ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Compose and Convert: Controlling Shape and Chemical Composition of Self-Organizing Nanocomposites

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Supplementary Information

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Content:

1. Conversion reactions

Conversion of $BaCO_3$ to $CdCO_3$:

Anhydrous $CdCl_2$ (458 mg, 50mM) was dissolved in 50 mL demineralized water. A substrate containing fresh $BaCO_3$ nanocomposites was placed in the solution for at least 12 minutes. This yields a $CdCO_3/SiO_2$ nanocomposite.

Conversion of $CdCO_3$ to CdSe:

A quartz substrate containing $CdCO_3$ nanocomposites was placed in a single zone tube furnace. An alumina boat, containing 99.9% pure selenium, was added upstream to the single zone tube furnace. The furnace was purged of oxygen and filled with nitrogen until a pressure between 20 and 50 mbar was reached. This pressure was maintained with a 6 sccm flow of N2 as the furnace was heated to 500°C at a rate of 60°C/min and maintained at this temperature for 1 hour.

Conversion of $CdCO_3$ to CdS:

A quartz substrate containing a $CdCO_3$ nanocomposite was placedin a single zone tube furnace. The furnace was purged of oxygen and filled with argon at atmospheric pressure with an argon flow rate of 90 sccm. The tube furnace was heated to 290°C at a rate of 10°C/min and maintained for 1 hour. Once 290°C was reached, 10 sccm of H_2S was added to the flow for 50 minutes. Afterwards the oven was purged using argon and allowed to cool. This resulted in a CdS nanocomposite.

Conversion of $CdCO_3$ to CdO:

A quartz substrate containing a $CdCO_3$ nanocomposite was placed in a single zone tube furnace. The furnace was purged of oxygen and filled with nitrogen gas till a pressure of 500 mbar was reached. This pressure was maintained with a 50 sccm flow of N_2 as the furnace was heated to 290°C for 4 hours. This resulted in a CdO nanocomposite.

Conversion of $BaCO_3$ to $Co(CO_3)x(OH)_{2-2x}$) (basic cobalt carbonate):

Cobalt nitrate hexahydrate ($Co(NO_3)_2$) (727 mg, 2.50 mM) was added to a sealable jar together with a quartz substrate containing $BaCO_3$ nanocomposites. The air in the jar was replaced by argon and 50 mL of degassed and demineralized water was added to the jar. After 50 minutes the substrate was removed and carefully washed using demineralized and degassed water followed by

a drying step using acetone. This yields a $Co(CO_3)x(OH)_{2-2x}/SiO2$ (basic cobalt carbonate) nanocomposite.

Conversion of basic cobalt carbonate to Co_3O_4:

A quartz substrate containing basic cobalt carbonate nanocomposites was placed in a single zone tube furnace and left open to air. The furnace was heated to 300°C at a rate of 20°C/min followed by a slowdown towards 380°C at a rate of 5°C/min. This temperature was maintained for 1 hour before approaching the final temperature of 540°C at a rate of 5°C/min. The final temperature of 540°C was maintained for 8 hours. This resulted in Co_3O_4 nanocomposites.

Conversion of $BaCO_3$ to $MnCO_3$:

Anhydrous $MnCl_2$ (650 mg, 0.1 M) was added to a sealable jar together with a quartz substrate containing $BaCO_3$ nanocomposites. The air in the jar was replaced by argon and 50 mL of degassed and demineralized water was added to the jar. After 60 minutes the substrate was removed and carefully washed using demineralized and degassed water followed by a drying step using acetone. This yields a $MnCO_3$ nanocomposite

Conversion of $MnCO_3$ to α-Mn_2O_3:

A quartz substrate containing an α-Mn_2O_3 nanocomposite was placed in a single zone tube furnace and left open to air. The furnace was heated to 540°C at a rate of 10°C/min and maintained for 24 hours. This yields a α-Mn_2O_3 nanocomposite.

Conversion of $MnCO_3$ to MnS:

A quartz substrate containing a $MnCO_3$ nanocomposite was placed in a single zone tube furnace. The furnace was purged of oxygen and filled with argon at atmospheric pressure with an argon flow rate of 90 sccm. The tube furnace was heated to 400°C at a rate of 10°C/min and maintained for 1 hour. Once 400°C was reached 10 sccm of H_2S was added to the flow for 50 minutes. Afterwards the oven was purged using argon and allowed to cool. This resulted in a MnS nanocomposite.

