Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

for

Enhanced dual photo/thermal initiating systems for preparation of few layer graphene filler-based composites and 3D printing

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Materials and Experimental Section

Chemical Reagents:

The 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (Irgacure369) and imidazole (2-Ethyl-4-Methylimidazle, EMIM) were purchased from sigma-Aldrich or TCI Chemicals. Di-tert-butyl-diphenyl iodonium hexafluorophosphate (Iod) was obtained from Lambson Ltd (UK). Trimethylolpropane triacrylate (TMPTA) and Di(trimethylolpropane) tetraacrylate (TA) was purchased from Sartomer (France). All the reactants were selected with high purity and used as received.

The preparation of FLG formulations (Prepreg solution)：

Among the many types of synthesis used to produce graphene (or FLG), the one used by the ICPEES for several years is certainly the least polluting, the most productive and the one that makes it possible to obtain a material with very few defects. The synthesis is carried out by gentle exfoliation under ultrasound in the presence of a surfactant, in particular a phenolic acid which, thanks to its aromatic rings, is able to "click" on the carbon network.

"Expanded graphite (EG - Mersen group) was put in the monomer solution in the presence of tannic acid (TA) (EG/TA mass ratio = 2). The solution was then placed under continuous ultrasonic (sonotrode) under magnetic stirring: the instrument used was a "Branson" ultrasonic arm (Digital sonifier 550) with a maximum power of 550 W. The treatment time is 4 h with 25% amplification, i.e. a power of 137.5 W."

Typical size of the FLG particles is several μm (see Figure S1) and the number of layers is typically comprised between one and ten.

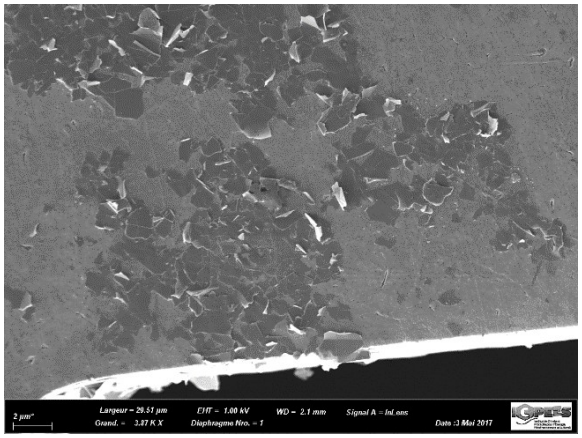


Figure S1. SEM picture of FLG.

