

Embedded Nanolamps in Electrospun Nanofibers

Enabling Online Monitoring and Ratiometric Measurements

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Synthesis of β -NaYF₄ (20% Yb, 2% Er, 10% Gd) nanoparticles. The synthesis of Ln³⁺ doped NaYF₄ UCNPs is based on a reported procedure.^[1] The following description is for 5 mmol of total rare earth chlorides. The synthesis was performed in a 250 mL three-necked round bottom flask under nitrogen flow. 1031.42 mg of YCl₃·6 H₂O (3.4 mmol) were dissolved together with 387.49 mg of YbCl₃·6 H₂O (1 mmol), 38.17 mg of ErCl₃·6 H₂O (0.1 mmol) and 185.65 mg of GdCl₃·6 H₂O (0.5 mmol) in 30 mL of methanol. 40 mL of oleic acid and 75 mL of octadecene were added and the cloudy solution was heated to 160 °C by a heating mantle with temperature control. The reaction mixture was stirred for 30 min in vacuo (200 Pa) at 160 °C in order to obtain a clear solution of the oleate coordinated yttrium and

lanthanide ions. Then, the solution was cooled to room temperature. Afterwards, a solution of 0.74 g of NH_4F (20.0 mmol) and 0.5 g of NaOH (12.5 mmol) in 50 mL of methanol was added. The suspension was heated up to 120 °C for 30 min to remove the methanol. A reflux cooler was assembled and the solution was heated to 325 °C to induce the growth of the nanoparticles. As soon as the temperature reached 300 °C, a timer was started and the occurring luminescence of the UCNPs was controlled with a 980 nm laser module (200 mW, cw). After the first luminescence was visible the nanoparticles were stirred for another 10 min for growth and self-focusing (Ostwald ripening). The solution was cooled to room temperature and the particles were precipitated by addition of ethanol (\approx 200 mL). The purification was done under air. The white particles were collected by centrifugation (1000 g, 5 min). The precipitate was dispersed twice in 20 mL chloroform and precipitated again with ethanol (\approx 200 mL). This washing step was repeated with cyclohexane and acetone until a clear solution in cyclohexane was obtained. In the last step, the particles were dissolved in 40 mL of cyclohexane and large aggregates were separated from the nanoparticle suspension by centrifugation (1000 g, 2 min). The oleate-capped nanoparticles were stored at 4 °C in a refrigerator.

Synthesis of $\alpha\text{-NaYF}_4$ nanoparticles. The synthesis was prepared in a three-necked round bottom flask under nitrogen flow. 3033.6 mg of $\text{YCl}_3 \cdot 6 \text{H}_2\text{O}$ (10 mmol) was dissolved in 20 mL methanol. 80 mL of oleic acid and 150 mL of octadecene were added and the cloudy solution was heated up to 160 °C by a heating mantle with temperature control. The reaction mixture was stirred for 30 min in vacuo (200 Pa) at 160 °C in order to obtain a clear solution of the oleate-coordinated precursors and then was cooled to room temperature. Afterwards, a solution of 1.48 g of NH_4F (40.0 mmol) and 1 g of NaOH (25 mmol) in 40 mL of methanol was added. The white suspension was heated to 120 °C for 30 min to remove the methanol. The clear solution was heated to 240 °C to induce the growth of the nanoparticles. After 30 min the solution was cooled to room temperature and the particles were purified like the core particles under air.

Synthesis of NaYF₄ (20%Yb, 2% Er, 10% Gd)@NaYF₄ nanoparticles. The synthesis was prepared in two three-necked round bottom flasks under nitrogen flow. 0.5 mmol of the NaYF₄ (20% Yb, 10% Gd, 2% Er) core particles were heated together with 2.5 mL of oleic acid and 2.5 mL of octadecene to 120 °C. 1 mmol of the shell-material dispersed in a few milliliters of cyclohexane was heated with 5 mL of oleic acid and 5 mL of octadecene also to 120 °C. The reaction mixtures were stirred for 30 min in vacuo (200 Pa) at 160 °C in order to remove cyclohexane. While the mixture of the core particles was heated to 325 °C under reflux cooling, the shell material was kept at 120 °C. The shell material was injected stepwise (0.5, 1, 1.5 and 2 mL) to the core particles. The time period after each injection was 10 min. During the injection of the shell material the temperature has to be above 300 °C to obtain a homogeneous shell growth. After the last injection the particles were stirred for another 10 min at reflux and were then cooled to room temperature. The particles were purified via centrifugation like the core particles.

