Electronic Supplementary Information

Novel Polystyrene Sulfonate-Silica Microspheres as a Carrier of a Water Soluble Inorganic Salt (KCl) for Its Sustained Release, via a Dual-Release Mechanism

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Experimental Section

Chemicals. Potassium chloride (KCl), poly(4-styrenesulfonic acid) (PSS) aqueous solution (M_w = ~75000, 18 wt. % in H_2O) and tetraethyl orthosilicate (TEOS) were purchased from sigma-Aldrich. Polyglycerol polyricinoleate (PGPR) was obtained from Palsgaard (Palsgaard 7130, Juelsminde, Denmark). Vegetable oil was bought from Aldi stores (Ireland), and hexane was ordered from Fisher Scientific.

Synthesis of PSS-SiO_2 microparticles with KCl encapsulated. To the PSS solution (3 ml) was added KCl (0.1 g), which allowed to be fully dissolved, followed by emulsification in vegetable oil (100 ml) containing dissolved polyglycerol polyricinoleate (PGPR) (0.8 g). The emulsification process was proceeded via mechanical stirring at a speed of 200 rpm with a marine impeller (ϕ 44 mm) at half liquid depth position in a vessel (ϕ 65 mm × 95 mm) for 2 h. TEOS (1 ml) was then added dropwise into the emulsion at an injection rate of 100 μl/min, which was stirred continuously for 4 h. The precipitate was centrifuged for 2 min at 4000 rpm (centrifugal force 1860 g), the supernatant decanted off, and the residue washed by hexane (35 ml x 3), and dried in a vacuum drier at room temperature for ~12 h, affording ~1 g of yellow microspheres.

Synthesis of PSS-0.7SiO_2 microparticles with KCl encapsulated. The same method as above was followed, but using 0.7 mL of TEOS, and afforded ~1 g of yellow microspheres.

Measurement of payloads, encapsulation efficiencies and release rates of KCl and the release percentages of PSS. Payload, encapsulation efficiency and release rates of KCl were measured by a flame photometer (PFP-7, Jenway, UK). The microsphere samples were ground using mortar and pestle to a fine powder, and dissolved in aqua regia ($HCl:HNO_3$ = 3:1) overnight. The particle debris was separated via centrifugation, and the supernatant solution was diluted with deionized water by a factor of 20. The concentration of K^+ in the solution was determined by the

flame photometer. The payload and encapsulation efficiency of KCl could be calculated by Equations (1) and (2) respectively as follows:

$$\text{Payload} = \frac{\text{Mass of KCl recovered from the obtained PSS-SiO}_2\text{ microspheres}}{\text{Mass of PSS-SiO}_2\text{ microspheres}} \quad (1)$$

$$\text{Encapsulation efficiency} = \frac{\text{Mass of KCl recovered from the obtained PSS-SiO}_2\text{ microspheres}}{\text{Mass of KCl input}} \quad (2)$$

The release of KCl and PSS from the microparticles was performed in deionized water (100 ml) in a Gallenkamp orbital shaker with a 150 rpm rotation speed at 37 ^{o}C. The released KCl samples (5 ml) were obtained periodically at fixed time intervals between 5 min to 2 days, and replaced by fresh deionized water (5 ml). The concentration of K^+ was measured by the flame photometer, and the concentration of PSS was detected by UV spectrophotometry at 254 nm (Cecil 2021 UV spectrophotometer).

Other Characterizations. The morphologies and cross-sections of the prepared microparticles were observed with an optical microscope (301-371.011, Leica, Germany) and SEM (Philips XL-30 FEG ESEM). Their size distribution, SPAN and the mean volumetric size (D_{43}) were measured by a laser light scattering technique (Mastersizer 2000, Malvern Instruments, UK). The phase of the sample was confirmed by a Bruker D8-Advance X-ray powder diffractometer using Cu Kα radiation (λ = 1.5406 Å), and the FT-IR spectra was performed on a Thermo Electron Nicolet 8700 spectrometer. The composition was recorded on a thermogravimetric analysis (STA 449 F3, NETZSCH). The chemical composition of the sample was evaluated by an energy disperse X-ray microanalysis (EDX) (Oxford, Inca 300) in

conjunction with SEM.