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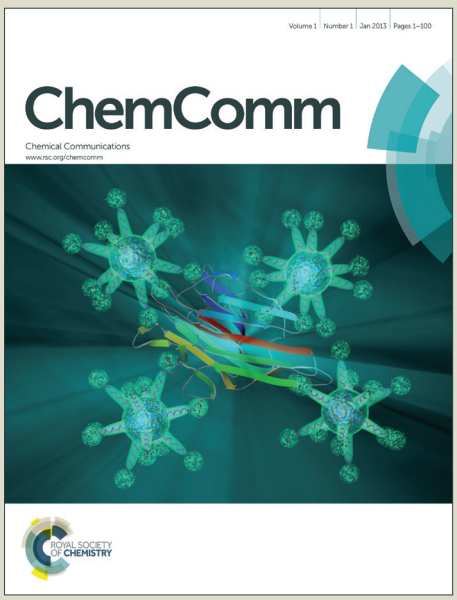

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Redox responsive organometallic microgel particles from poly(ferrocenylsilane)s generated by microfluidics †

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We describe a novel, versatile method for the fabrication of poly(ferrocenylsilane) (PFS) based microspheres using microfluidics. Cross-linked microgel particles were obtained by UV-induced crosslinking of precursor droplets. By variation of the substitution of the silane units of PFS, organogel as well as hydrogel particles were prepared. Applications of these redox active microspheres to form *in-situ* Ag nanoparticles, as well as loading and release of guest molecules were demonstrated.

Microgels are spherical particles, consisting of cross-linked, three-dimensional polymer networks, with dimensions ranging from the submicrometers to tens of micrometers.[1] These gel particles have been used for preparing sensors, regulating cell culture, controlling drug release, and in many other areas.[2-4] It is evident that engineering of gel particle size and morphology has a major impact for gel performance in these applications. Here we used microfluidic particle synthesis which offers a facile approach to the continuous production of microgels with precise control over their size, shape and morphology.[1,3,5-9]

Poly(ferrocenylsilane)s, (PFS)s, composed of skeletal ferrocene and silane repeat units, are established redox responsive materials.[10-15] Water soluble PFSs have been developed e.g. by side group modification[16] to allow one to process PFS to obtain nanostructures from water. For example, capsules possessing a PFS shell in aqueous environment, fabricated by template layer-by-layer assembly of polyionic PFSs, showed expansion accompanied by a drastic permeability change in response to a small chemical oxidation trigger.[11] PFS microspheres constitute a novel class of redox-responsive structures. Manners et al.[17,18] used a precipitation polymerization method for the formation of hydrophobic PFS microspheres. Relatively well-defined microparticles with average diameters of 1–3 μm (polydispersity index, PDI 1.1–1.5) were obtained by this method. Depending on the composition of the reaction medium employed during polymerization, xylene-swellable microgel particles were formed. Chemical oxidation of the PFS particles allowed the Manners group to electrostatically bind negatively charged silica spheres to the PFS microparticle surface. Examples of organic solvent-swellable, redox-active, crosslinked networks, gels and nanogels formed from PFS homopolymers and block copolymers were also reported.[19] However, in all these microsphere preparation procedures, particle size control (size and its uniformity, cross-linking) was cumbersome.

In contrast, microfluidic techniques allow one to prepare microparticles with precise control of (monodisperse) size, shape and composition.[4] The microfluidic approach can be used to break up a liquid jet formed by two immiscible phases (e.g. aqueous and organic) to form colloids of reactive monomers. These can then be polymerized (e.g. by UV polymerization).[20] In this study we demonstrate the use of this technique to obtain novel PFS microgels in both organic and aqueous phases. Applications of these redox responsive microspheres are illustrated for in-situ preparation of Ag nanoparticles (e.g. for catalysis) and in redox triggered release systems.

The organometallic microgels reported here are fabricated from PFS macro-crosslinkers featuring either acrylate side groups (PFS M1; soluble in organic solvents; Fig. 1b)[21] or vinylimidazole side groups (PFS M2; soluble in water; Fig. 2b).[22] PFS microgels were produced by the generation of monodisperse PFS macro-crosslinker droplets in a microfluidic device and subsequent off-chip photopolymerization. The PFS particles were then washed several times to remove residual surfactant. By careful selection of fluidic chip device parameters, dispersed phase, continuous phase and surfactants,[23] monodisperse PFS microgels were obtained.

