

## Electronic Supporting Information

### Photobleaching-resistant ternary quantum dots embedded in a polymer-coated silica matrix

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#### 1. Experimental details

**1.1 Materials:** Copper (I) iodide (CuI, 99.99 %), indium acetate (In(OAc)<sub>3</sub>, 99.99 %), zinc stearate (ZnSt<sub>2</sub>, 12 % Zn basis), zinc acetate dihydrate (Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, 99.9 %) 1-dodecanethiol (DDT, 97 %), 1-octadecene (ODE, 90 %), oleic acid (OA, 90 %), 3-mercaptopropionic acid (MPA, 97 %), tetraethyl orthosilicate (TEOS, 99 %), (3-mercaptopropyl)-trimethoxysilane (MPS, 95 %), hydrochloric acid (HCl, 37 %), manganese (II) acetate tetrahydrate (Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O, 99.99 %) sodium sulfide hydrate (Na<sub>2</sub>S·xH<sub>2</sub>O, 60 %), cysteamine hydrochloride (NH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>SH·HCl, 97 %), were obtained from Sigma-Aldrich and used without further purification. The two-component epoxy resin CeTePox 100R and the hardener for LED encapsulation were obtained from CTP GmbH.

**1.2 CuInS<sub>2</sub>/ZnS-MPA QDs synthesis:** To prepare green-emitting QDs (540 nm), 8 mg CuI (0.0417 mmol), 146 mg In(OAc)<sub>3</sub> (0.5 mmol) and 5 mL of DDT were loaded into a 100 mL 3-neck flask and filled with argon. The mixture was heated to 120 °C for 15 min. QDs were then grown at 220 °C for 5 min to obtain core crystals emitting at ca. 630 nm. The Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O shell precursors were added directly to the reaction solution: 1.0975 g Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (5 mmol), 2 mL OA, 5 mL ODE and 1 mL DDT followed by a slow heating to 220 °C and annealing at this temperature for 1 h under argon. Next, the ZnSt<sub>2</sub> precursor, consisting of 3.16 g ZnSt<sub>2</sub> (5 mmol), 1 mL DDT and 5 mL ODE dissolved at 130 °C under argon, was injected dropwise into the QD solution at 220 °C and left to react for an additional hour. In-situ ligand exchange reaction with MPA was performed by injecting 10 mL MPA into the growth solution and letting it react at 170 °C for 1 h. Finally, the reaction was left to cool down naturally below 100 °C and 10 mL pH 10 buffer solution was injected to separate the MPA-QDs from the

organic solvents and precursors. The aqueous phase was collected, precipitated with acetone and centrifuged. The QDs were washed with buffer/acetone mixtures and the particles were finally dispersed in distilled deionized water (DI). Yellow (580 nm), orange (600 nm) and red (640 nm) QDs were synthesized in the same manner by varying the Cu:In ratio: 12 mg (0.0625 mmol, 1:8), 24 mg (0.125 mmol, 1:4) and 48 mg (0.25 mmol, 1:2), respectively.

**1.3 ZnS:Mn<sup>2+</sup>-Cysteamine QDs synthesis:** For the precipitation reaction 3.005 g Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (13.7 mmol), 0.374 g Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.5 mmol) and 0.692 g cysteamine (6.1 mmol), were dissolved in 50 ml DI in a 250 mL round bottom flask. Separately, 1.472 g Na<sub>2</sub>S·xH<sub>2</sub>O (ca. 13 mmol) was dissolved in 12 ml DI and added dropwise into the reaction solution within 10 min under vigorous stirring. Next, the mixture was annealed at 95 °C for 3 h to obtain a transparent solution. The orange luminescent QDs were then precipitated and washed with ethanol three times using a centrifuge and finally redispersed in DI at a pH of 4.5.

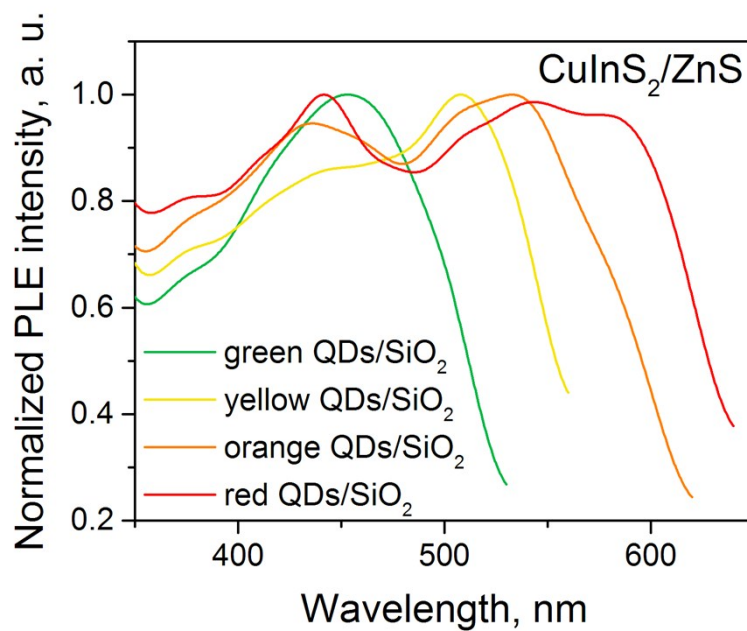
**1.4 Silica nanocomposites preparation:** 8.9 mL TEOS (40 mmol), 0.9 mL MPS (5 mmol) and 9.1 mL methanol were mixed together in a beaker under stirring. Next, 3.15 mL DI and 50  $\mu$ L HCl were added dropwise into the alkoxide solution under vigorous stirring. The solution was covered and stirred for another 48 h at room temperature to complete the hydrolysis. The molar ratio of TEOS:MPS:H<sub>2</sub>O:HCl was *ca.* 8:1:35:0.23. To form silica monoliths, 1 mL MPS/TEOS sol was mixed with 0.5-1.25 mL QD stock solution (20-30 mg/mL) by dropwise addition under stirring to produce composites with *ca.* 10-20 % QD loading (wt/wt). Gelation took place within 2-24 h depending on the amount of water and QDs in the system (QD solutions were slightly basic). Samples were then dried in a methanol rich atmosphere at 40 °C for a specified period of time. The monolithic gels were put into an oven set to 100 °C for 8 h to complete the drying process. Powder samples were obtained by drying the gels at 100 °C for at least 24 h and grinding in a mortar.

