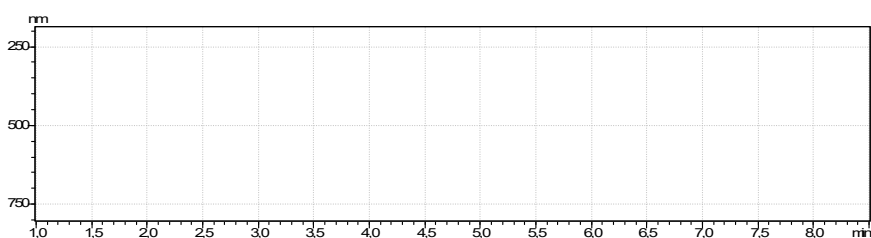
(1)



(2)



(3)



(4)

Fig. S6. Analysis by LC-DAD-MS of synthesised (after purification) (1) CA-CDs, (2) CA-ED₂-CDs, (3) CA-NH₃-CDs and commercial carbon dots (4) GQDs

XPS analysis

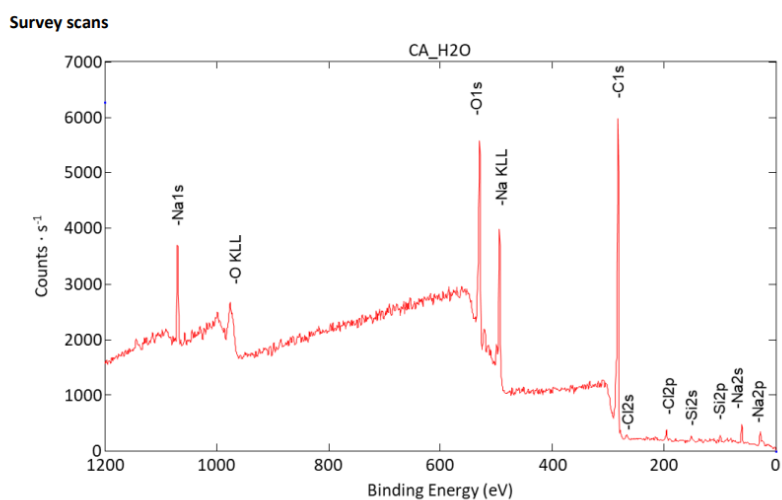


Fig.S7. Survey XPS spectrum of carbon dots from citric acid

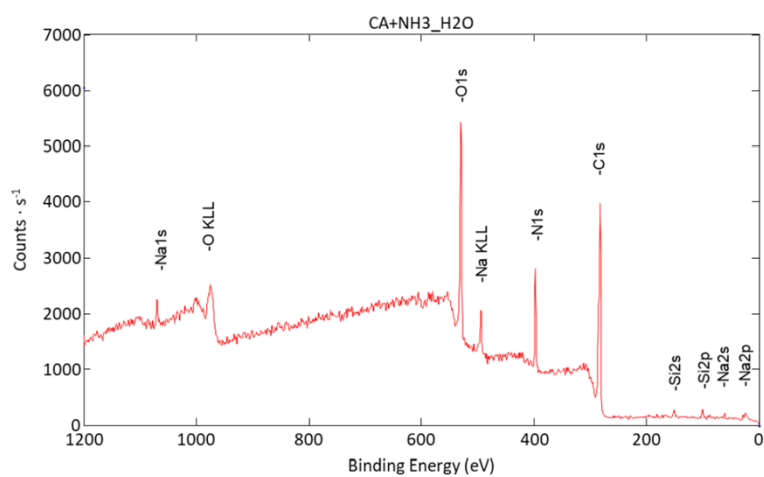


Fig.S8. Survey XPS spectrum of carbon dots from citric acid and ammonia

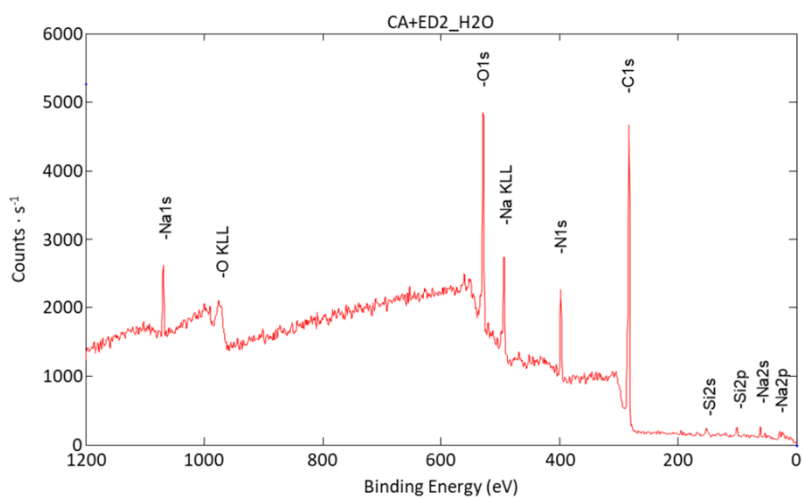


Fig.S9. Survey XPS spectrum of carbon dots from citric acid and ethylenediamine

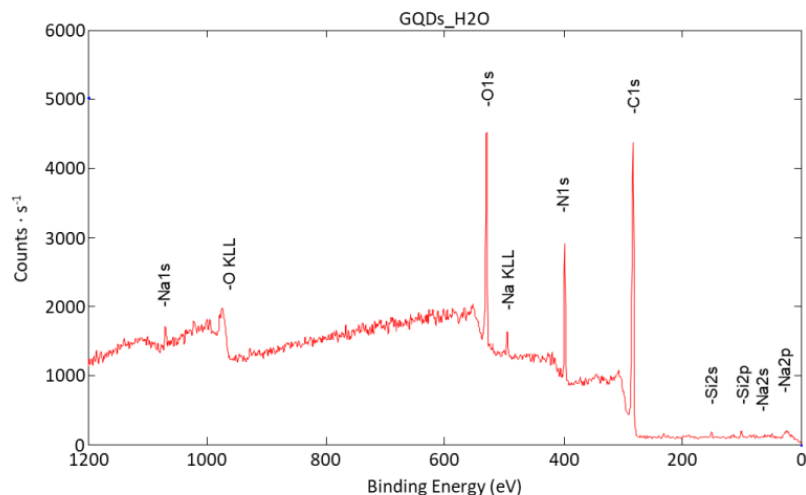


Fig.S10. Survey XPS spectrum of carbon dots from commercial carbon dots (GQDs)

The N 1s spectra were fitted with single line centered at 399.9 eV which indicate presence of either C-NH and/or N-(C=O) type bonds in organic compounds². The Na 1s spectra were fitted with single line