Surface modification of NaYF₄ nanoparticles. For the preparation of uncapped NaYF₄ particles a ligand exchange method was used. Equal volumes of cyclohexane, containing the oleate capped upconversion nanoparticles, and DMF were stirred at 30 °C. Nitrosyl tetrafluoroborate was put directly into the stirring solution (one mg NOBF₄ was inserted per one mg nanoparticle). NOBF₄ led to a protonation of the oleate, leading to a detachment of the ligand from the particle surface. The uncoated nanoparticles are at the same time stabilized by BF₄⁻ ions in the DMF phase. After 15 min of stirring at 30 °C, the upper phase (cyclohexane) was removed and the DMF phase was washed with an excess of chloroform (10 - 20 mL). After being centrifuged (1000 g, 5 min), the jelly-like precipitate was washed again with 1 - 2 mL of DMF and chloroform (10 - 20 mL). In the last step, the particles were dispersed in the desired volume of DMF and aggregates were separated by centrifugation (1000 g, 3 min). The uncapped nanoparticles were stored in the dark at 4 °C in the refrigerator.

Surface modification for water dispersible NaYF₄ nanoparticles. Poly(acrylic acid) (PAA) (1 mg for 10 mg nanoparticles) was dissolved in 2 mL of double distilled water. The solution was heated to 30 °C. BF₄⁻ coated UCNP dispersed in DMF were added quickly dropwise to the stirring polymer solution. After 15 min the particles were centrifuged at 21.000 g for one hour. Afterwards the supernatant was removed and the particles were dispersed again in water by sonication. The particles were centrifuged again for one hour at 21.000 g and were finally dispersed in the desired aqueous solution by sonication (Fig. S2).

Leakage of UCNP from microfluidic channels. Double distilled water was flown through the microfluidic channel containing the modified nanofibers (40 mg·mL⁻¹, spinning time 15 min) at a flow rate of 25 μL·min⁻¹. The solution was collected for 3 h and prepared for ICP-OES measurements after drying in an oven at 70 °C. With a detection limit of 600 nM (0.0533 μg·mL⁻¹) for Y³⁺-ions no leakage of the UCNP from the nanofibers and from the microfluidic channel was observed. Y³⁺ ions were chosen since they have the highest concentration inside the nanocrystals.

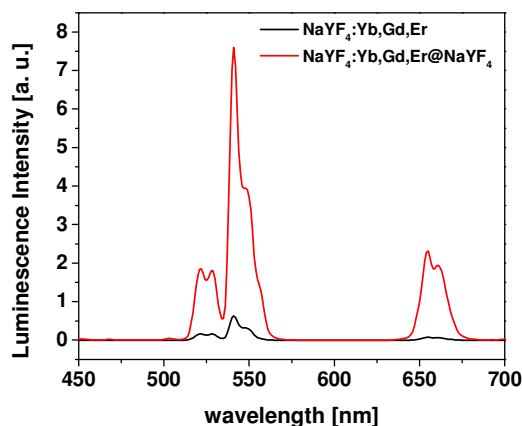


Fig. S1. The luminescence spectra of the core and the core-shell particles inside the spinning solution (14 %(e/v) PVP, 1:1 DMF/ethanol, UCNP) were compared. The spectra were

normalized to the same number of nanoparticles regarding ICP-OES measurements. The particles were excited with a 980 nm cw laser (200 mW).