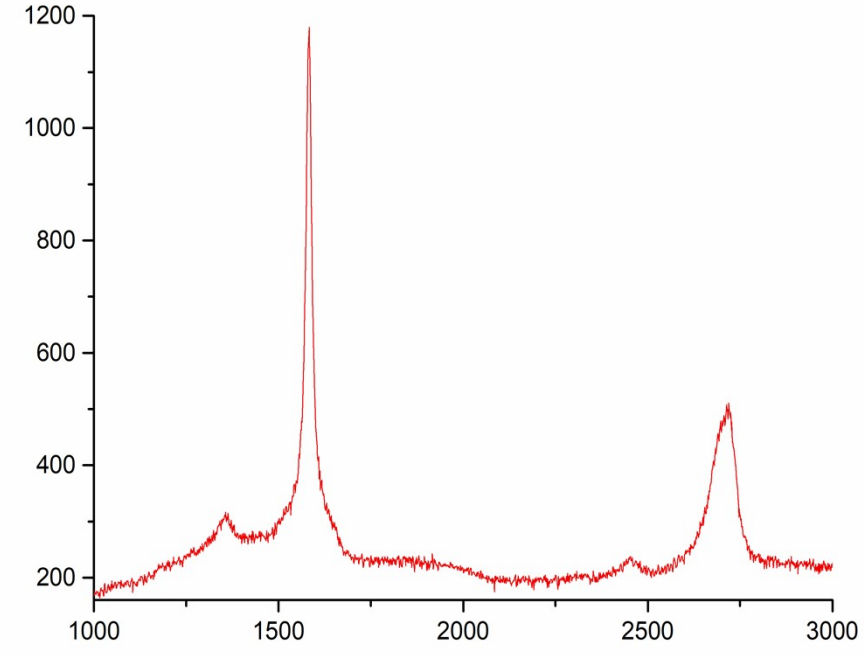


Figure S2. Raman spectrum of FLG. The Figure shows a typical spectrum of high-quality FLG used in this study. The most intense peak is the G band that originates from the sp^2 bonded carbon atoms of the hexagonal lattice of a graphitic structure, and it is well visible around 1580 cm^{-1} . The D band, around 1350 cm^{-1} , is related to sp3 defects present in the sp^2 carbon atom network. ID/IG is very low attesting the high structural quality of the FLG.

Testing and characterization:

Real-Time Fourier Transformed Infrared Spectroscopy (RT-FTIR): The photopolymerization was evaluated by Real-Time Fourier Transformed Infrared Spectroscopy JASCO FTIR-4100. Specific procedure: the sample was either injected into a circular mold (10 mm inner diameter) that was pasted onto polypropylene film or laminated in-between two polypropylene film. Then it was

placed on a sample holder in a horizontal accessory (transmission mode). RT-FTIR was used to follow the C=C double bond conversion (functional groups of the two acrylates) versus time for polymerizations of 25 μm thin laminated and 2.5 mm thick samples. For 25 μm thin samples, the vibration peak of acrylate C=C double bond at ~1600 cm^{-1}; For 2.5 mm thick samples, the decrease of the C=C double bond at 6130–6200 cm^{-1} was followed. A LED@405 nm having an intensity of 0.11 W/cm^2 at the sample position was used for the photo-polymerization experiments within the FTIR spectrometer.

DSC testing: Different formulations (≈10-30 mg) in the presence of CTCs were inserted in an aluminum 100 μL crucible. Thermal polymerization (Mettler-Toledo DSC) was carried out from 0 °C to 250 °C at a heating rate of 10 °C /min under nitrogen flow (100 mL/min). Conversion calculation: The heat released for acrylate double bond is ΔH_{theory} = 78.61 kJ mol^{-1} which leads to 795.9 J g^{-1} and 674.8 J g^{-1} for 100% of acrylate function conversion for TMPTA and TA, so final acrylate function conversion (FC) = (heat released g^{-1})/ 795.9 or (heat released g^{-1})/ 674.8 is obtained in thermal polymerization.

Thermal imaging camera information: an infrared thermal imaging *camera Fluke* TiX500.

The investigation of DoCs of composites:

First of all, taking Irgacure 369 (PI 369) as an example, we prepared the resin prepregs of TMPTA or TA (containing 2% or 4% graphene) within $2.5*10^{-5}$ mol/g PI 369 (or $5.5*10^{-5}$ mol/g CTC, based on 4 g monomer). Then it is mixed well by high speed stirring and keep stirring overnight for more homogeneous and the better formation of charge transfer complex. After that, in a LED-curing box, a mold filled with the investigated resin was placed vertically under the light (LED@405 nm for a certain time; 1 W/cm^2, the reaction setup was exhibited in Figure below **(**Figure S4, A**)**, the distance from the samples of composite to the light source is about 5 cm). Flow diagram of the composite preparation was shown in Figure S4, B. The polymerized products were used to measure the Depth of Cure (DoC) with an Absolute LCD Digimatic Indicator (Mitutoyo).