centered at 1071.6 eV which indicate Na⁺ oxidation state of sodium³. The Cl 2p spectra were fitted with doublet structure (doublet separation $p_{3/2} - p_{1/2}$ equals 1.6 eV) with $2p_{3/2}$ line centered at 198.4 eV which indicate presence of Cl ions in chlorides⁴. The Si 2p spectra show two doublet structures (doublet separation $p_{3/2} - p_{1/2}$ equals 0.6 eV) with first $2p_{3/2}$ line centered at 101.9 eV which indicate C-Si-O type compounds like in e.g. siloxanes or silicones and second $2p_{3/2}$ line centered at 103.2 eV which indicate presence of SiO₂ type compound⁵. As for the presence of silicon compounds, they often appear on XPS analyses and probably originate from PDMS, but do not affect the value of the results obtained.

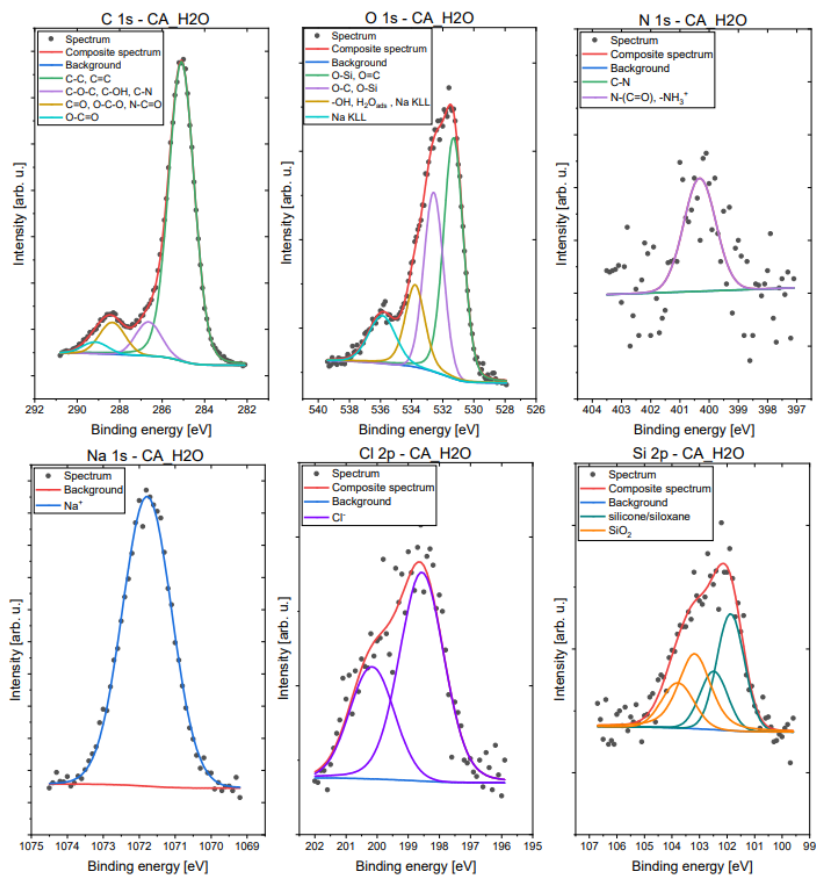


Fig.S11. High resolution spectra of different peaks and analyzes for carbon dots from citric acid

