



### **3D** Printable Conducting Hydrogels Containing Chemically Converted Graphene

## **Supporting Information**

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The following document presents further work and clarification of the synthesis and characterization of UV-crosslinkable chitosan hydrogels using GO and CCG.

S1. UV-vis spectroscopy

Figure S1 shows the UV–vis spectroscopy of ChiMA and ChiMA 3CCG aqueous solutions before and after addition of photoinitiator (Irgacure 2959) at the same weight ratio as used in the film preparation (4:1 Irgacure:filler). The characteristic absorption peak of CCG is around

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270,<sup>1</sup> but, as observe by Wang et al.<sup>2</sup> for a composite of GO with chitosan, the broad graphene absorption is weakened by the ChiMA CCG interaction, showing only a tailing shoulder out to 800 nm on the ChiMA band at 250 nm. In contrast, the characteristic absorption peak of Irgacure 2959 is clearly observable at 280 nm at the same degree of dilution. After exposure to UV for 10 min the photoinitiator peaks are replaced with a shoulder at 248 nm that can be attributed to polymer-incorporated chromophoric groups from the photoinitiator. Therefore, the presence of 3 wt.% graphenic filler does not interfere with the UV absorption of the photoinitiator and subsequent formation of crosslinks.



Figure S1. UV-vis absorption spectra of ChiMA and ChiMA 3CCG solutions.

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#### S2. SEM and Particle Size of the Dispersions

SEM images of aqueous GO and CCG are shown in Figure S2a,b. The largest nanoplatelet size is about 400 nm with the smallest around 70 nm. The average size of the sheets as estimated by the Zetasizer in the GO and CCG dispersions is between 430 to 460 nm (Figure S2c). The particle size of the dispersions prepared for printing varies between 1 to 2.5  $\mu$ m, far below the diameter of the printing nozzle that is 200  $\mu$ m (Figure S2c).



Figure S2. Scanning electron microscopy of (a) CCG and (b) GO. (c) Average particle size of CCG and GO as well as ChiMA and composite solutions as measured by the Zetasizer.

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#### S3. TGA of GO/ChiMA composites

The TGA curves (Figure S3) indicate that the decomposition temperatures of the ChiMA samples are almost similar, falling between 210-216°C. Considering 10% weight loss as the point of comparison, the thermal decomposition temperature (T 0.1) for the crosslinked ChiMA samples is increased from 104°C in ChiMA to around 215°C for GO/ChiMA composite with 3 wt.% GO. This temperature increase can be due to the moisture trapped inside the condensed structure of the crosslinked ChiMA, as evidenced by the SEM. Furthermore, increasing the GO content makes the sample less hygroscopic and more resistant to thermal decomposition.

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Figure S3. TGA curves of GO, ChiMA films before and after UV irradiation and ChiMA composites with 0.5, 1.5 and 3 wt.% GO content.

#### S4. Raman Spectra of GO/ChiMA composites

In the Raman spectra (Figure S4), the D and G bands of the GO/ChiMA composites are shifted toward lower wavelengths, close to that of CCG, with an increase in the  $I_D/I_G$  ratio compared to the Raman spectrum of GO. The bands also show significant broadening particularly for the 3 wt.% composite. These changes can be attributed to some reduction of  $GO^{3-5}$  during the UV irradiation, as it has been shown that UV irradiation has the potential to convert GO to reduced GO.<sup>6-8</sup>

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Figure S4. Raman spectra of GO and ChiMA composites with 0.5 and 3 wt.% GO (b).

S5. Mechanical properties of GO/ChiMA

The addition of GO has significantly improved the mechanical properties of ChiMA in the dry state (Figure S5). The tensile strength of the ChiMA film was increased, by increasing the GO content, to around 75 MPa in the composite with 3wt.% GO. The Young's modulus also increased from 1.8 GPa in ChiMA film to 3.3 GPa in ChiMA 3GO.

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Figure S5. Mechanical properties of ChiMA samples with different GO contents.

Table S1.	Mechanical	properties	of ChiMA	composites	with d	lifferent G	O contents	in dry
state.								

Sample	Tensile	Elongation	Young's	
	Strength	at Break	Modulus	
	(MPa)	(%)	(GPa)	
ChiMA	47.8±1.6	3.7 ±0.4	1.8±0.1	
ChiMA 0.1GO	50.6 ± 1.2	3.2±0.2	2.5±0.1	
	57.2 + 2.1	2 1 + 0 2	2.010.2	
Chima 0.5GO	$57.3\pm 2.1$	3.1±0.3	2.8±0.2	
ChiMA 1.5GO	61.2±2.8	3.6±0.2	2.9±0.2	
ChiMA 3GO	75.5±2.2	4.2±0.4	3.3±0.1	

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