Conversion of $BaCO_3$ to Ag_2CO_3:

Silver nitrate (1.7 grams, 10 mM) was dissolved in 15 mL of degassed and demineralized water. A quartz substrate containing a fresh $BaCO_3$ nanocomposite was placed in this solution for 1 second before being removed and washed in water followed by a wash with acetone. The resulting nanocomposite consists of Ag_2CO_3 which will naturally decay to Ag_2O in air over the course of a few days.

Conversion of Ag_2CO_3 to Ag_2O:

A quartz substrate containing a Ag_2CO_3 nanocomposite was placed in a single zone tube furnace. The furnace was purged of oxygen and filled with nitrogen at atmospheric pressure with a flow of 30 sccm. The furnace was heated to 120°C at 5°C/min and maintained for 24 hours. This yields a black colored Ag_2O nanocomposite.

Conversion of $SrCO_3$ to $PbCO_3$:

Lead Nitrate ($Pb(NO_3)_2$, 15 g, 906 mM) was dissolved in 50 mL degassed and demineralized water under a nitrogen atmosphere. A quartz substrate containing a fresh $SrCO_3$ nanocomposites was placed in this solution for 45 seconds. Afterwards, the substrate containing the white nanocomposite was removed and washed in three demineralized water baths followed by an acetone bath. This yields a $PbCO_3$ nanocomposite.

Conversion of $PbCO_3$ to $MAPbBr_3$ perovskite:

A quartz substrate containing a $PbCO_3$ nanocomposite was placed in a saturated solution of MABr in IPA for 5 seconds before removing the substrate and washing with methanol. This yields a $MAPbBr_3$ perovskite nanocomposite.

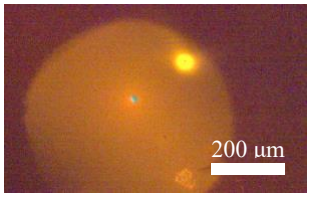
Table S1. Conversion reactions

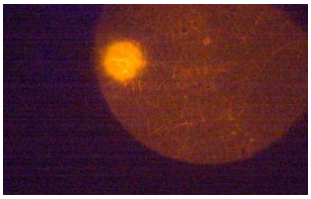
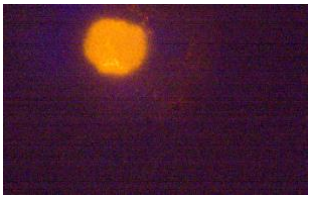
Fig. #	**Cationic conversion**	**Anionic conversion**	**Additional comments**
2A An array of corals	Conversion of $BaCO_3$ to $CdCO_3$.	Conversion of $CdCO_3$ to CdO.	
2H triangular shaped	Conversion of $BaCO_3$ to $Co(CO_3)x(OH)_{2-2x}/SiO_2$ (basic cobalt carbonate).	Conversion of basic cobalt carbonate to Co_3O_4.	Slower initial heating rates cause more breakage of the nanocomposite
2O line with two turns	Conversion of $BaCO_3$ to $MnCO_3$	Conversion of $MnCO_3$ to MnS	The cationic conversion time was extended to 120 minutes to compensate for the denser structure.
3A, 3 in a row, first structure	Conversion of $BaCO_3$ to Ag_2CO_3	Conversion of Ag_2CO_3 to Ag_2O	