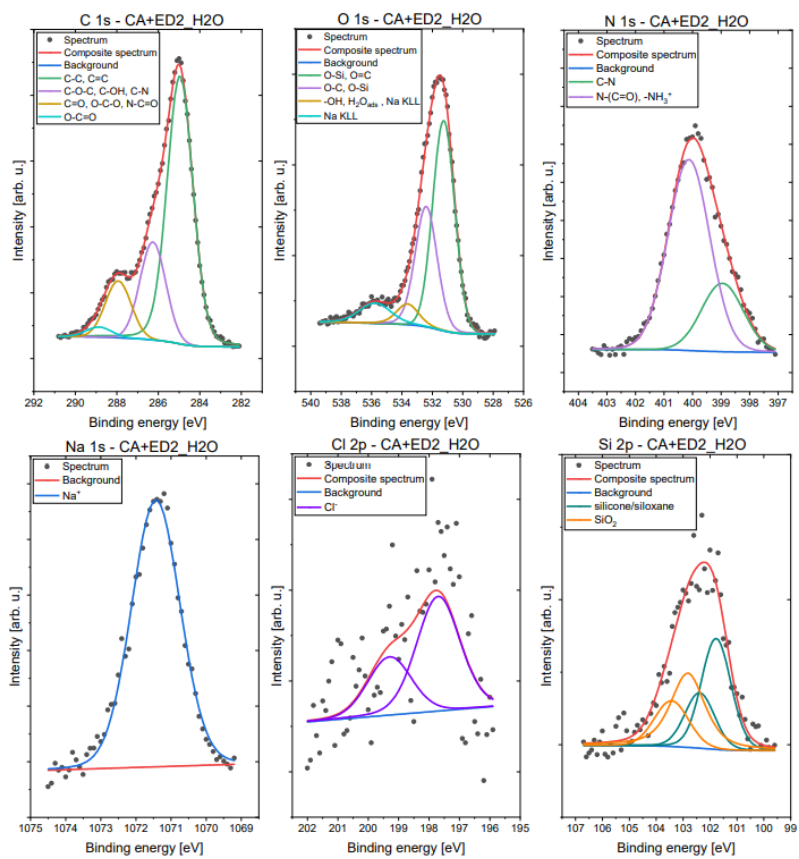


Fig.S12. High resolution spectra of different peaks and analyzes for carbon dots from citric acid and ethylenediamine

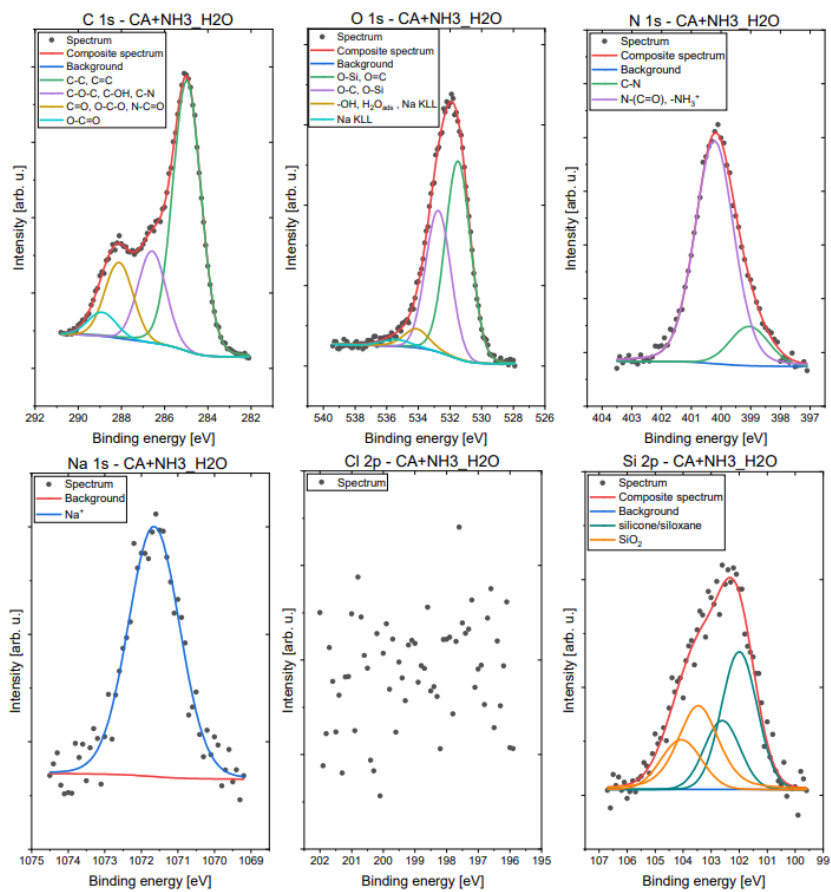


Fig.S13. High resolution spectra of different peaks and analyzes for carbon dots from citric acid and ammonia