Scanning electron microscope (SEM):

The graphene-containing morphology and their corresponding composites were investigated by scanning electron microscope (SEM) with a JEOL JSM-7900F microscope. All samples were prepared to obtain pellets with a thickness of around 1.5 mm and test the surface and cross-section of samples in various observation scales. (Sample preparation was performed as usual, referring to composite preparation of Depth of Cure (DoC) formulations and procedures)

Thermogravimetric analysis (TGA):

TGA was carried out using a METTLER-TOLEDO TGA/DSC 3+ thermoanalyzer. 30 mg of samples was heated from 30 to 800 °Cata scan rate of 10 °C/min under a N_2 atmosphere (purge of 100 mL/min of N_2 protection gas).

Dynamic thermomechanical analysis (DMA):

Sample preparations were performed based on 2% or 4% graphene-containing resins by combination of $2.5*10^{-5}$ mol/g Irg 369 and $5.5*10^{-5}$ mol/g CTC under the irradiation of LED@405 nm for a certain time. Then, all round samples were polished to obtain pellets with a thickness of around 1.5 mm, and then experiments were performed on a Visconalyse METTLER DMA 861at a frequency of 1.00 HZ.

DLW experiment: The letter patterns were produced through the computer-controlled movement of laser diode (CNI laser diode, wavelength**:** 405 nm and light intensity: 0.11 W, resins: $2.5 *10^{-5}$ mol/g and $5.5*10^{-5}$ mol/g CTC(EMIM) in TMPTA or TA containing graphene fillers) (spot size ~50 μm, The x-y resolution can be 50 μm (size of the laser beam)) under air, the printing time is about 5 mins-10 mins, the y-axis is <2 mm and the pattern was characterized by numerical optical microscope (OLYMPUS DSX-HRSU).

Supplementary Figures:

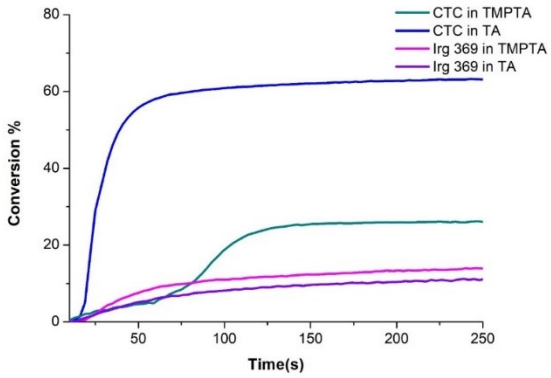


Figure S3. Photopolymerization profiles for CTC (C=C bond conversion vs. irradiation time) (≈ 25 μm thickness) measured by RT-FTIR under 405 nm LED irradiation (the irradiation starts at t = 10 s, 0.11 W cm^{-2}). resin: Irgacure 369 (2.5×10^{-5} mol g^{-1} in monomer) or CTC (5.5×10^{-5} mol g^{-1} in monomer) in 0.5% FLG-containing monomer.

