Graphitic Carbon Nitride Stabilizers Meet Microfluidics: From Stable Emulsions to Photoinduced Synthesis of Hollow Polymer Spheres

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Graphitic carbon nitride (g-CN) has been utilized as a heterogeneous catalyst, but is usually not very well dispersible. The amphiphilic character of g-CN can be altered by surface modifications of g-CN nanopowders. Introducing hydrophilicity or hydrophobicity is a promising avenue for producing advanced emulsion systems. In this study, a special surface-modified g-CN is used to form stable Pickering emulsions. Using a PDMS-based microfluidic device designed for stable production of both single and double emulsions, it is shown that surface-modified g-CNs allow the manufacture of unconventionally stable and precise Pickering emulsions. Shell thickness of the double emulsions is varied to emphasize the robustness of the device and also to demonstrate the extraordinary stabilization brought by the surface-modified carbon nitride used in this study. Due to the electrostatic stabilization also in the oil phase, double emulsions are centered. Finally, when produced from polymerizable styrene, hollow polymer microparticles are formed with precise and tunable sizes, where g-CN is utilized as the only stabilizer and photoinitiator.

The search for sustainable photocatalysts for solar fuel production has led to the (re)discovery of graphitic carbon nitride (g-CN), a metal-free semiconductor with favorable photoactivity in the visible light range.[1] This photocatalyst is metal-free and easily synthesized via thermal polymerization of nitrogen-rich and cheap precursors, such as melamine, which makes it a superior choice over traditional semiconductors with metal content.[2] g-CN as used in the literature is not a single compound, but represents a class of materials with tunable properties, for example, light absorption, bandgap, photoluminescence, all of which can

be tailored via pre- or post-modification methods.[3] g-CN has been utilized in water splitting,[4] CO_2 reduction,[5] photoelectrochemistry,[6] and polymer chemistry.[7] Abundant aromaticity together with functional edge termination (–OH and –NH_2 groups) grants a partial amphiphilic character to g-CN, so that even unmodified g-CN can stabilize emulsions (Pickering style)[8] and be utilized as a photoinitiator to synthesize nano-/micron-sized polymer particles;[9] the performance of which is comparable to classical Pickering stabilizers such as cellulose,[10] clay,[11] Fe_3O_4,[12] and graphene oxide.[13] The presence of g-CN in polymer particles opens further potential applications in bioimaging,[14] photonics,[9] and photocatalysis.[15] Traditional g-CN materials are sheet-like and dominated by strong π–π interactions leading to restricted dispersibility; however, the surface of g-CN can be modified via photoinduced grafting processes to provide hydrophilicity or hydrophobicity. Our recent work demonstrated that photoinduced modification of g-CN by vinylthiazole (vTA) groups grants stable organic dispersions via electrostatic stabilization, even in organic solvents.[16] By such modifications, g-CN can actually detach from the interface and move into the single phases. These modifications therefore allow cheap and photoactive g-CN dispersion in either hydrophilic or hydrophobic media for multiple applications, such as traditional emulsion polymerization.[17]

Microfluidics has developed into a strong technique for versatile hierarchical material synthesis,[18] while offering high reproducibility and scalability. Microfluidic channel designs with *T*– junctions can easily produce emulsion droplets, and pairs of flow-focusing cross-junctions can be used to produce double emulsions.[19] Researchers have shown that it is even possible to make higher-order multiple emulsions with high precision and reproducibility.[20] In this work, we take advantage of microfluidics to produce single and double emulsions containing vTA-modified g-CN. To the best of our knowledge, it is the first attempt to make g-CN emulsions using microfluidics for reliable monodisperse production of complex emulsions. We show that using our microfluidic design we can not only tune the emulsion droplet-size for single emulsions, but also the thickness of the associated oil-layer within double emulsions. Center-stabilized double emulsions are utilized to form hollow polymer spheres when styrene is chosen as the oil phase, and where g-CN acts as a stabilizer and photoinitiator (**Scheme 1**).

