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Supporting information for

Low solids emulsion gels based on nanocellulose for 3D-printing

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This Supporting Information document contains two tables and seven figures in eight pages.

Formulation of inks and respective dry mass ratio of CNF/alginate and PLA

Table S1. Formulation of the emulsion gels with given fraction of the organic (oil) phase f_o in the emulsion and PLA concentration in such phase. The relative amount of (CNF+alginate) and PLA in the printed materials expressed as % weight on dry basis is also listed. Equal amounts of CNF and alginate were used in most cases discussed in the main document (see also **Figure S2** for the effect of CNF: alginate composition).

Ink	f_o or %PLA	CNF + alginate (%)	PLA (%)
%PLA = 0	f_o = 0.2	100	0
4		75	25
8		60	40
12		50	50
f_o = 0.1	%PLA = 12	53	47
0.2		50	50
0.3		37	63
0.4		27	73
0.5		20	80

Effect of CNF/alginate ratio on the properties of emulsion gel and corresponding cast objects. The emulsion gels with different CNF/alginate ratios were prepared according to the same procedure for other variables. After equilibrating for 24h, produced emulsion gels were gently cast into round-shape rubber plates. Several drops of $CaCl_2$ solution were slowly added to pre-crosslink the cast samples so that the sample surface can be strong enough to hold the impact of liquid when immersing into $CaCl_2$ bath. After 24h, the crosslinked samples were taken out for observation.

The stability and ability to maintain shape of emulsion gel with different CNF/alginate ratios are shown in **Figure S1 and S2,** respectively. The emulsion with alginate only in aqueous phase was separated rapidly (less than 2h), while increasing loadings of CNF, the droplets of emulsion gels were more homogeneous, leading to stable emulsions (**Figure S1**). As shown in **Figure S2**, significant shape deformation occurred at low CNF addition, and the deformation decreased correspondingly by loading more CNF in the aqueous phase. This is attributed to the fact that high alginate concentrations lead to quick and strong gelation which can affect the shape of cast emulsion gel, leading to the fact that the printed objects could also lead to deformation. The amount of CNF has a decisive role in determining the stability of emulsion gel and its ability to maintain the designed shape after printing. Accordingly, the ratio of CNF and alginate was fixed at 50:50 for all formulations.