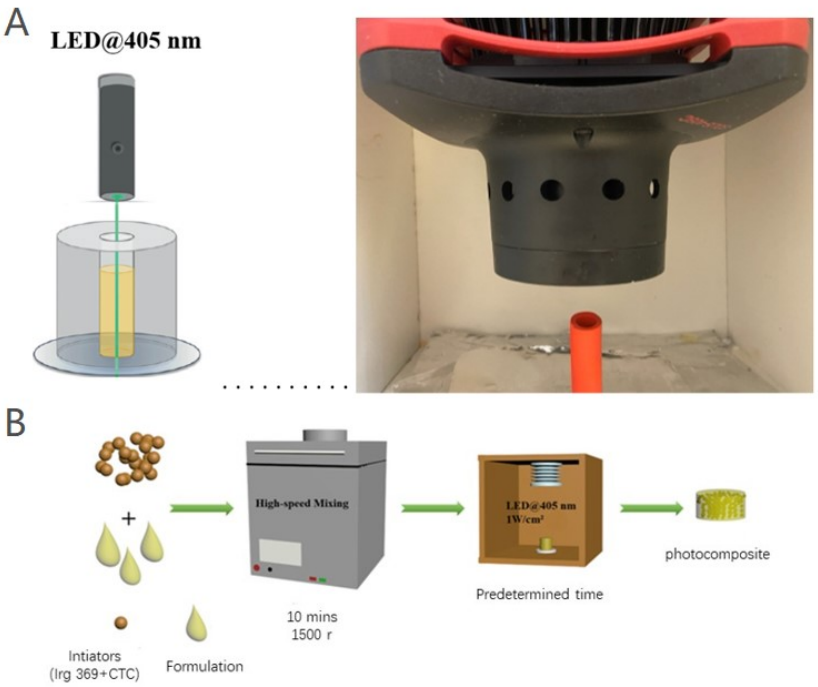


Figure S4. A). Schematic diagram (left) and the original device diagram (right) of the light reaction set-up. B). Flow diagram of the composite preparation.

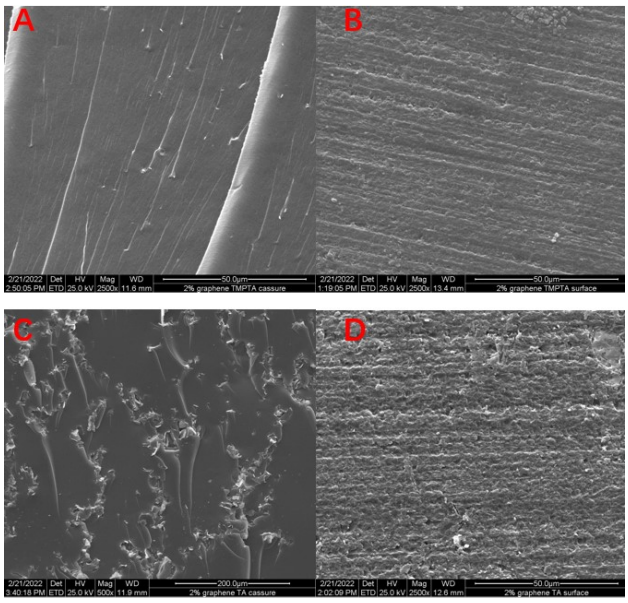
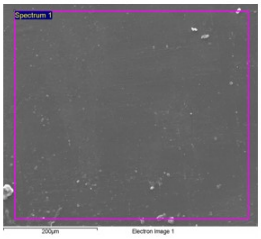
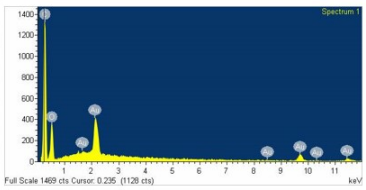


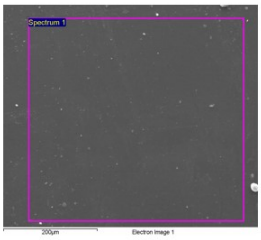
Figure S5. Scanning electron microscope (SEM) images of the photocomposites (A,B for poly(TMPTA) and C,D for poly(TA)). products with 2% graphene in the composite (left: cross-section and right: surface). The scale bar is 50-200 μm.

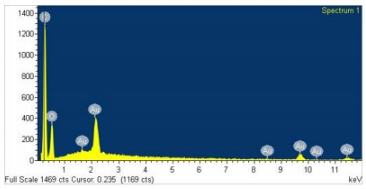
A





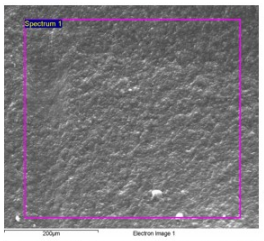
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	40.62	1.1846	60.84	1.18	67.42
O K	7.03	0.3178	39.16	1.18	32.58
Totals			100.00		