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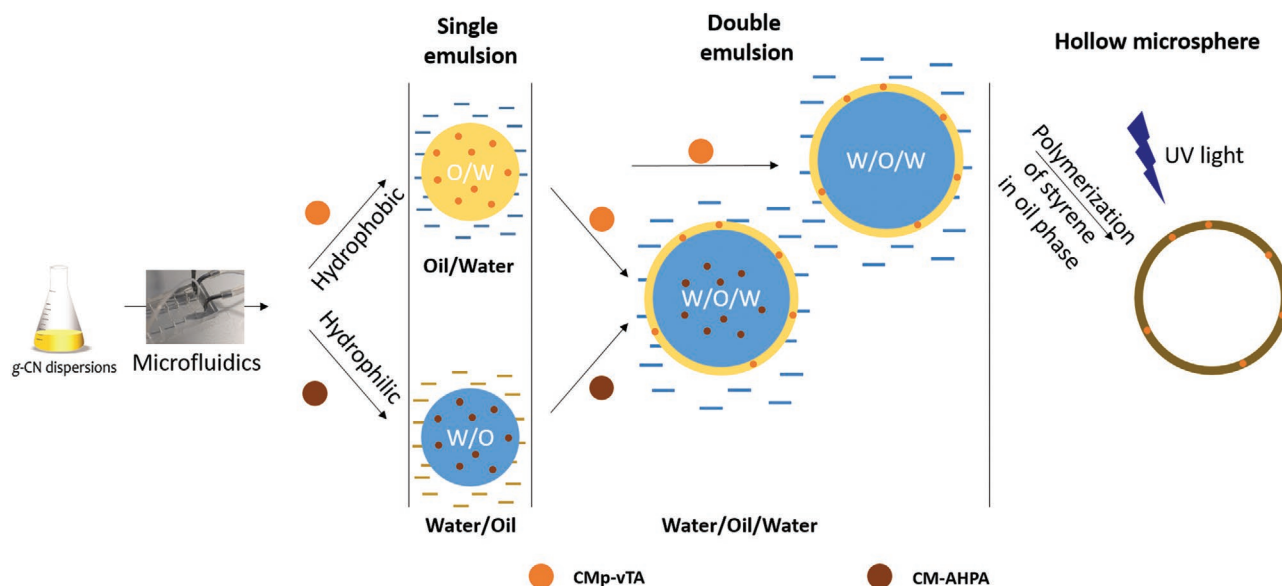
Scheme 1. General pathway toward emulsions. Surface modified g-CNs are used to produce single emulsions (oil/water and water/oil), double emulsions (water/oil/water), and double emulsions leading to the synthesis of hollow polymer spheres using g-CN as both a stabilizer and a photoinitiator in the presence of a monomer as the oil phase.

Graphitic carbon nitrides were synthesized and modified according to previous reports. Namely, g-CN was synthesized from cyanuric acid–melamine mixture and denoted as CM,[21] the alternative synthesis from cyanuric acid–2,4-diamino-6-phenyl-1,3,5 triazine mixture is denoted as CMp (details in Supporting Information).[22] CM was modified via one pot visible light induced grafting with hydrophilic groups (denoted as CM-AHPA)[23], while CMp was modified via one pot visible light induced grafting with vinyl thiazole groups (denoted as CMp-vTA).[16] CM-AHPA retains its absorption profile indicating the photoactivity after AHPA modification (Figure S1a, Supporting Information). AHPA modification leads to slight changes in the packing structure disordering in the crystal structure due to grafted organic moieties and introduction of charged species (Figure S1b, Supporting Information). Both samples however present similar fingerprint region at FT-IR spectra (Figure S1c, Supporting Information) and similar powder morphologies (Figure S1d, Supporting Information). For CMP-vTA, the absorption is enhanced and shifts after vTA grafting (Figure S2a, Supporting Information), however, preserving perfect sheet stacking (Figure S2b, Supporting Information).[16] FT-IR (Figure S2c, Supporting Information) and morphology (Figure S2d, Supporting Information) of particles are retained after modification as well. Successful modification can also be confirmed via elemental combustion analysis via the increased sulfur content and C/N ratios after both modifications (Table S1, Supporting Information). An important parameter for the stability of dispersions is the zeta potential, which showed a decrease after AHPA grafting (from −28.6 mV down to −41.3 mV in water, Table S1, Supporting Information) hinting toward increased water stability. vTA modification on CMp allows grafting on the edges of sheets, which allows autonomous charge delocalization in organic solvents (Table S1, Supporting Information) where the negative charge migrates to thiazole edges leaving the carbon

nitride core partially positive, which is the key phenomenon to access electrostatic stabilization in organic solvents. CM-AHPA water dispersion (0.1 wt%) and CMp-vTA 1-octanol dispersion (0.1 wt%) were both prepared via sonication for 4 h and allowed to rest for 1 h for the sedimentation of large sheets.