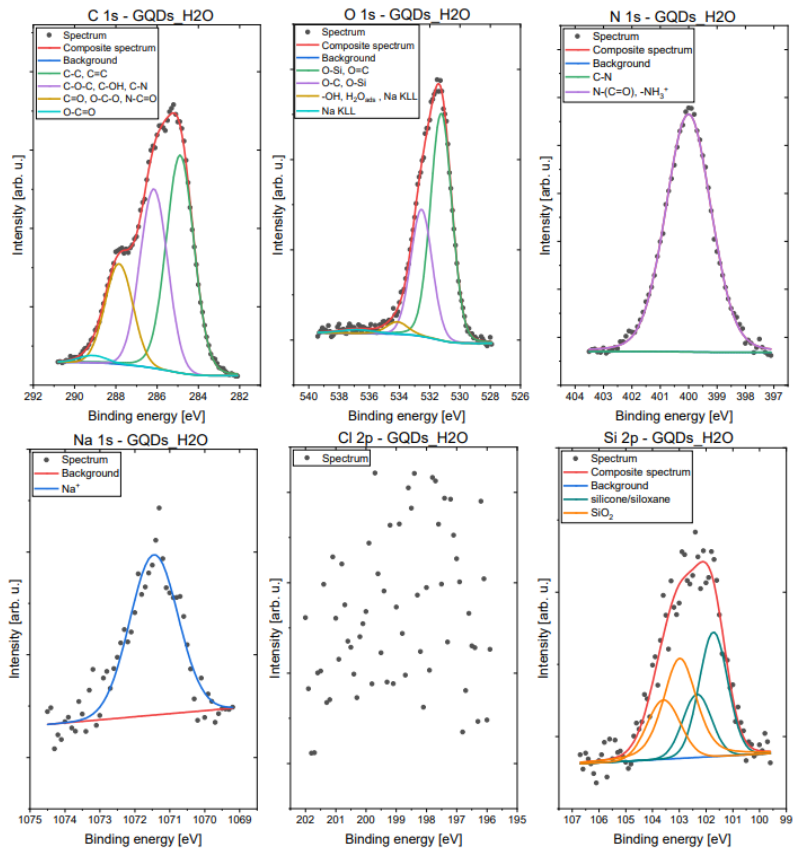


Fig.S14. High resolution spectra of different peaks and analyzes for commercial carbon dots (GQDs)

Real-Time FT-IR photopolymerization experiments

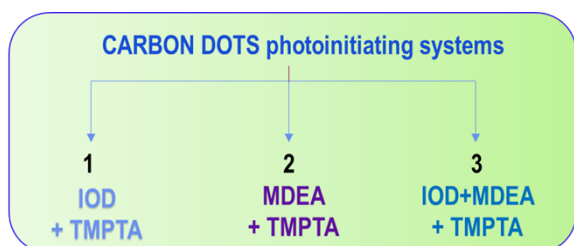


Fig.S15. Initiating systems used in free-radical photopolymerization processes.

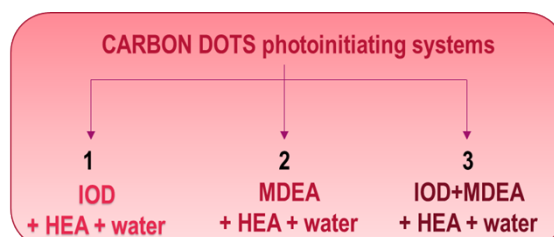


Fig.S16. Initiating systems used in free-radical photopolymerization processes of acrylate-water resin.

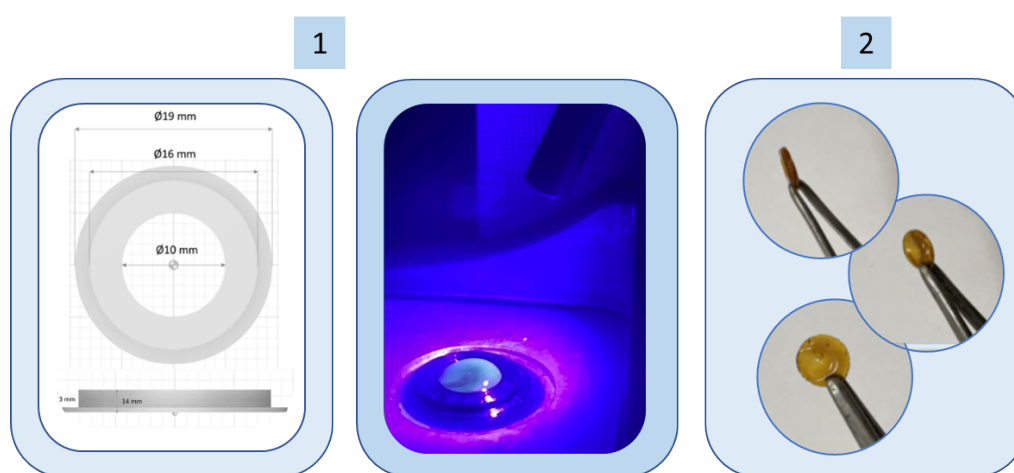


Fig.S17. (1) Ring designed to carry out photopolymerization processes (2) and the resulting hydrogel material after photopolymerization of the initiator system containing synthesized carbon dots.