3A, 3 in a row, second structure	Conversion of $BaCO_3$ to $MnCO_3$	Conversion of $MnCO_3$ to α-Mn_2O_3	This reaction goes over 300°C. At this temperature Ag_2O is known to be converted from Ag_2O to Ag.
3A, 3 in a row, third structure	Conversion of $BaCO_3$ to $Co(CO_3)x(OH)_{2-2x}/SiO_2$ (basic cobalt carbonate).	Conversion of basic cobalt carbonate to Co_3O_4	
3F, 3 in a row, first structure	Conversion of $BaCO_3$ to $CdCO_3$	Conversion of $CdCO_3$ to CdSe	
3F, 3 in a row, second structure	Conversion of $BaCO_3$ to $CdCO_3$	Conversion of $CdCO_3$ to CdS	
3F, 3 in a row, third structure	Conversion of $BaCO_3$ to $CdCO_3$	Conversion of $CdCO_3$ to CdO	
Figure 4A, triangle w circle. Triangle	Conversion of $BaCO_3$ to $CdCO_3$	Conversion of $CdCO_3$ to CdSe	
Figure 4A, triangle w circle. Circle	Conversion of $BaCO_3$ to Ag_2CO_3	Conversion of Ag_2CO_3 to Ag_2O	
Figure 4F, Perovskite **Pb core**	Conversion of $SrCO_3$ to $PbCO_3$	N/A	
Figure 4F, Perovskite overgrowth	N/A	Conversion of $PbCO_3$ to $MAPbBr_3$ perovskite	

2. Light-induced nucleation and growth of $BaCO_3/SiO_2$ structures using 365 nm and 1435 nm

Table S2. Light-induced nucleation and growth of $BaCO_3/SiO_2$ structures

Fig. #	**Precursor solution (mM)**	**Light irradiation for nucleation (A= area, I= light intensity, t= time)**	**Light irradiation for growth (A= area, I= light intensity, t= time)**	**Additional comments**
2A An array of corals	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM Ketoprofen, 50 mM DTAB	275 nm, A= radius 50 μm, I = 100 μW/mm2, t = 15- 35 s per nucleationsite, in a constant irradiation of overlapping 365 nm, A= radius 250 μm, I = 4.5 μW/mm^2	365 nm, A= radius 250 μm, I = 4.5 μW/mm^2, t = 1 h 20 min	Overlapping light irradiation:  Increasing irradiation time for later nucleation site.
2H triangular shaped	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, 50 mM DTAB	275 nm, A= triangular shaped projection with arms of 350 μm , I = 75 μW/mm^2, t = 60 s per nucleation site	275 nm, A= triangular shaped projection with arms of 350 μm, I = 75 μW/mm^2, t = 5.5 h per nucleation site	Triangular light projection:  Grown in a series of subsequent growth of triangular shaped BaCO3/SiO2.

2O line with two turns	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, and 50 mM DTAB	365 nm, A= radius 125 µm, I = 535 µW/mm^2, t = 3 s	1. 365 nm, A= radius 125 µm, I = 32 µW/mm^2, t = 3 min 2. 365 nm, A= radius 25 µm, I = 400 µW/mm^2, t = 5 min 3. 365 nm, A= radius 25 µm, I = 435 µW/mm^2, t = 3 h 20 min, additional 1435 nm overlapping with UV, ramping I= 10-25 mW within the first 10 min, then after 50 min to 30 mW.	365 nm irradiation:  NIR irradiation:  Moving sample: growth in x-direction for 50 min, then in 75 min in y-direction, then 50 min in x-direction.*
3A, 3 in a row, first structure	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, 50 mM DTAB	275 nm, A= radius 50 µm, I = 100 µW/mm^2, t = 6 s per nucleationsite, in a constant irradiation of overlapping 365 nm, A= radius 250 µm, I = 10 µW/mm^2	365 nm, A= radius 250 µm, I = 10 µW/mm^2, t= 1 h 45 mi	Overlapping irradiation: 
3A, 3 in a row, second structure	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, 50 mM DTAB	275 nm, A= radius 100 µm, I = 100 µW/mm^2, t= 4 s	275 nm, A= radius 100 µm, I = 10 µW/mm^2, t= 2 h	275 nm irradiation: 
3A, 3 in a row, third structure	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, 50 mM DTAB	275 nm, A= radius 100 µm, I = 100 µW/mm^2, t= 12 s	275 nm, A= radius 100 µm, I = 25 µW/mm^2, t= 2 h	275 nm irradiation 