In the next step, both dispersions were introduced into the microfluidic device for the preparation of water-in-oil (W/O) and oil-in-water (O/W) emulsions. **Figure 1**a shows the microfluidic device with a single cross-junction producing CMp-vTA containing O/W droplets (see Movie S1, Supporting Information). This process is facilitated by rendering the surface of the channels hydrophilic (see Supporting Information). Upon collection of the droplets, a few microliters of the dispersion were spread onto a coverslip for observation under confocal microscopy.

Morphological examination reveals that the produced O/W droplets retain their spherical shape after transferring to the glass coverslip, (inset Figure 1a) and the produced emulsion droplets were stable for more than 24 h (data not shown). Furthermore, confocal images also reveal that modified carbon nitride retains its fluorescence properties, and that the carbon nitride is distributed evenly across the droplets (Figure 1b). In addition to this, it can be deduced that the modified carbon nitride is exclusively confined within and along the interface of the droplets unlike the unmodified version that can move across the interface and settle at the bottom as aggregates.[24]

One of the major assets of microfluidic production of emulsion droplets is the possibility to produce populations with a narrow size distribution. Monodispersity in the emulsion size can provide consistent content or product for a given volume—a necessary aspect for reproducible functionality. Predictably, the produced emulsion droplets are highly mono-disperse (Figure 1d). Moreover, by altering the flow rates of inner solution, we could change the size of the O/W droplets while still retaining a narrow size distribution as depicted in Figure 1d. By
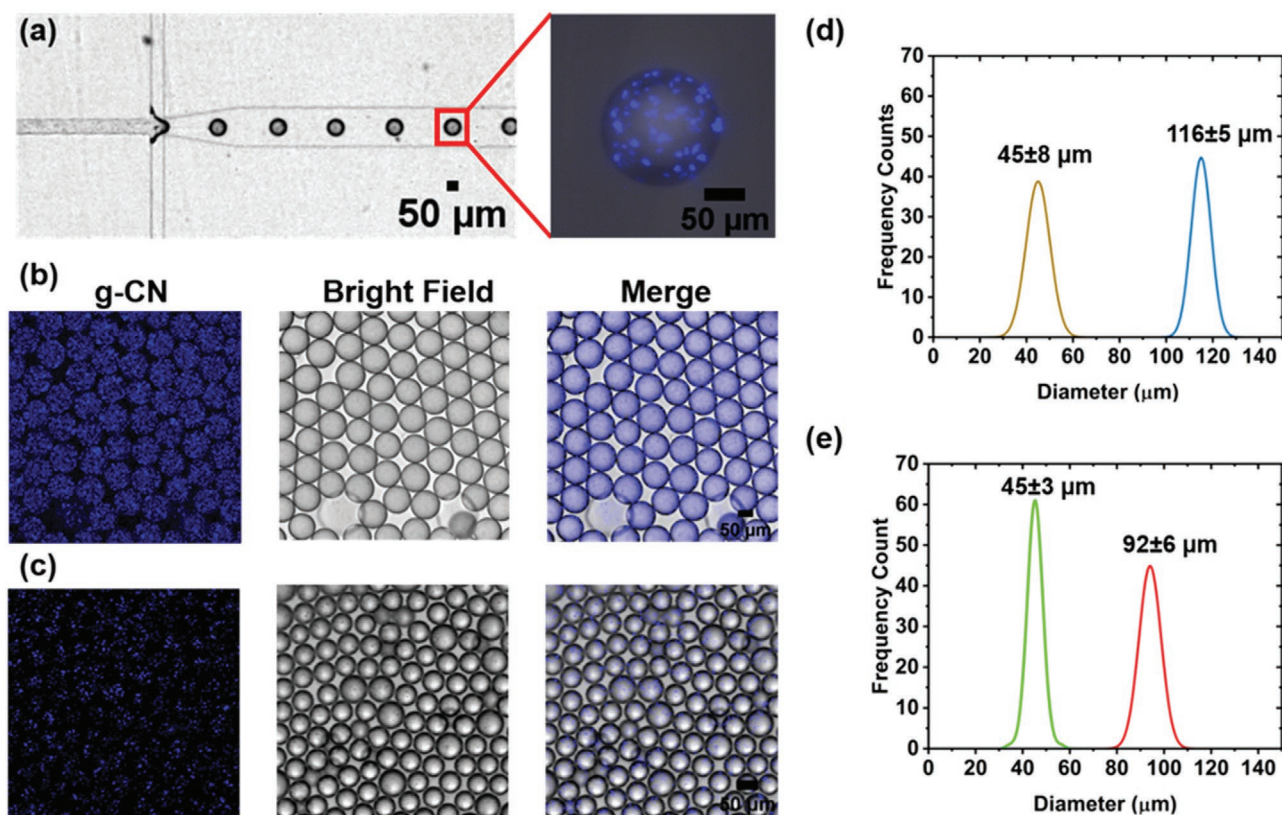
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Figure 1. Microfluidic production of a carbon nitride Pickering emulsion. a) High-speed microscopy of the on-chip emulsion production (inset showing O/W droplet with CMp-vTA). Confocal images of monodisperse b) O/W with CMp-vTA in oil phase (74 mbar aqueous phase and 87 mbar oil phase for smaller size droplets and 110 mbar for larger size droplets) and c) W/O droplets with CM-AHPA in aqueous phase (96 mbar aqueous phase and 80 mbar oil phase for smaller size droplets and 70 mbar in oil phase for larger size droplets). Size distributions for monodisperse d) O/W and e) W/O droplets. Mean sizes are shown together with the standard deviations.