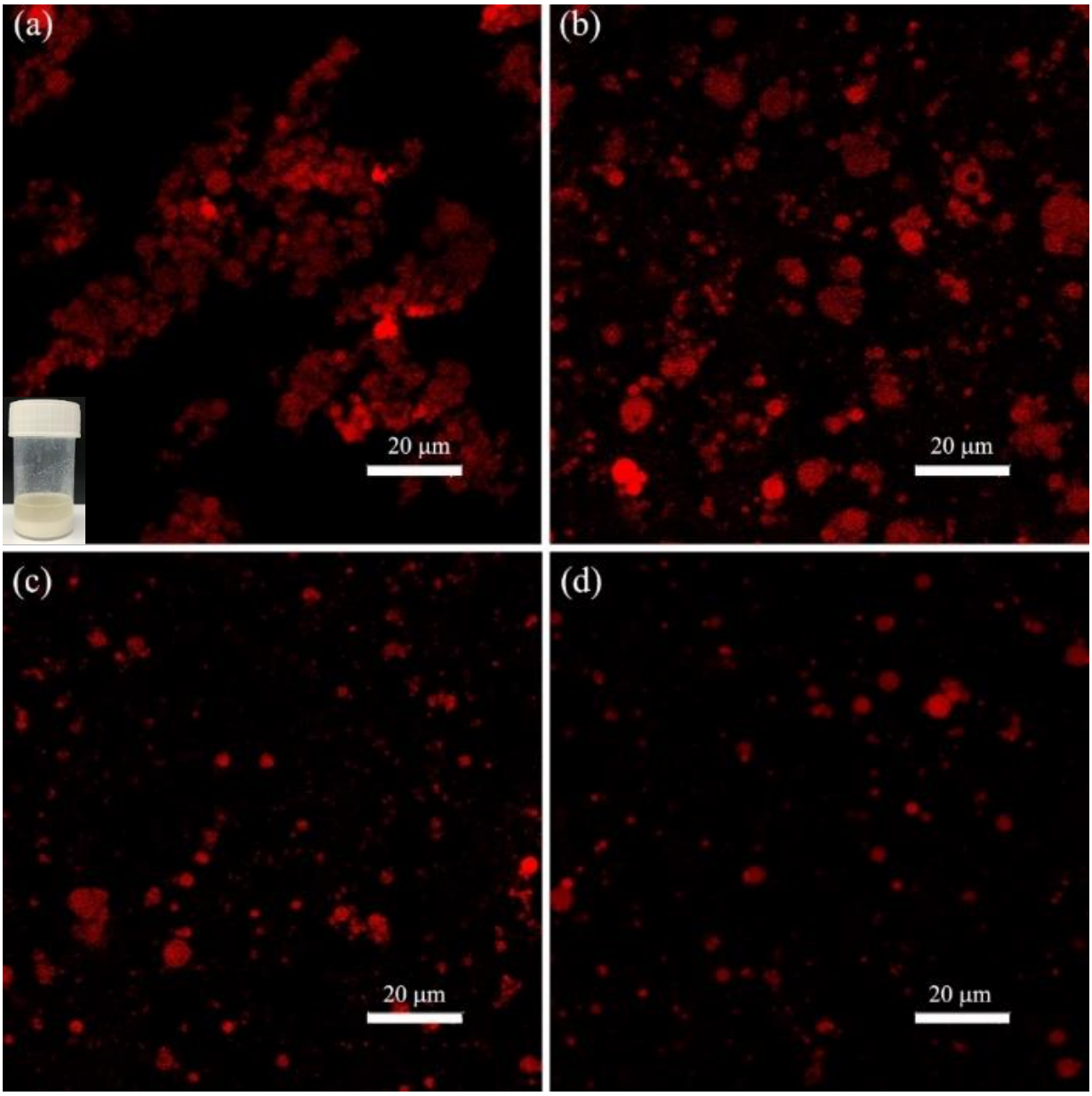

Figure S1. CLSM micrographs of emulsion gel produced with CNF-to-alginate ratio of (a) 0:100, (b) 20:80, (c) 33:67 and (d) 50:50, in the presence of 8 wt% PLA concentration. The f_o = 0.2. The solid content of CNF and alginate in the aqueous phase was kept constant at 3 wt%. The oil phase was stained with Nile red. The prepared emulsions were imaged immediately after emulsification to avoid rapid macroscopic separation.

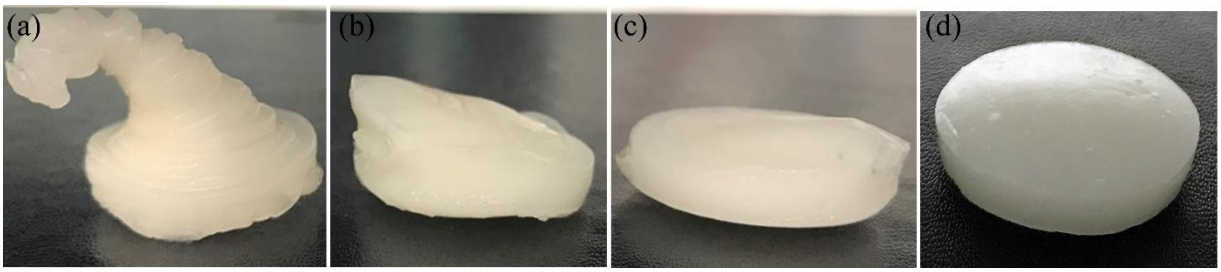

Figure S2. Visual appearance of emulsion gel crosslinked by Ca^{2+} after casting into round plates with CNF-to-alginate ratio of (a) 0:100, (b) 20:80, (c) 33:67, (d) 50:50. The PLA concentration was 8 wt%, and the f_o = 0.2. The solid content of CNF and alginate in the aqueous phase was kept constant at 3 wt%.