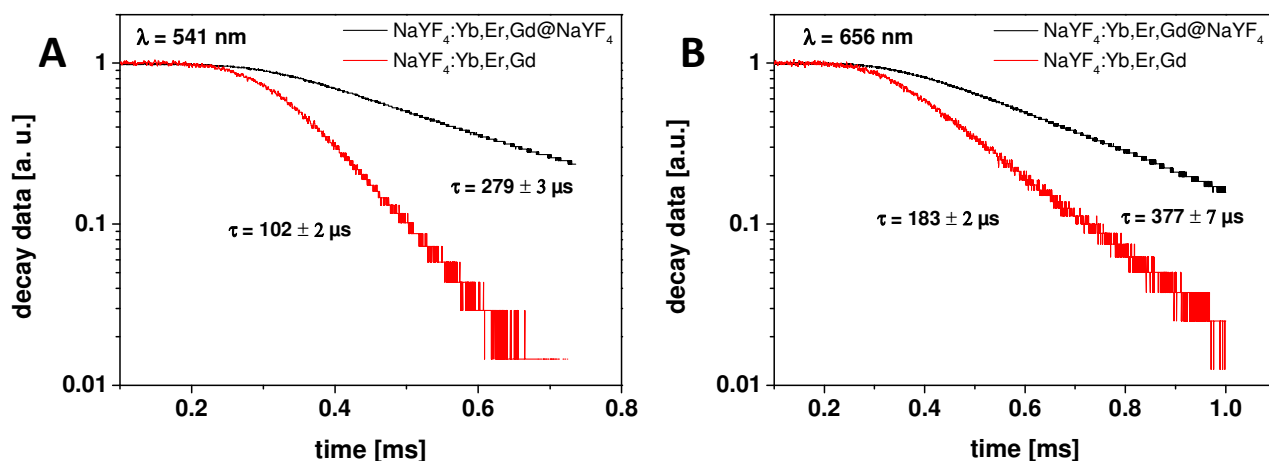


Fig. S2. Cut and normalized decay data of $\text{NaYF}_4:\text{Yb,Er,Gd}$ and $\text{NaYF}_4:\text{Yb,Er,Gd}@NaYF_4$ nanoparticles dispersed in the spinning solution (14%(w/v) PVP, 1:1 DMF/ethanol, UCNPs). Particles were excited at 980 nm and the luminescence decay of the green upconversion emission around 541 nm and the red emission around 656 nm were recorded.

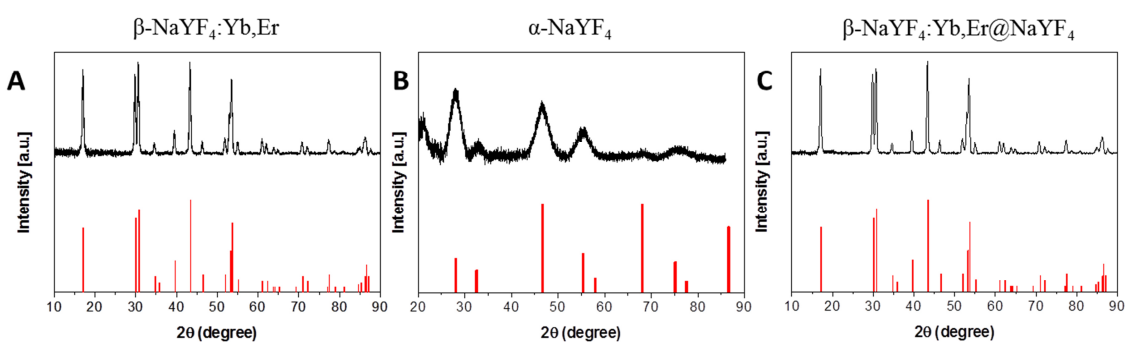


Fig. S3. (A) XRD patterns of $\beta\text{-NaYF}_4$ (20% Yb, 10% Gd, 2% Er (21.9 nm, black) and a reference pattern of $\beta\text{-NaYF}_4$ (red, JCPDS no. 16-0334). (B) XRD patterns of cubic $\alpha\text{-NaYF}_4$ nanoparticles (black) and a reference pattern of $\alpha\text{-NaYF}_4$ (red, JCPDS no. 039-0724). (C) XRD patterns of $\beta\text{-NaYF}_4:\text{Yb,Er}@NaYF_4$ nanoparticles (black) and a reference pattern of $\beta\text{-NaYF}_4$ (red, JCPDS no. 16-0334).

NaYF₄ (20% Yb, 10% Gd, 2% Er)@NaYF₄ (25.5 nm, black) and a reference pattern of β-NaYF₄ (red, JCPDS no. 16-0334).