increasing the flow of the inner solution, we produced droplets with mean size distributions of 45 ± 8 and 116 ± 5 µm.

Following this, CM-AHPA containing W/O droplets are generated using the single cross-junction microfluidic channel. Unlike O/W droplet production, the surface of the microfluidic channels need not be modified in advance thanks to the inherent hydrophobic nature of the PDMS channels. W/O droplets are visualized under confocal microscope for morphology and stability studies (Figure 1c). Droplets were stable for the 24 h period tested (data not shown). Fluorescence emission of CM-AHPA is similar to that of CMp-vTA (Figure 1c). Monodispersity of the W/O droplets was high, and the morphology highly spherical, as observed for the of O/W droplets containing CMp-vTA. W/O droplets of various size distributions are made by altering the flow rates. Narrow size distribution (45 ± 3 µm and 94 ± 5 µm) of various populations is shown in Figure 1e. In order to clarify the differences in intensities of the confocal images for CM-AHPA- and CMp-vTA-based emulsions, fluorescence spectroscopy was applied, which shows emission intensity differences between both species, indicating that a higher fluorescence signal is an intrinsic property of CMp-vTA (Figure S3, Supporting Information).

Unlike single emulsion production (W/O or O/W droplets), production of double emulsion requires careful flow focusing of two successive cross-junctions (see Figure S4, Supporting

Information, for optimization steps). The first junction forms W/O droplets while the second junction injects them into an outer aqueous phase thus producing water-in-oil-in-water (W/O/W) double emulsions. First, CM-AHPA was used in the aqueous inner solution, CMp-vTA in the oil phase (1-octanol), and MilliQ water in the outer aqueous phase (see Movies S2 and S3, Supporting Information). Using this configuration, double emulsions with ultra-thin shells could be made which are stable during and after the preparation process, as visualized under the confocal microscope (**Figure 2**a,b). Interestingly, such an ultra-thin oil-phase in the double emulsion resulted in a ring in the fluorescence emission channel. Such a ring-like structure is not observed when double emulsion with thick oil phase is produced (Figure 2c,d). A thin oil shell could result in better packing of the particles along the interface unlike in double emulsions with a thick oil shell. Note that the size of the inner aqueous droplet is same in both the double emulsions, that is, ≈50 µm. No matter the thickness of the oil phase, the double emulsions are stable during an observed period of 12 h (data not shown). Importantly, the ability to produce double emulsions with varying shell thicknesses can have major implications for catalysis and drug delivery.[25] Moreover, with catalysts in both the phases, one can perform biphasic photocatalysis.[26]