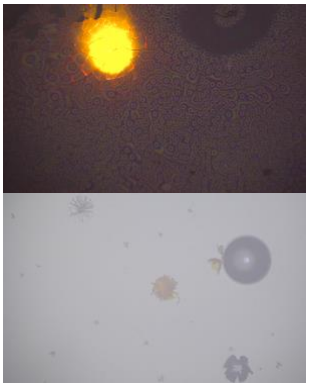
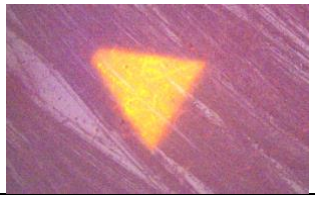
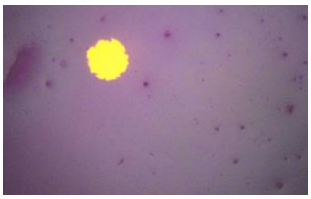
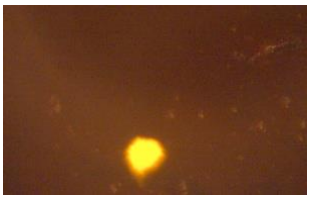
3F, 3 in a row, first structure	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 3 mM KP, 30 mM DTAB	365 nm, A= radius 75, µm, I = 400 µW/mm^2, t = 7 s	365 nm, A= radius 75 µm, I = 45 µW/mm^2, t= 1 h 20 min	365 nm irradiation: 
3F, 3 in a row, second structure	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, 50 mM DTAB	365 nm, A= radius 75 µm, I = 400 µW/mm^2, t = 2 s	275 nm, A= radius 75 µm, I = 25 µW/mm^2, t= 1 h 40 min	365 nm irradiation: 
3F, 3 in a row, third structure	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, 50 mM DTAB	365 nm, A= radius 75 µm, I = 535 µW/mm^2, t = 10 s	275 nm, A= radius 75 µm, I = 45 µW/mm^2, t= 1 h	365 nm irradiation: 
Figure 4A, triangle w circle. Triangle	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, 50 mM DTAB	275 nm, A= triangular shaped projection with arms of 250 µm , I = 100 µW/m µW/mm^2, t = 3 s	275 nm, A= triangular shaped projection with arms of 250 µm , I = 50 µW/mm^2, t = 6 h	Triangular light projection: 
Figure 4A, triangle w circle. Circle	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, 50 mM DTAB	275 nm, A= radius 150 µm , I = 100 µW/mm^2, t = 2 min with overlapping 365 nm, A= radius 50 µm, I = 5 µW/mm2	275 nm, A= radius 150 µm , I = 100 µW/mm2, t = 3 h with overlapping 365 nm, A= radius 50 µm , I = 5 µW/mm^2, last hour 365 nm off	275 nm irradiation: 

Figure 4F, Perovskite Pb core	20 mM $SrCl_2$, 7.75 mM Na_2SiO_3, 3.75 mM KP, 75 mM DTAB	365 nm, A= radius 75 µm, I = 535 µW/mm^2, t = 5 s	365 nm, A= radius 75 µm, I = 32 µW/mm^2, t = 30 min	365 nm irradiation: 
Figure 4F, Perovskite overgrowth	20 mM $BaCl_2$, 9 mM Na_2SiO_3, 2.5 mM KP, 25 mM DTAB	365 nm, A= radius 50 µm, I = 400 µW/mm^2, t = 10 s	1. 365 nm, A= radius 50 µm, I = 15 µW/mm^2, t = 1 h 2. 365 nm, A= radius 50 µm, I = 5 µW/mm^2, t = 1 h 30 min moving sample	365 nm irradiation:  Moving sample.

*To grow a line with an arbitrarily shaped line we prepare a precursor solution of 20 mM $BaCl_2$, 9 mM Na_2SiO_3, 5 mM KP, and 50 mM DTAB. We fill the reaction cell and upon irradiation of an area with a radius of 125 µm with high intensity 365 nm light (535 µW/mm^2) for 3 seconds we induce nucleation. We directly lower the light intensity to 32 µW/mm^2 to enable growth for 3 minutes. Then we reduce the illuminated area to a spot size with a radius of 25 µm. We place the growing structure in the middle of the spot and increase the light intensity to 400 µW/mm^2 to continue growth. After 5 minutes, we additionally turn on the 1435 NIR laser irradiation, of which the focal spot is located in the middle of the UV spot. We ramp the intensity of the NIR laser from 10 mW output power to 25 mW in 10 minutes, while we simultaneously increase the UV light irradiation to 435 µW/mm^2. We start moving the sample away from the light spots with a pace that matches the growth rate to keep the growth front in a constant location in the irradiated area and selectively enable growth in one direction. After 50 minutes of growth, we increase the NIR output power to 30 mW. We change direction of movement after 75 minutes of growth in x- direction, to movement in y-direction. After one hour in growth in y-direction, we change the movement again in x-direction. We enable growth for another 50 minutes to complete a total growth time of 3 hours and 20 minutes. We observe a faster growth at the end, which can indicate a gradual increase of the bulk solution.