Table S1. The composition of the core NaYF₄:Yb,Er,Gd and the core-shell NaYF₄:Yb,Er,Gd@NaYF₄ nanoparticles as determined by ICP-OES measurements.

lanthanide ions	Y ³⁺	Yb ³⁺	Gd ³⁺	Er ³⁺
composition core particles [%]	68.2	19.9	9.9	2.0
composition core-shell particles [%]	84.2	9.7	5.2	1.0

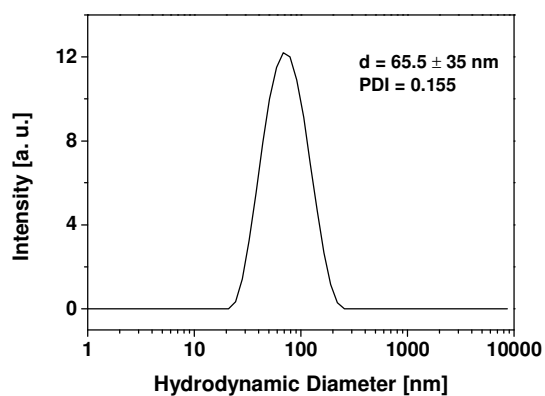


Fig. S4. DLS measurements of polyacrylic acid coated NaYF₄:Yb,Er,Gd in double distilled water.

The hydrodynamic diameter was 65.5 ± 35 nm with a polydispersity index of 0.155.

Table S2. Conditions for optimized solution and processing parameters for electrospun PVP nanofibers.

Concentration (w/v)	Flow rate ($\mu\text{L}\cdot\text{min}^{-1}$)	Voltage (kV)	Morphology
9	1	7-9	bead
	3	7-9	bead
	5	8-10	bead
	8	6-11	bead
	10	7-12	bead
10	1	11-13	bead
	3	11-13	bead
	5	8-11	bead
	8	8-10	bead
	10	11-13	bead
11	1	9-11	bead
	3	8-12	bead
	5	9-11	bead
	8	8-10	bead
	10	7-9	bead
12	1	8-10	bead
	3	8-10	bead
	5	8-10	bead
	8	9-11	bead
	10	8-11	bead
13	1	8-10	bead
	3	7-9	bead
	5	7-9	bead
	8	6-11	bead
	10	7-12	bead
14	1	9-11	smooth
	3	8-10	smooth
	5	8-12	smooth
	8	8-14	smooth
	10	6-17	smooth

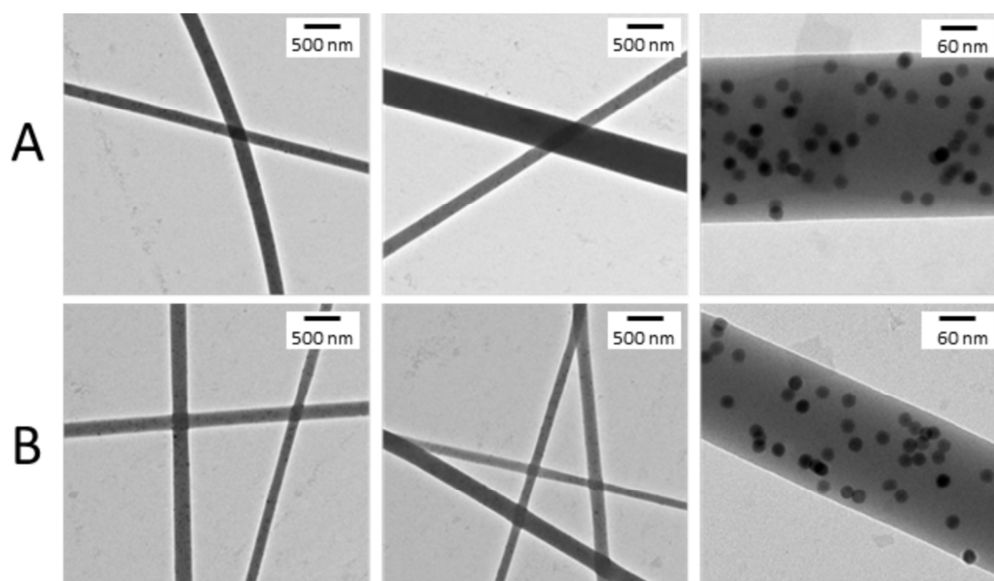


Fig. S5. TEM-images of the PVP nanofibers containing $10 \text{ mg}\cdot\text{mL}^{-1}$ UCNPs. (A) shows the morphology of the nanofibers before and (B) after heat-treatment. The diameter of the fibers and the distribution of the UCNPs inside the nanofibers are comparable, additionally in (B) cross-linking of the PVP nanofibers occurs.