**1.5 LED converters preparation:** commercial 450-455 nm surface mounted device (SMD) LEDs were used in the experiments with an LE of 11 lm/W at 20 mA. QD/silica composites were either placed directly on top of the chip or embedded in an epoxy resin first (CeTePox, CTP GmbH). Ultrastable composites were prepared by immersing thoroughly dried gels in a polyvinyl chloride (PVC) solution (100 mg/mL THF) for 45 min and drying under ambient conditions. white light emitting diodes (WLEDs) and single colour converters were made from powdered silica (*ca.* 15 % QDs) stirred in a PVC solution and later embedded in epoxy (1:10

PVC:epoxy). Conversion efficiencies were measured from free-standing semi-transparent QD/sil/PVC/epoxy samples.

**1.6 Characterization:** UV-Vis transmittance spectra were obtained using an Ocean Optics HR4000 spectrometer equipped with an Avalight deuterium-halogen light source. PLQYs (photo-luminescence quantum yields) and emission spectra were measured via an absolute method on a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a 150 W/CW Xenon light source, a photonic multi-channel analyser, and an integrating sphere. Excitation spectra were obtained on a Perkin Elmer LS55 spectrometer equipped with a pulsed Xe-lamp. Hydrodynamic diameters were assessed using a Malvern Zetasizer NanoZS. Thermogravimetric (TG) measurements were conducted on a Netzsch STA 409 in a temperature range of 25-900 °C under a nitrogen atmosphere. BET isotherms and porosity data were obtained from a BELSORP-max from BEL JAPAN, INC. A calibrated Avantes ULS2048XL spectrometer coupled with an integrating sphere was utilized to measure the properties of LED colour converters. LED stability was measured by integrating the QD PL signal (500-800 nm) either using an Avantes ULS2048XL or an Ocean Optics USB650 spectrometer in an integrating sphere. Colour quality was assessed by the CIE (Commission Internationale de L'Eclairage 1931) colorimetry system.

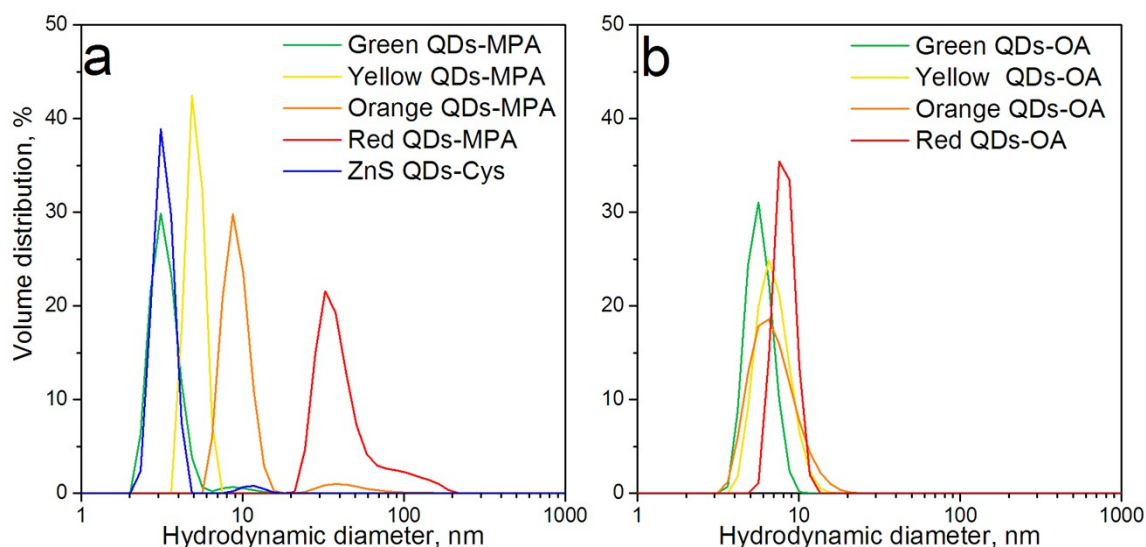
## 2. Silica monoliths excitation spectra



**Fig. S1** Photoluminescence excitation (PLE) spectra of solid composite gels with different CuInS<sub>2</sub>/ZnS QDs at *ca.* 10 % solid loading.