3. Zoom in on fine-detail

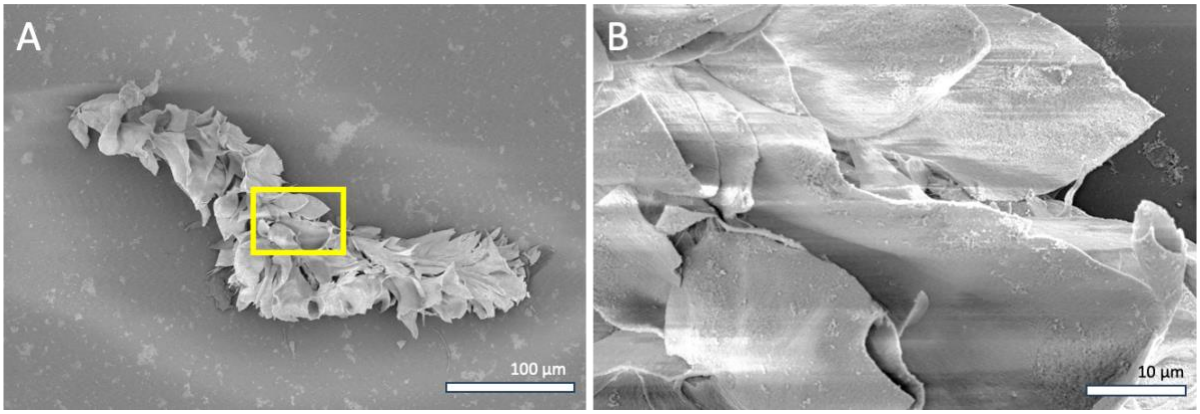


Figure S1. Electron microscopy image of (A) MnS/SiO_2 line-shape of Figure 2, with (B) zoom in showing the fine-details of the structure after conversion.

4. Crystal lattice shrinkage

Due to the different size of the crystal lattice between $BaCO_3$ and Co_3O_4, the converted structures shrinks in volume (Figure S2).

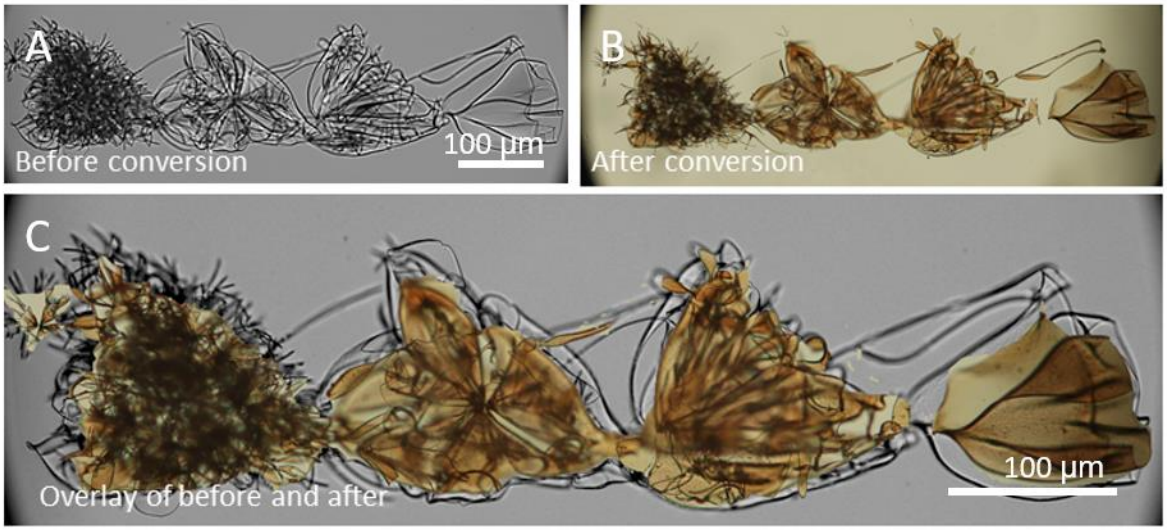


Figure S2. Comparison of the volume change due to conversion. A) triangular shaped $BaCO_3/SiO_2$ structures before conversion (top left). B). Co_3O_4 triangular shaped after conversion. C) overlay of B (colored) on top of A (greyscale).