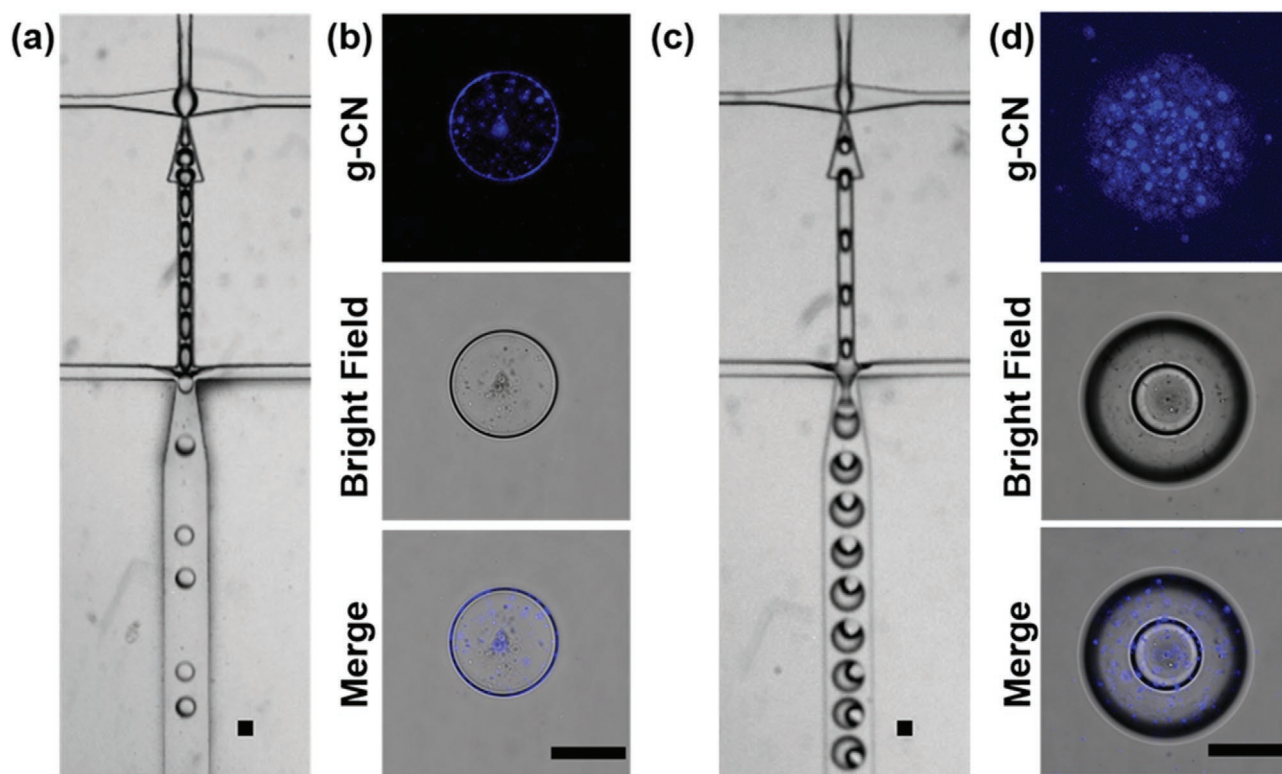Following the successful production of double emulsions containing carbon nitride in both aqueous and oil phases, we

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Figure 2. Microfluidic production of W/O/W double emulsions with CM-AHPA in inner aqueous phase and CMp-vTA in oil phase. a) High-speed microscopy of ultra-thin double emulsion shell production with corresponding confocal images in (b). Pressures in the inner aqueous phase, oil phase, and outer aqueous phase inlets were 62, 58, and 127 mbar, respectively. c) High-speed microscopy of thick double emulsion shell production with corresponding confocal images in (d). Pressures in the inner aqueous phase, oil phase, and outer aqueous phase inlets were 72, 77, and 70 mbar, respectively. Scale bar corresponds to 50 μm.

aimed to exploit the photoinitiating properties of carbon nitride. For this purpose, double emulsions were produced with an oil phase comprising 5% 1-octanol, 95% styrene, and CMp-vTA (0.1 wt%). Note that CMp-vTA is not dispersible in 100% styrene (Figure S5, Supporting Information), and 1-octanol had to be added as the dispersing agent. Using this oil phase, double emulsions were produced with MilliQ water in both inner and outer phases (**Figure 3** and Movie S4, Supporting Information). Confocal images of the emulsions show a distinct fluorescent ring from the oil phase (Figure 3b) and not from the internal aqueous phase indicating that the CMp-vTA is indeed confined to the oil phase. It is also important to underline that the inner aqueous phases of our double emulsions are always localized in the center of the assembly, which strongly hints at long-range electrostatic stabilization even through the non-dissociative oil phase arising from CMp-vTA.[16] These styrene-containing double emulsions were found to be stable at room temperature over a period of 12 h (data not shown). Size analysis shows that these double emulsions are also highly monodisperse and have an average outer diameter of 92 ± 5 μm (Figure 3c).