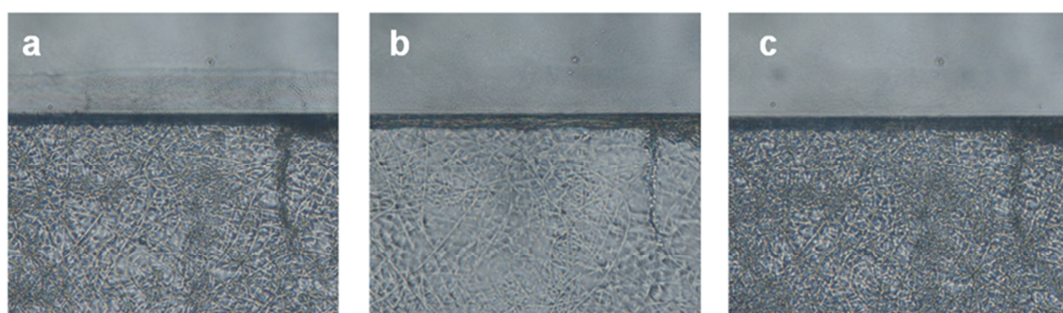


Fig. S6. The morphology of PVP nanofibers ($20 \text{ mg}\cdot\text{mL}^{-1}$, 10 min) were investigated inside the microfluidic channel, (A) the nanofibers before the water flow, (B) during water flow and (C) after drying of the microfluidic channel.

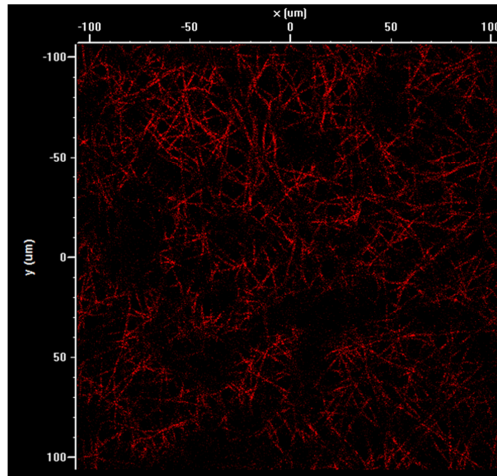


Fig. S7. UCNP-nanofibers embedded in a microfluidic channel while excited at 543 nm. The scattered light caused by the nanofibers was collected with a long pass filter at 650 nm.

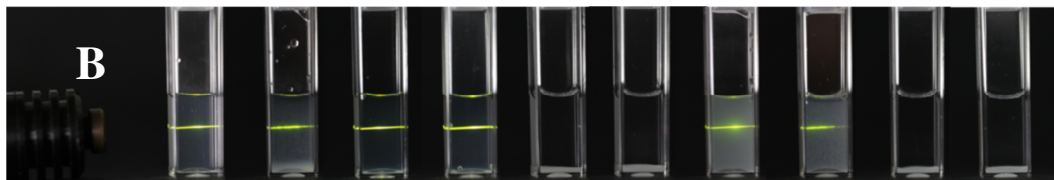
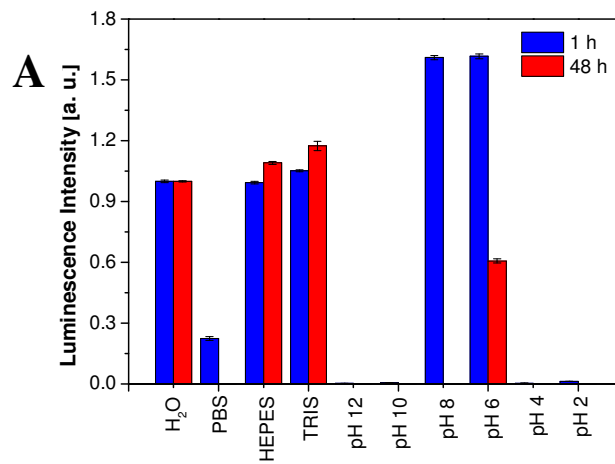