For PFS M1, a glass chip with T-junction[7,24] was chosen to generate oil-in-water droplets, using toluene as the hydrophobic solvent. The two immiscible streams in this case were a solution of PFS M1 in toluene and 1% Tween 20 in water as the dispersed and continuous phases, respectively. Fig. 1a is a representative image of the microfluidic T-junction taken by a CCD camera (Orca ER) to illustrate particle formation. Subsequent UV-irradiation yielded cross-linked microparticles and led to the formation of spherical PFS microgels. Near monodisperse (PDI<1.1) microspheres can easily be produced with a range of diameters, depending on the fluid flow rates. Fig. 1c and 1d display SEM images of representative PFS microgels with different sizes and smooth surfaces. We observed that microsphere size decreased monotonically with increasing water-to-oil flow rate ratios, in agreement with the literature.[25,26] Particle diameters obtained with our device were in the range of 5−12 μm. This range can be easily extended by varying device design and flow rate ratio to produce spheres with submicrometer

to many tens of micrometers sizes. A 2D packed assembly of highly monodisperse spheres on silicon substrates can be seen on Fig. 1c, with a high degree of order and symmetry.

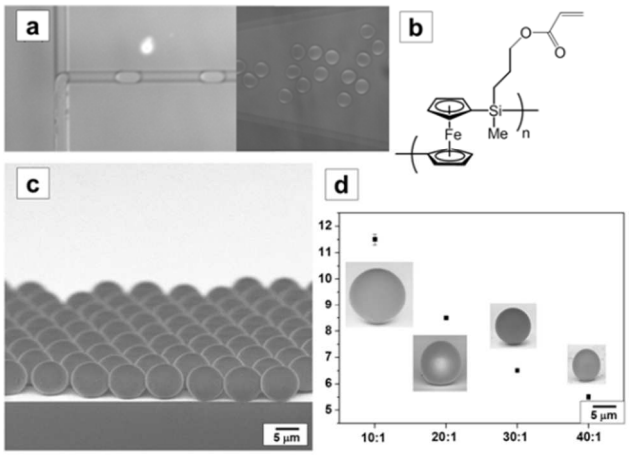

Fig. 1 PFS microgels prepared from PFS M1. (a) Images taken by a high speed camera of head-on forming droplets. (b) PFS M1. (c) SEM images of PFS M1 microgels. (d) Diameter of PFS M1 microspheres produced at increasing water-to-oil flow rate ratios, (10:1) Q_w=1 μL/min, Q_{PFS}=0.1 μL/min; (20:1) Q_w=2 μL/min, Q_{PFS}=0.1 μL/min; (30:1) Q_w=3 μL/min, Q_{PFS}=0.1 μL/min and (40:1) Q_w=4 μL/min, Q_{PFS}=0.1 μL/min.

For the formation of water soluble, crosslinkable PFS M2 based particles, a flow-focusing[27] PDMS device was used (see Fig. 2a). The polymer shown in Fig. 2b was a vinyl imidazole-functionalized PFS polycation, which we recently reported as constituent of a PFS polyionic liquid.[22] The immiscible liquid streams in this case included an aqueous solution of PFS M2 and a 1% Span 80 in hexadecane solution as the dispersed and continuous phases, respectively. A representative image captured by a high speed camera during droplet formation is shown in Fig. 2a. A highly periodic break-up of the thread of the dispersed phase yields droplets with a narrow size distribution. Subsequent UV-irradiation led to the formation of PFS M2 microgels. Fig. 2c shows SEM images of the beads obtained, possessing a uniform size of about 20 μm. The PFS M2 particles displayed a rough surface morphology after drying (Fig. 2d), likely resulting from aggregation of the hydrophobic PFS backbone chains at high concentrations in the dispersing water forming micelles prior to polymerization.[28,29]

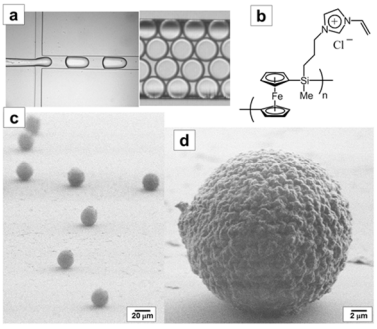

Fig. 2 PFS microgels prepared from PFS M2. (a) Images taken by a high speed camera of hydrogel precursor droplets formed in a flow-focusing microfluidic device, (b) PFS M2, (c) SEM images of PFS M2 microgels and (d) SEM image of a single PFS M2 microgel particle.

PFS chains have been shown to reduce silver ions to the corresponding metal.[30-32] For cylindrical micelles possessing a PFS core, this redox reaction led to the formation of fascinating one-dimensional arrays of silver nanoparticles in the micellar core, as shown by Winnik, Manners and coworkers. [30,31] When the PFS microspheres (M1) were immersed in a saturated solution of $AgPF_6$ in toluene, a color change from light yellow to black was observed. Silver nanostructures gradually formed on the surface of the microspheres, covering the surface through a nucleation and growth process (Fig. 3 and Fig. S1). The PFS microspheres not only acted as a reducing agent for the formation of metallic Ag but also served as templates that directed the growth of Ag structures, which can find applications in catalysis.