Obtaining double emulsion with aqueous core stabilized in the center would grant access to structurally perfect hollow polymer spheres if the styrene monomer in oil phase could be subjected to polymerization. Such facile fabrication of hollow polymer spheres would be superior compared to traditional methods such as using templates or self-assembly.[27] In our

case, g-CN can be utilized as a photoinitiator in addition to being an emulsion stabilizer. There, our double emulsions were placed between glass cover slips in water and irradiated via near UV light for 4 h in order to initiate styrene polymerization. An increased darker contour (bright field) suggests that indeed polymerization has taken place, and confocal images demonstrate similar fluorescent rings as before, confirming the presence of g-CN within the polymerized styrene (**Figure 4**a). Importantly, during the entire process, the emulsion remained stable to finally form the solid hollow microspheres. Subsequently, polymer spheres were freeze-dried, and their morphology was investigated via SEM. After freeze-drying, polymer spheres preserved their shape and smooth surface morphologies for individual particles were observed (Figure S6, Supporting Information). Furthermore, the spherical particles were subsequently cracked manually to reveal their inner morphology by SEM, and indeed they were found to be hollow inside (Figure S7, Supporting Information). This also underlines the stability of W/O/W system during polymerization. Peaks were obtained for freeze-dried hollow polystyrene particles via powder XRD indicating partial crystallinity (Figure S8, Supporting Information). Close-up confocal images of individual microspheres are shown in Figure 4a inset.

Interestingly, after the 4 h polymerization period, the emulsions shrunk significantly into smaller spherical structures with increased shell thickness (Figure 4b,c). Utilizing 2D
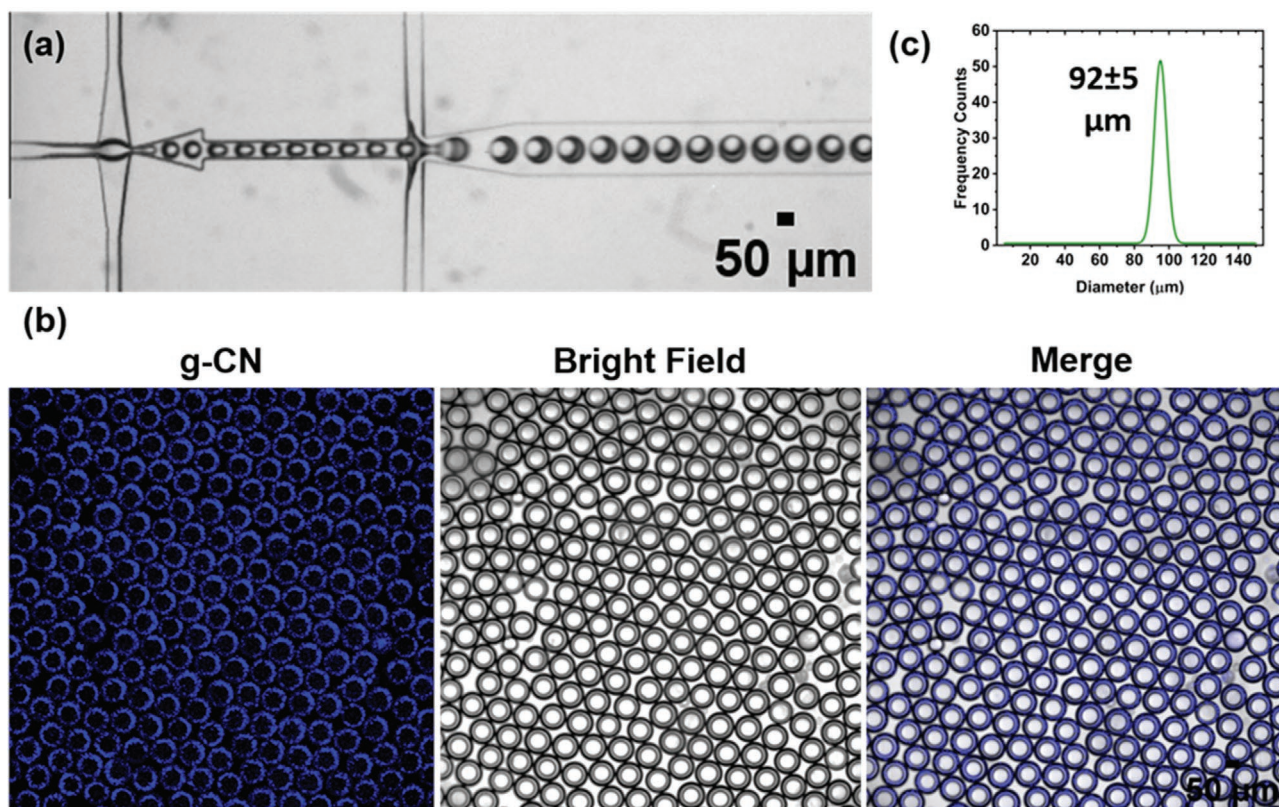
Figure 3. Production of CMp-vTA containing W/O/W double emulsions with 95% styrene in the oil phase. a) High-speed microscopy of the double emulsion production process with fluid pressures set at 64, 64, and 70 mbar for the inner aqueous, middle oil phase, and outer aqueous phase inlets, respectively. b) Confocal images of the highly monodisperse center-stabilized double emulsions. c) The narrow size distribution with a mean outer diameter of 92 ± 5 µm.