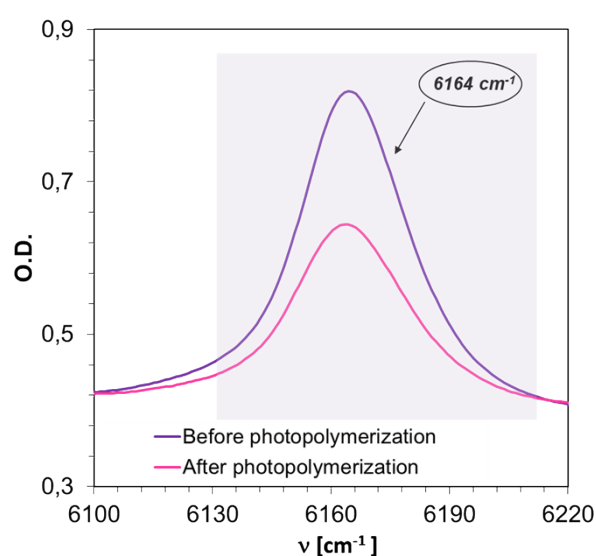


Fig.S18. Intensity variation of the band at wavenumber 6164 cm^{-1} during measurement of the radical photopolymerization kinetics of the acrylate monomers studied

Free-radical photopolymerization of acrylate monomers and hydrogel formulations in two and three initiating systems based on Carbon Dots.

Table S2. Conversions obtained for acrylate monomer during free radical photopolymerization after visible wavelength @405nm for different carbon dot-based initiating systems.

Bulk photopolymerization of ACRYLATE monomer monitored at ~ 6164 cm ⁻¹		
Type of carbon dots	Ingredients of compositions	Conversion [%] @405nm current = 1.4 A power out = 1.50 W irradiance = 22.0 cW/cm ²
CA-CDs	IOD+TMPTA	8
	MDEA+TMPTA	3
	IOD+MDEA+TMPTA	100
CA-NH ₃ -CDs	IOD+TMPTA	31
	MDEA+TMPTA	6
	IOD+MDEA+TMPTA	64
CA-ED ₂ -CDs	IOD+TMPTA	83
	MDEA+TMPTA	9
	IOD+MDEA+TMPTA	64
GQDs	IOD+TMPTA	20
	MDEA+TMPTA	5
	IOD+MDEA+TMPTA	50
References	IOD+TMPTA	8
	MDEA+TMPTA	1
	IOD+MDEA+TMPTA	26

Photocatalytic properties of carbon dots during free-radical polymerization of the water-based coating hydrogel

Table S3. Conversions obtained for acrylate monomer during free radical photopolymerization dedicated to obtain hydrogels after visible wavelength @405nm for different carbon dot-based initiating systems.

Free-radical photopolymerization of HEA/WATER monomer (1:1 wt. %) mixture, monitored at ~6164 cm ⁻¹		
Type of carbon dots	Ingredients of compositions	Conversion [%] @405nm current = 1.4 A power out = 1.50 W irradiance = 22.0 cW/cm ²
CA-CDs	IOD+TMPTA	48
	MDEA+TMPTA	16
	IOD+MDEA+TMPTA	100
CA-NH ₃ -CDs	IOD+TMPTA	23
	MDEA+TMPTA	17
	IOD+MDEA+TMPTA	100
CA-ED ₂ -CDs	IOD+TMPTA	26
	MDEA+TMPTA	4
	IOD+MDEA+TMPTA	97
GQDs	IOD+TMPTA	80

References	MDEA+TMPTA	20
	IOD+MDEA+TMPTA	91
	IOD+TMPTA	3
	MDEA+TMPTA	6
	IOD+MDEA+TMPTA	73

Absorption and fluorescence spectra for the determination of the excited singlet state energy for investigated of carbon dots in water

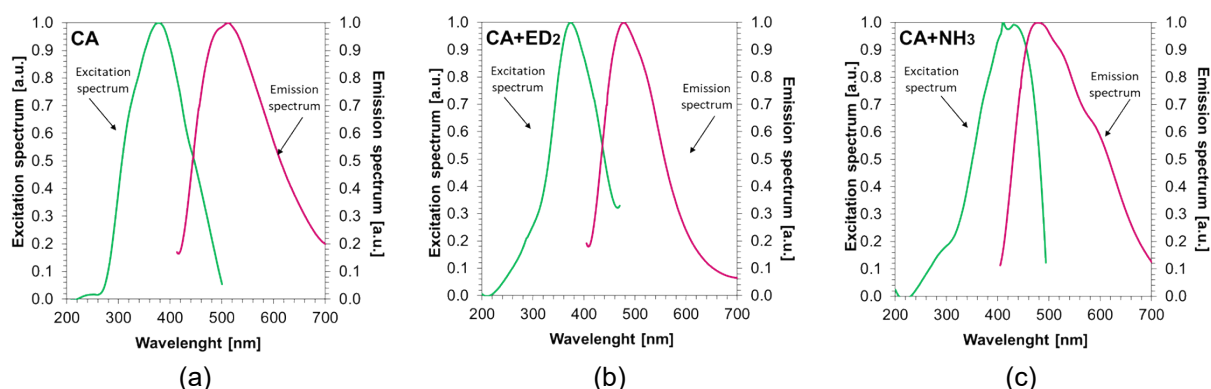


Fig.S19. Excitation and emission spectra for determination of excited singlet state energies for citric acid carbon dots (a), for citric acid materials with ethylenediamine (b), and for citric acid materials with ammonia (c). The solvent is water.