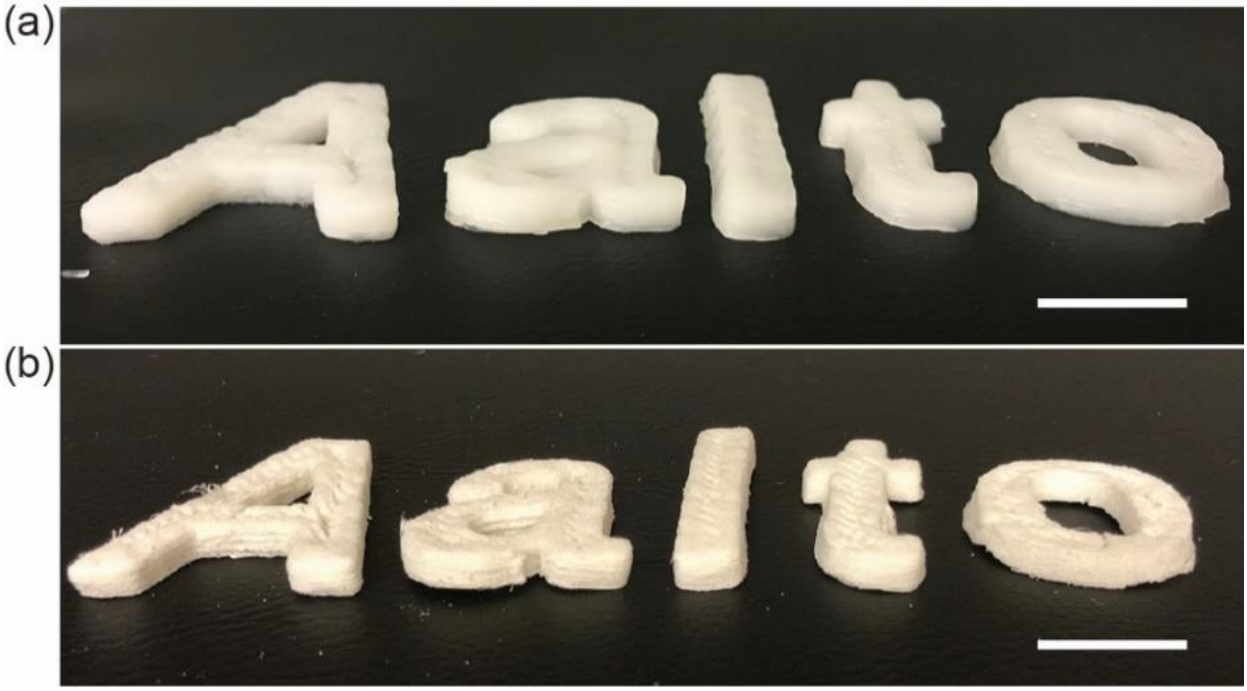

Figure S3. Side view of 3D-printed "Aalto" shape at (a) hydrated and (b) freeze-dried state. The formulation in (a) and (b) was identical: the concentration of CNF and alginate was equal in aqueous phase (3 wt%). The PLA concentration was 12 wt%, and the f_o = 0.3. The scale bar is 2.5 cm.