sheet-like g-CN as a photoinitiator results in polymer-initiating species on both sides of the sheets; therefore, g-CN also acts as crosslinker, which was proven by our previous studies.[17]. Similarly, hollow polymer microspheres were not soluble in tetrahydrofuran (data not shown), a common solvent for polystyrene, which indicates cross-linked species. Furthermore, we have performed polymerization of a reference sample that does not contain CMp-vTA, but instead BAPO as photoinitiator and a commercial surfactant (F-108, 0.5 wt%). The original size of the emulsions were 70.25 ± 2 µm and they shrunk to 10.2 ± 3 µm (Figure S9, Supporting Information), similar to that of the hollow spheres formed when g-CN is used as a photo-initiator. Combining this data with the fact that the emulsions remained stable with no change in size when they are not polymerized (over a period of 12 h, Figure S10, Supporting Information), it can be hypothesized that, upon polymerization, polymerized chains of styrene tend to pack assisted by π–π stacking and repulsion from hydrophilic environment resulting in an observable shrinkage in size. This could most likely be the cause of the observed shrinkage of microspheres compared to original double emulsions. Overall, this is a proof of straightforward synthesis of hollow polymer spheres utilizing CMp-vTA as emulsion stabilizer and photoinitiator. Electrostatic stabilization arising from autonomous charge delocalization on CMp-vTA sheets allows fabrication of centered double emulsions without any additional dissolved ions/stabilizers.[28]

Adjusting surface properties of g-CN by photografting of organic modifiers provides stable aqueous and organic dispersions, which are key for utilization in successful production of emulsions. In this project, g-CN and microfluidics were combined for the fabrication of O/W and W/O single emulsions as well as W/O/W double emulsions. Thanks to microfluidic technology, it is possible to produce highly monodisperse particles at specific sizes and with high precision. Not only the surface modification of g-CN avoided aggregation of carbon nitride, the modification rendered them phase specific while stabilizing the emulsions, thanks to their amphiphilic nature. Both configurations provide an attractive platform for O/W and W/O based biphasic photocatalysis based on photoredox chemistry. Taking advantage of the stabilization properties of the modified g-CN, we have managed to produce double emulsions that contain both hydrophilic and hydrophobic variants. Double emulsions with a photoactive stabilizer is highly promising for the discovery of patched polymer nanoparticles, photocatalysis, and charge transport phenomenon. By altering the flow rates in the microfluidic chip, double emulsions with both ultra-thin and thick shells were produced, suggesting the robustness of the microfluidic device design.