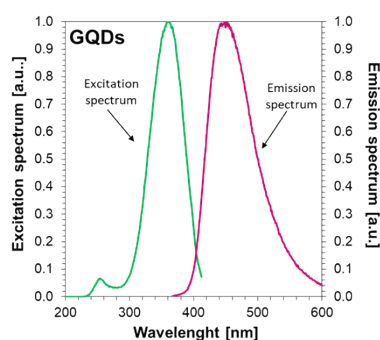


Fig.S20. Excitation and emission spectra for determination of excited singlet state energies for carbon dots from Sigma Aldrich. The solvent is water.

Cyclic voltammetry profiles showing oxidation and reduction processes of carbon materials in water.

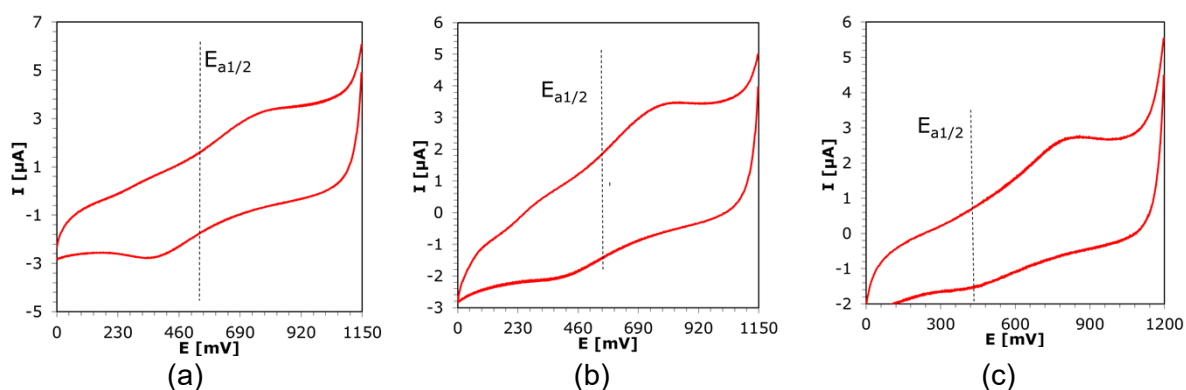


Fig.S21. Cyclic voltammetry for the oxidation process (CV_{ox} , vs. Ag/AgCl) in aqueous solution (containing 0.1 M KCl) for citric acid dots (a) for citric acid dots doped with ethylenediamine (b) and for citric acid dots doped with ammonia (c).

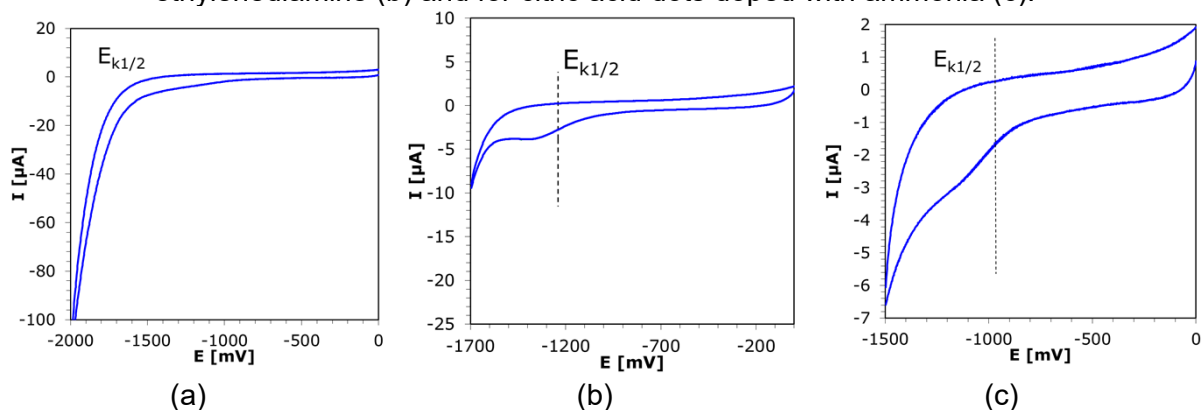


Fig.S22. Cyclic voltammetry for the reduction process (CV_{ox} , vs. Ag/AgCl) in aqueous solution (containing 0.1 M KCl) for citric acid dots (a) for citric acid dots doped with ethylenediamine (b) and for citric acid dots doped with ammonia (c).

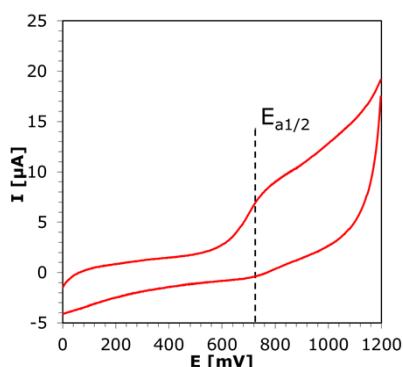


Fig.S23. Cyclic voltammetry for the oxidation process (CV_{ox} , vs. Ag/AgCl) in aqueous solution (containing 0.1 M KCl) for commercial carbon dots from Simga Aldrich.