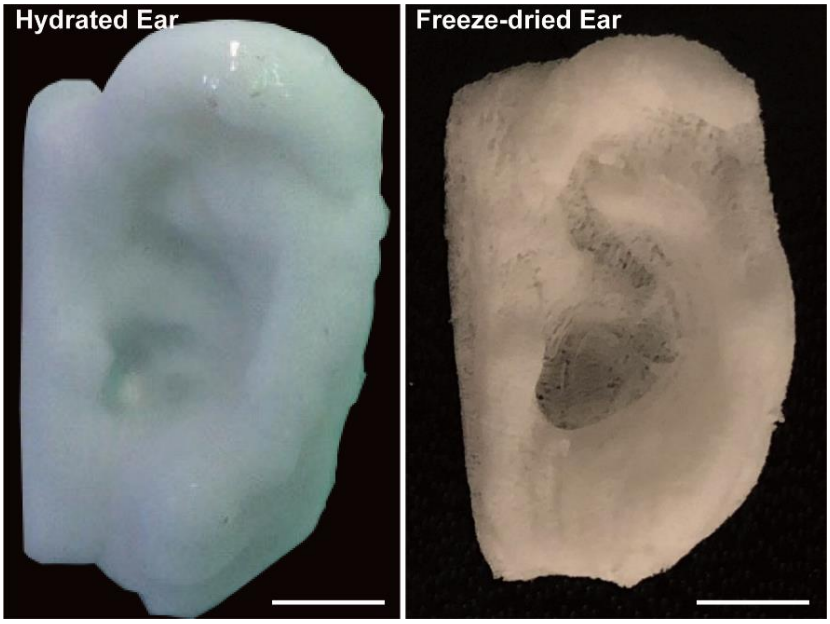

Figure S4. Top view of 3D-printed asymmetrical "ear" shape at hydrated and freeze-dried state, respectively. In the formulation, the concentration of CNF and alginate was equal in the formulation (3 wt%), the PLA concentration was 12 wt%, and f_o = 0.3. The scale bar is 2.5 cm.

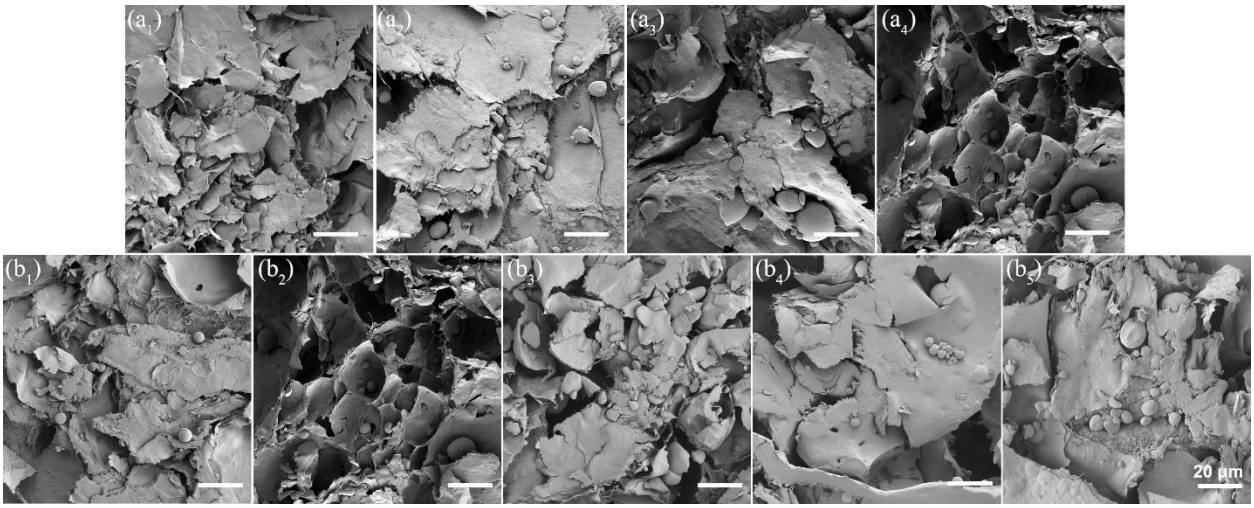

Figure S5. SEM images of the internal microstructure of freeze-dried scaffolds prepared from emulsion gels at (a1-a4) increased PLA concentrations (0, 4, 8, and 12 wt%, respectively) and (b1-b5) increased volume fraction of the internal phase (f_o = 0.1, 0.2, 0.3, 0.4, 0.5, respectively). In (a), f_o = 0.2 for all samples. In (b), %PLA is 12 wt%. The amount of CNF and alginate in the aqueous phase was the same for all the formulations (1.5 wt% each, based on the aqueous phase). The internal of samples were cut out by a knife. The scale bar is 20 μm.

Mechanical performance. Compression test of printed scaffolds at hydrated (after crosslinking) and dry state were conducted by using a dynamic mechanical analysis (DMA, TA Instruments Q800, United States) equipped with a 18N load cell. Measurements were performed in displacement control mode at a rate of 0.05 N/min until reaching the final loading level of 18N. Three replicates were performed for each formulation.