Fig. S8. A) The luminescence intensity of NaYF₄:Yb,Er,Gd nanoparticles in different aqueous dispersions was measured at 541 nm (n = 10). The PAA modified nanoparticles were excited

with a 980 nm laser module (cw, 200 mW). The measurements were performed 1 h and 48 h after their surface modification. The particles were dispersed in double distilled water, PBS buffer, HEPES buffer (50 mM, pH 7.4), TRIS buffer (50 mM, pH 7.4) and Britton-Robinson buffers of different pH (0.04 M H₃PO₄, 0.04 M acetic acid, 0.04 M boric acid, pH 12-2). The mass concentration of the particles was 2 mg·mL⁻¹. B) Images of PAA modified particles in different aqueous dispersion under NIR excitation 1 h after synthesis. From left to right the particles were dispersed in double distilled water, PBS buffer, HEPES buffer (50 mM, pH 7.4), TRIS buffer (50 mM, pH 7.4) and Britton-Robinson buffers of different pH (0.04 M H₃PO₄, 0.04 M acetic acid, 0.04 M boric acid, pH 12-2).

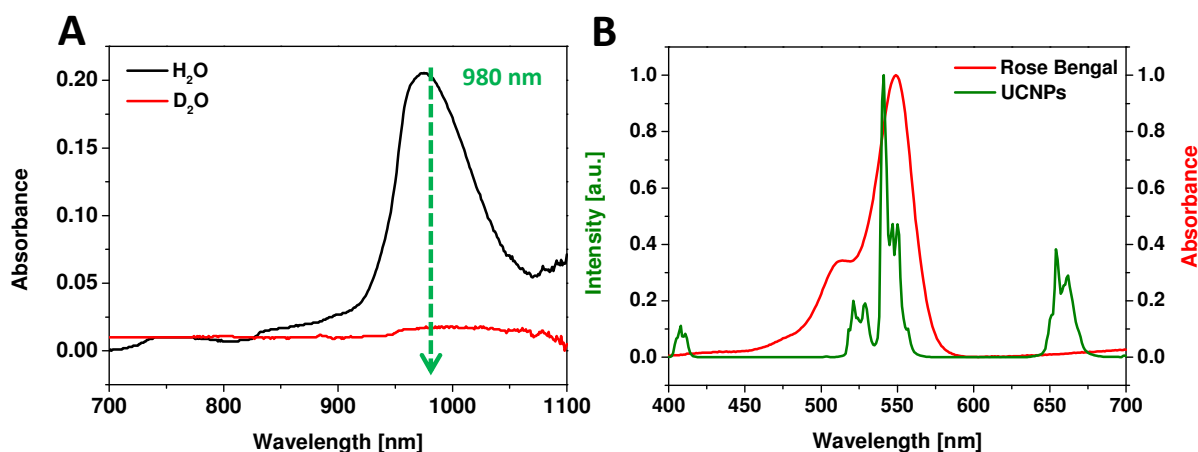


Fig. S9. (A) Absorption spectra of D₂O and H₂O were collected from 700 nm to 1100 nm. The dashed line indicates the absorption at 980 nm. (B) The spectral overlap between the absorbance spectra of Rose Bengal (red) and the green emission of erbium doped upconversion nanoparticles is shown. The UCNPs were excited at 980 nm. The spectra were collected in water.

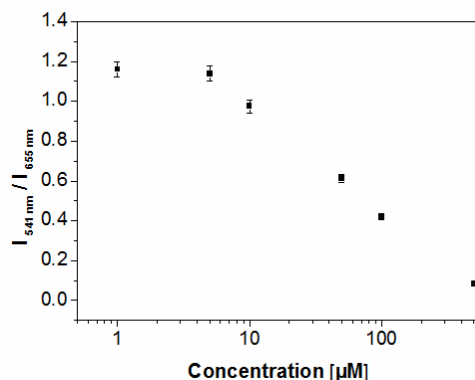


Fig. S 10. The ratio of the green (541 nm) to red (656 nm) emission of $\text{NaYF}_4:\text{Yb,Er,Gd}@poly(\text{acrylic acid})$ ($\beta(\text{UCNPs}) = 2 \text{ mg}\cdot\text{mL}^{-1}$) as a function of the dye concentration (RB) is shown. The particles were excited in water with a 980 nm laser module (cw, 200 mW) in cuvettes. The LOD for RB was $7.6 \mu\text{mol}$.

REFERENCES

- 1 S. Wilhelm, M. Kaiser, C. Wurth, J. Heiland, C. Carrillo-Carrion, V. Muhr, O. S. Wolfbeis, W. J. Parak, U. Resch-Genger and T. Hirsch, *Nanoscale*, 2015, **7**, 1403–1410.