During generating the particles from PFS M2, we incorporated a fluorescent dye (Rhodamine 6G, R6G) as molecular cargo into the microparticle network of this water dispersable colloid (Fig. 2a). Cross-sectional confocal microscopy images taken at 2.6 μm depth steps through a single microsphere revealed that the dye molecules were uniformly distributed within the bead volume (Fig. 2b). In water, the microgel particles retained their dye cargo (fig. 2c). Oxidation by ferric chloride ($FeCl_3$) has previously been shown to be an effective trigger for the release of cargo molecules from PFS capsules[11,33,34] and multilayer films. We employed this approach to release the dye from the hydrogel particles. Fig. 4c and 4d display fluorescence microscopy images of PFS microgels before and after chemical oxidation. PFS microgels that originally showed no release of dye (Fig. 4c and Fig. S3) were treated with aqueous $FeCl_3$ solution (5 mg/mL) during *in-situ* imaging. As a result, the PFS microgels exhibited a continuous release of dye molecules accompanied by an increasing size expansion (Fig. 4d and Fig. S4). After oxidation, the PFS microgels remained intact due to their covalently crosslinked structure (Fig. S5). Upon oxidation, the polarity of the PFS network chains increases as they become positively charged. Therefore, swelling of the gel particles in water increases, resulting in an enlarged average pore size and enhanced dye release. Moreover, R6G is a weakly basic dye with a pKa value of ~8.3, making it positively charged at pH=7.4.[35] Electrostatic repulsion between the positively charged R6G dye molecules and the positively charged microgel network chains is expected to drive dye release from the microgel particles.

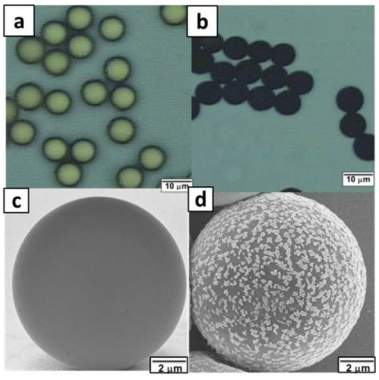

Fig. 3 Redox induced formation of PFS-silver hybrids. (a) An optical microscopy image of the PFS M1 microgels before adding $AgPF_6$ in toluene. (b) An optical microscopy image of the PFS M1 microgels after adding $AgPF_6$. (c) SEM image of a single PFS M1 microgel particle

before adding $AgPF_6$ and (d) SEM image of a single PFS M1 microparticle after adding $AgPF_6$.

In summary, two PFS macro-crosslinkers of different polarity, including PFS chains with acrylate side groups (soluble in organic solvents) and PFS chains with vinyl imidazole groups (soluble in water), were used as microgel precursors. Microfluidic processing enabled us to generate redox responsive microparticles with precisely controlled dimensions using these two polymers. We demonstrate potential applications of these responsive microspheres to obtain Ag nanoparticles in-situ, and in molecular release.

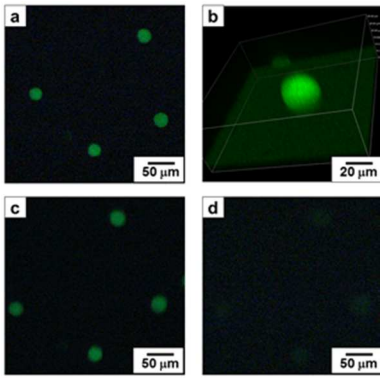

Fig. 4 Redox-induced molecular release. (a) Fluorescence microscopy images of Rhodamine 6G-loaded PFS M2 spheres. (b) Scanning confocal cross-sectional z-scan of a single PFS M2 microsphere, the dye is uniformly distributed throughout the bead volume. (c) After immersion of the loaded microgels in water for 30 min and (d) After immersion in 5 mg/mL $FeCl_3$ aqueous solution for 30 min.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Materials and Methods, Microfluidic device and operation, Characterization equipment, SEM images showing the redox-induced formation and growth of silver nanostructures on the surface of a redox-active PFS M1 microsphere; Cross-sectional confocal microscopy of a single PFS M2 microsphere loaded with Rhodamine 6G dye; Dye-loaded PFS M2 microspheres immersed in water; Dye-loaded PFS M2 microspheres immersed in $FeCl_3$; PFS M2 microspheres before and after oxidation with $FeCl_3$]. See DOI: 10.1039/b000000x/

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