5. Light-microscope set-up

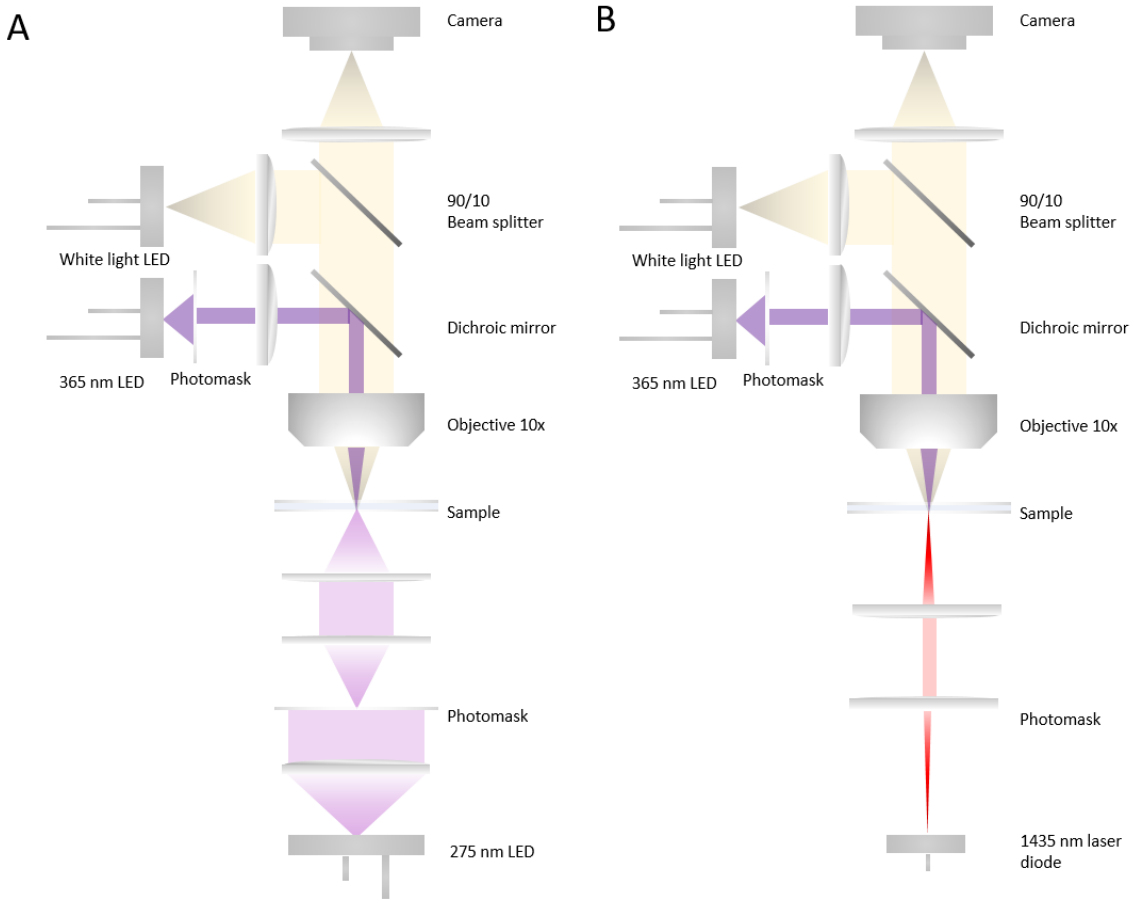


Figure S3. Schematic overview of a double UV irradiation using (A) a 365 nm and 275 nm LED and (B) a 365 nm LED and 1435 nm laser diode.