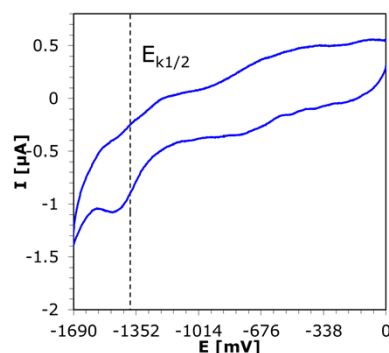


Fig.S24. Cyclic voltammetry for the reduction process (CV_{ox} , vs. Ag/AgCl) in aqueous solution (containing 0.1 M KCl) for commercial carbon dots from Simga Aldrich.

Table.S4. Electrochemical and thermodynamic properties of carbon dots in the photo-oxidation and photo-reduction mechanisms

Carbon Dots	E ₀₀ [eV]	Foto-oxidation		Foto-reduction	
		E _{ox} vs Ag/AgCl [mV]	ΔG _{et} [eV]	E _{red} vs Ag/AgCl [mV]	ΔG _{et} [eV]
CA	2,78	549	-1,59	*	<i>no</i>
CA +ED ₂	2,84	580	-1,62	-1241	-0,73
CA + NH ₃	2,72	544	-1,54	-937	-0,92
GQDs	3,08	726	-1,71	-1383	-0,83

calculated using the Rehm-Weller equation: $\Delta G_{et} = F[E_{ox}(D/D^+) - E_{red}(A^-/A)] - Ze^2/\epsilon a - E_{00}$

E_{ox} (D/D⁺) - electron donor oxidation potential (0.864 vs, Ag/AgCl for MDEA amine)

E_{red} (A⁻/A) - electron acceptor reduction potential (-0.68V vs, Ag/AgCl for IOD idonium salt)

E₀₀ - transition energy 00 for the singlet state

*no signal detected at given measurement parameters

no - no calculation

3D printing experiments

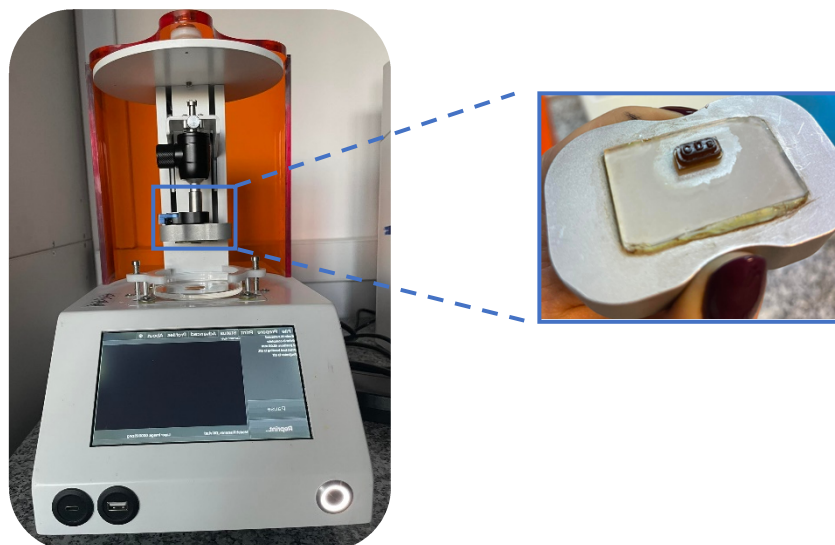


Fig.S25. A 3D material made by free-radical photopolymerization of an TMPTA/PEGDA mixture (1/1 wt. %) in the presence of a three-component photoinitiating system based on CA-ED₂-CDs (0.2 wt. %), IOD (2 wt. %) and MDEA (2 wt. %).