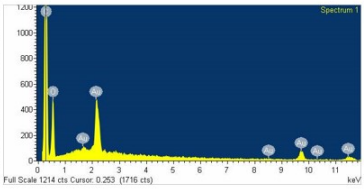




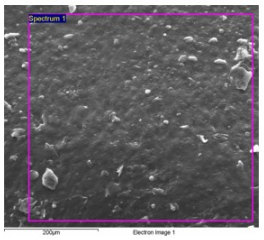
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	41.75	1.1882	61.09	1.15	67.65
O K	7.10	0.3164	38.91	1.15	32.35
Totals			100.00		

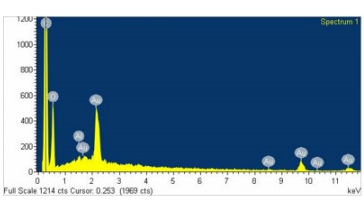
B





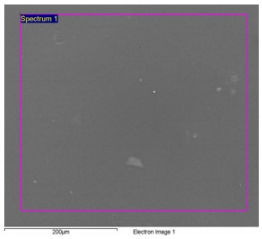
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	54.92	1.1842	60.82	0.99	67.40
O K	9.52	0.3180	39.18	0.99	32.60
Totals			100.00		

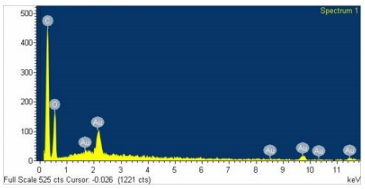




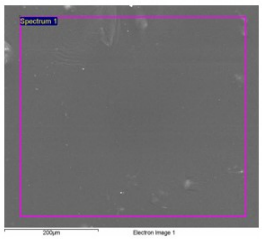
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	62.35	1.1826	60.81	0.92	67.39
O K	10.82	0.3186	39.19	0.92	32.61
Totals			100.00		

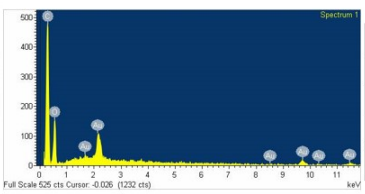
C





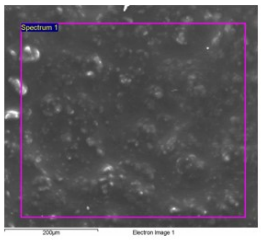
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	13.91	1.1228	56.36	1.76	63.24
O K	3.32	0.3452	43.64	1.76	36.76
Totals			100.00		

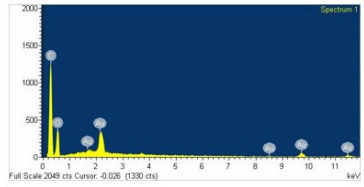




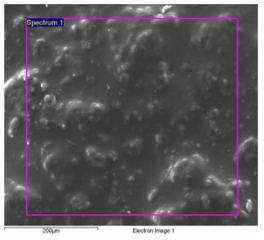
Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	15.25	1.1520	58.54	1.74	65.29
O K	3.11	0.3314	41.46	1.74	34.71
Totals			100.00		

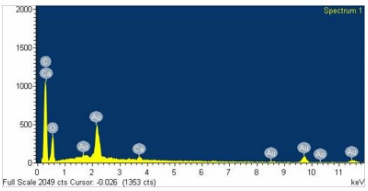
D





Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	38.07	1.1522	58.56	1.13	65.30
O K	7.77	0.3313	41.44	1.13	34.70
Totals			100.00		





Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	33.95	1.1470	58.07	1.22	65.00
O K	6.98	0.3294	41.47	1.23	34.85
Ca K	0.24	1.0248	0.45	0.06	0.15
Totals			100.00		

Figure S6. Energy Dispersive X-Ray Spectroscopy (EDX) analysis for the surface of photocomposites [A: 0% and B: 2% graphene content for poly(TMPTA); C: 0% and D: 2% graphene content for poly(TA)].