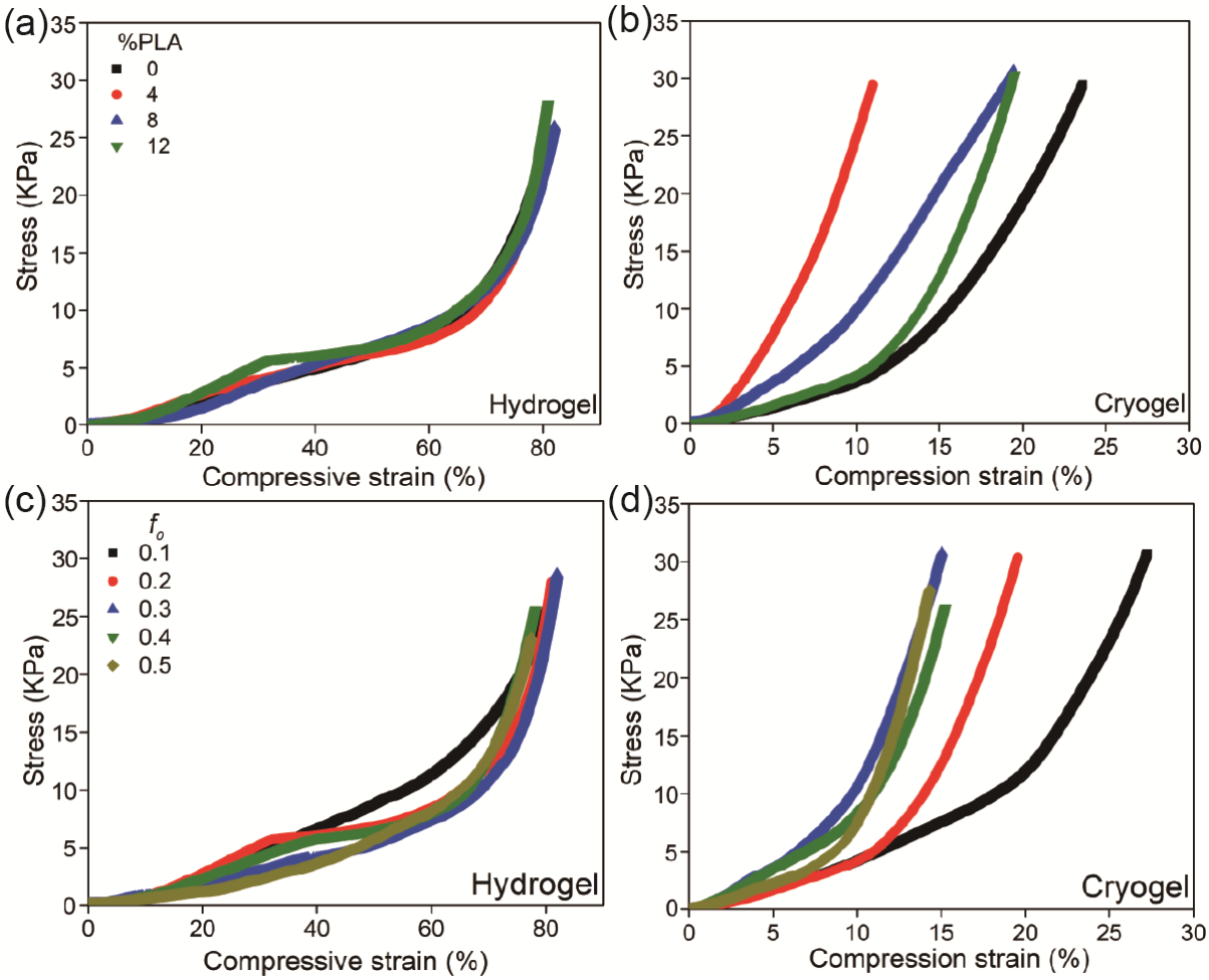

Figure S6. Compression tests for printed cubic scaffolds obtained from emulsion gels of (a,b) varying PLA concentrations and (c,d) different values of the oil fraction, f_o. In (a) and (c), crosslinked scaffolds in the hydrated stated were tested. In (b) and (d), scaffolds were tested in the dry condition. All the measurement was conducted at ambient temperature.