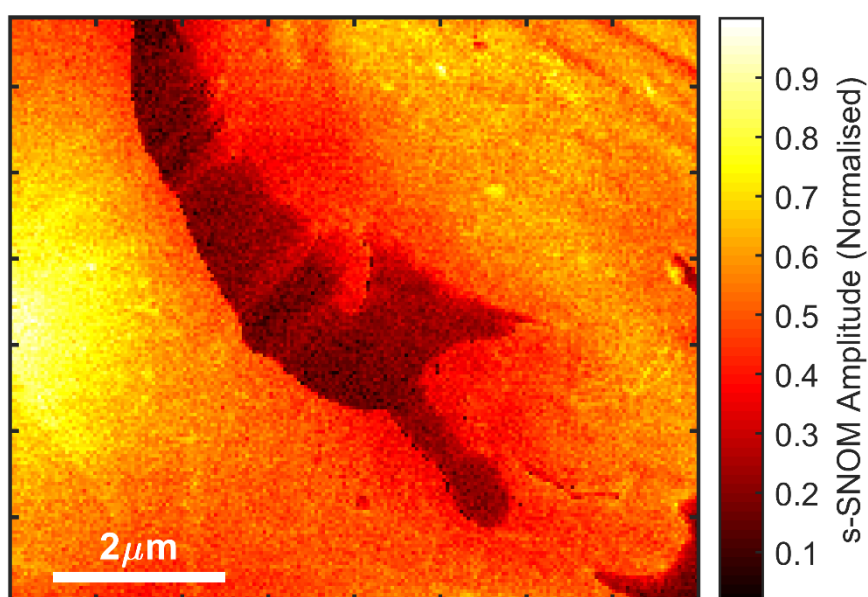


Fig.S26. s-SNOM amplitude data taken simultaneously with the data in Figure 17 in the main text, with incident illumination at 1490 cm⁻¹. The data was demodulated at the 3rd harmonic of the AFM tapping frequency to reduce the influence of background effects, and the data has been normalised to the maximum recorded value.

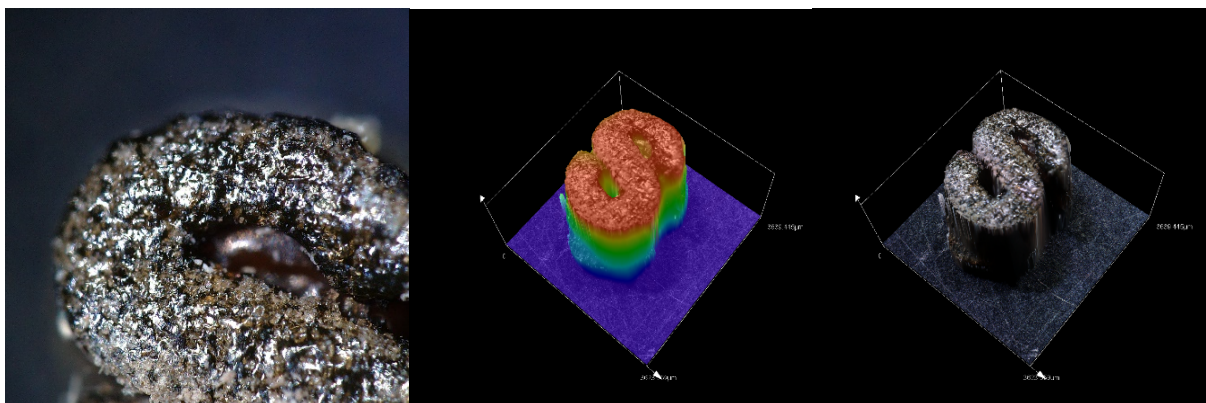


Fig.S27. A 3D hydrogel material made by free-radical photopolymerization of an HEA/water mixture (1/1 wt. %) in the presence of a ternary photoinitiating system based on CA-NH₃-CDs(0.2 wt. %) and IOD (2 wt. %).

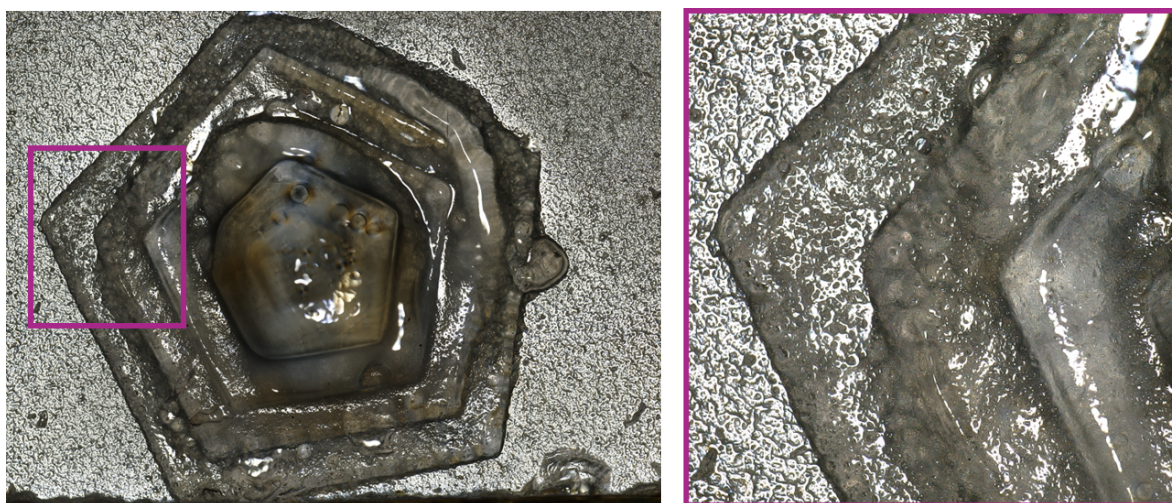


Fig.S28. A printout made by photopolymerization of a HDDA/PEGDA/WATER (40/40/20 wt%) mixture in the presence of N-phenylglycine (2 wt%). Printing parameters: layer thickness – 100um, time to cure 1st layer – 45 s, time to cure layer – 15 s.

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