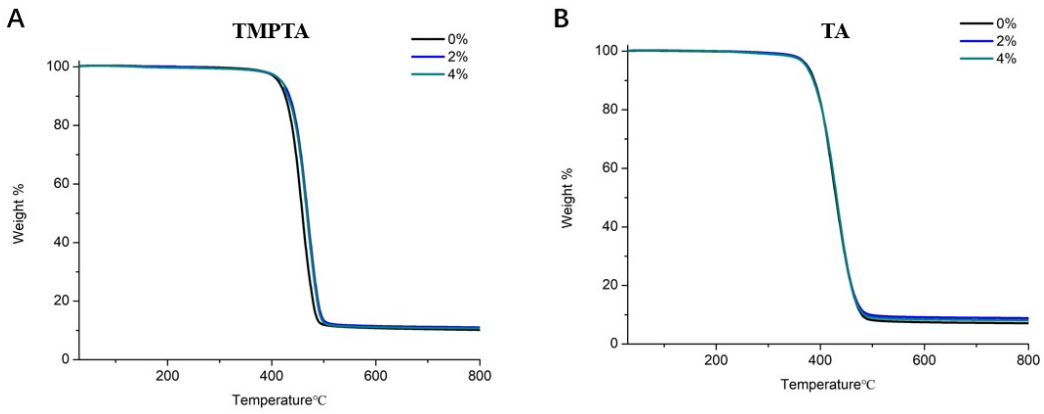


Figure S7. TGA tests for the photocomposites [poly(TMPTA) and poly(TA)] containing 0%, 2%, 4% (w%) graphene filler.

elastic modulus (G') at 25 °C

Entry	graphene filler		G' (MPa)
1	TMPTA	0%	183
2		2%	155.5
3		4%	142.6
4	TA	0%	200.6
5		2%	167
6		4%	114

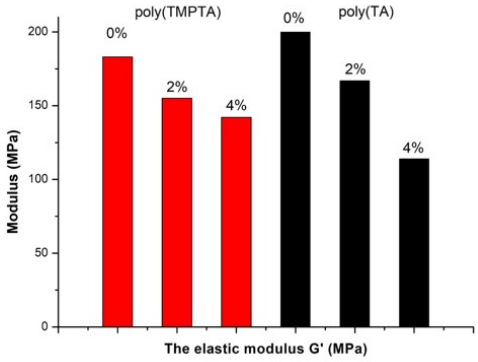


Figure S8. DMA tests at 25°C for the photocomposites [poly(TMPTA) and poly(TA)] containing 0%, 2%, 4% (w%) graphene filler.

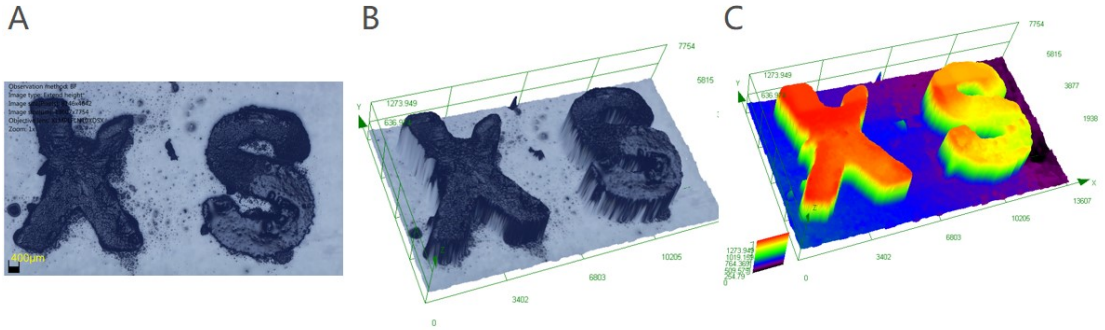


Figure S9. Optical microscopy of 3D patterns printed from TA with 2% graphene content. (A). Top

surface morphology and (B,C). 3D overall appearance in black and color patterns. The scale bar is 2000 μm (A is 400 μm).