Double emulsions pave the way for facile synthesis of hollow structures if the inner phase is stabilized and prevented from rupturing. Placing styrene in the oil phase and utilizing g-CN ability as an emulsion stabilizer and photoinitiator, we are able
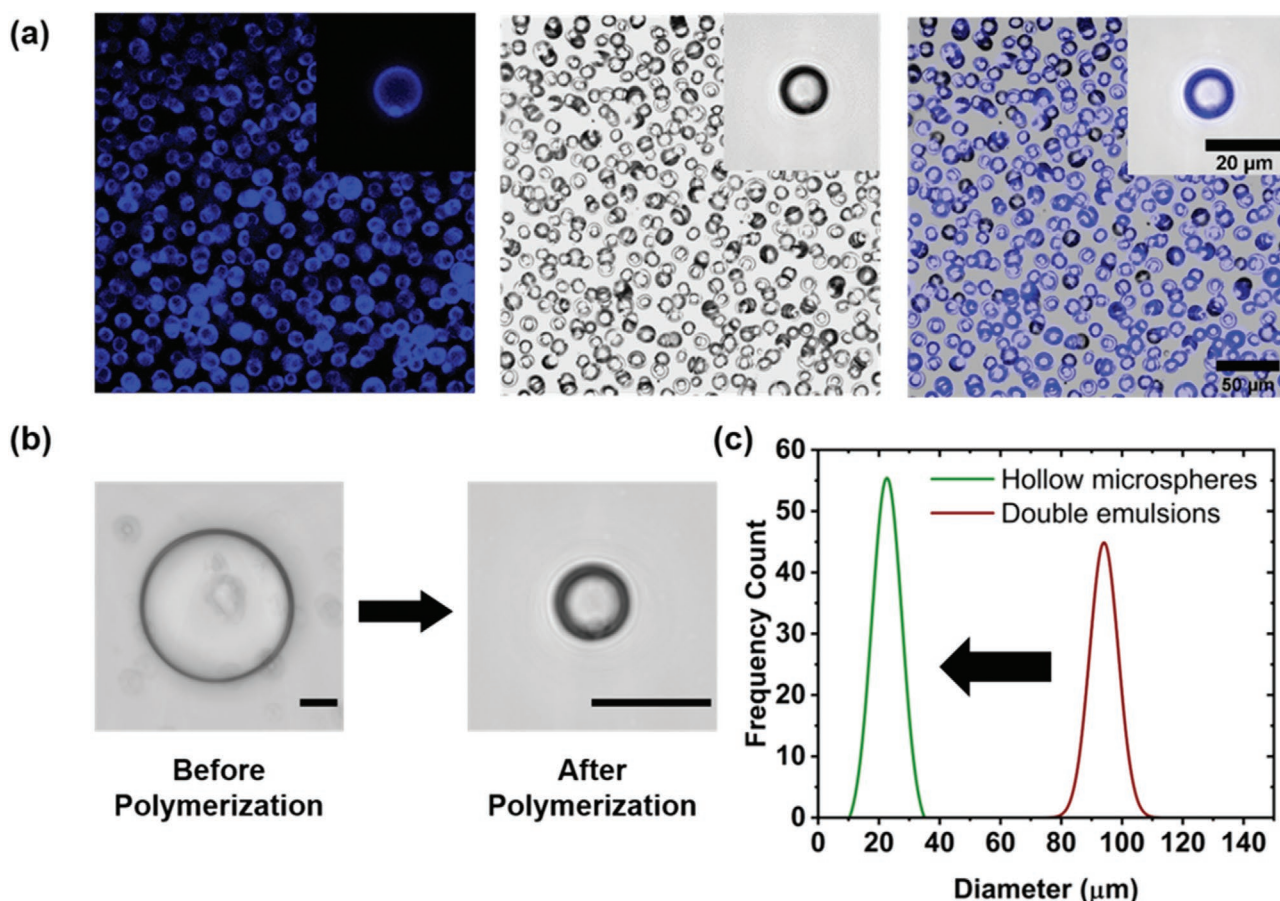
Figure 4. Polymerized microspheres via carbon nitride. a) Confocal images of the hollow structures after exposure to UV light (inset showing the zoomed in confocal images of the hollow microsphere. b) Bright-field images of a double emulsion (before polymerization) and a hollow microsphere (after polymerization) as shown. Scale bar corresponds to 20 μm. c) Change in size distribution of the double emulsions with preserved monodispersity before (92 ± 5 μm) and after (20 ± 3 μm) polymerization.

to synthesize hollow polymer particles in the presence of UV irradiation. From the SEM data, it can be concluded that the produced microspheres are indeed hollow. Overall, this work demonstrates the combination of surface-modified g-CNs and microfluidic technology to form advanced droplets which can be utilized for bioimaging, catalysis, and photonics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Keywords

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