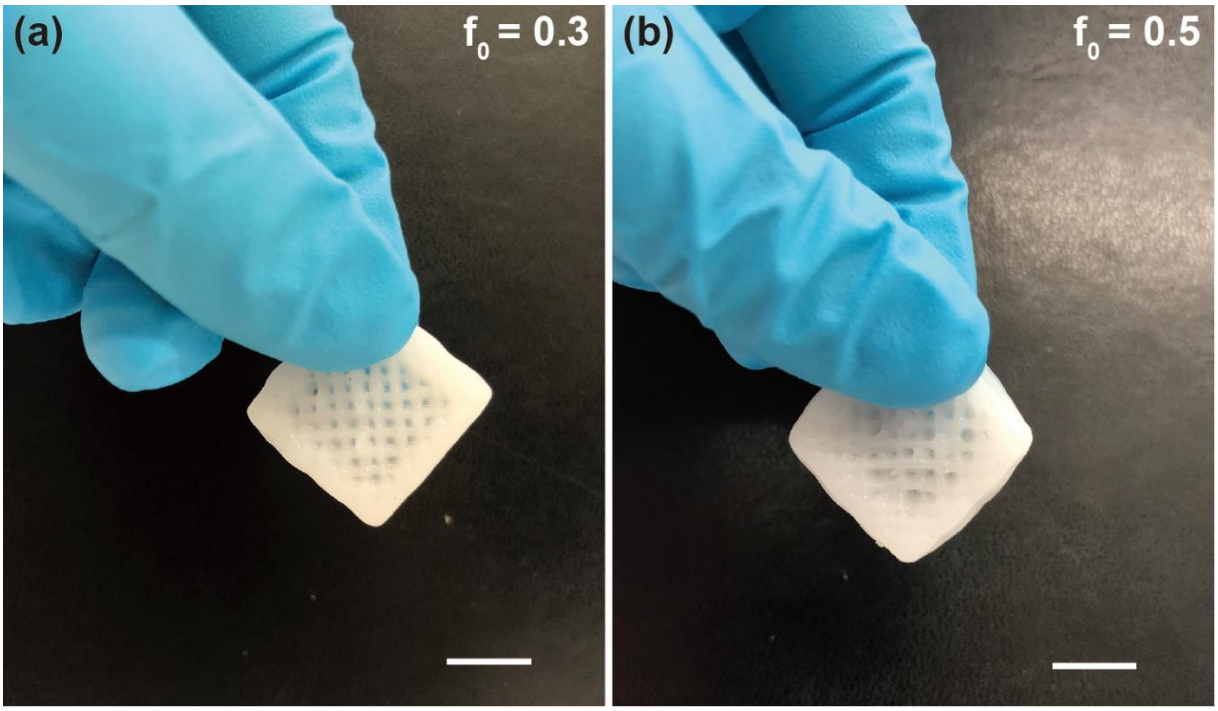

Figure S7. Visual appearance of printed cubic scaffolds at (a) f_o = 0.3 (or water-to-oil fraction = 70:30) and (b) f_o = 0.5 (or water-to-oil fraction = 50:50) after swelling in water. The PLA concentration in both samples was 12 wt%.

Table S2. Shrinkage % of printed cubic scaffolds after room temperature (RT) and freeze drying. The shrinkage is expressed for measurements on the plane and height directions. The original emulsion gels were formulated with varying values of the oil fraction f_o and PLA concentration, as indicated (see **Table S1** for details on the formulation)

Inks	**Surface Shrinkage (%)**		**Height shrinkage (%)**	
	RT drying	Freeze drying	RT	Freeze drying
%PLA= 0	57.5	5	60	0
4	55	5	60	0
8	52.5	5	60	0
12	52.5	5	60	0
f_o = 0.1	60	10	60	0
0.2	52.5	5	60	0
0.3	46	5	60	0
0.4	45	5	60	0
0.5	45	5	60	0