QYs of solid composites were measured by exciting above the apparent PLE maximum to exclude inner filter effects. Exciting the samples in the UV resulted in large absorption factors along with lower excitation light penetration depths and higher reabsorption.

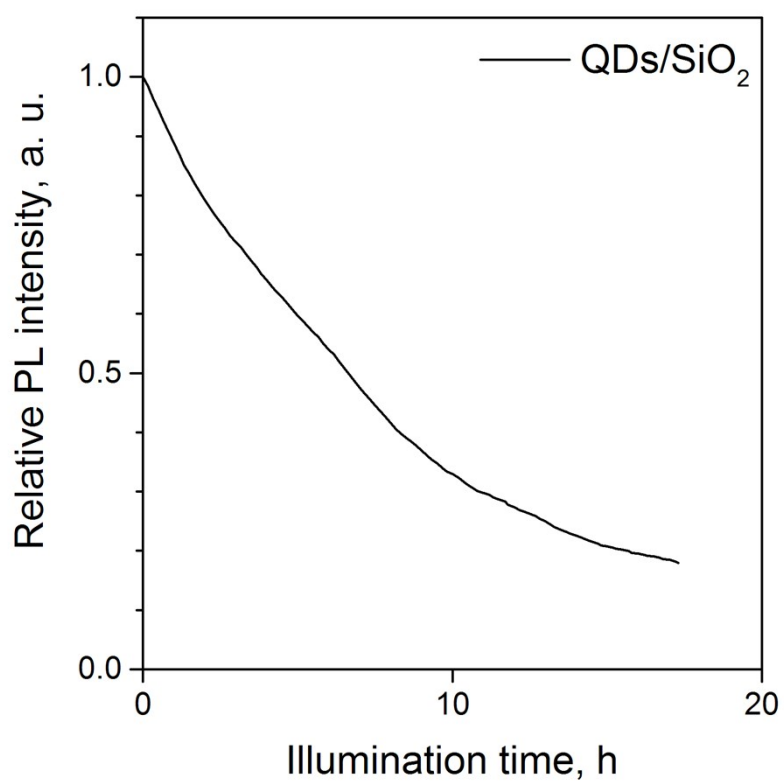
### 3. DLS particle sizes



**Fig. S2.** CIS/ZnS and ZnS:Mn<sup>2+</sup> QD particle sizes represented as volume fractions for: a) hydrophilic QDs after ligand exchange for MPA and b) hydrophobic oleic acid-capped QDs before the ligand exchange.

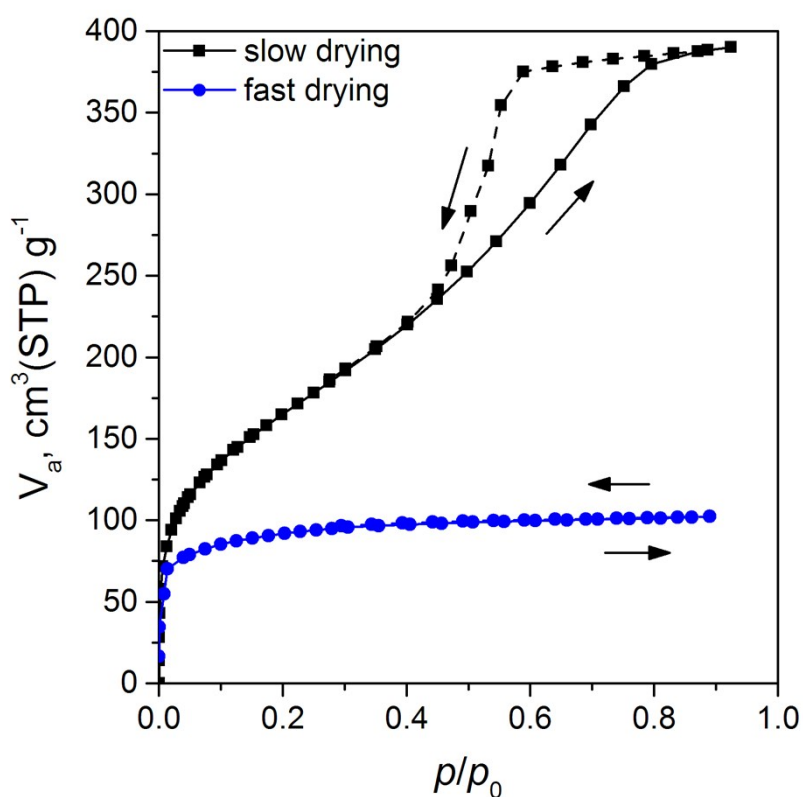
Mean hydrodynamic diameters were 3, 5, 9 and 33 nm for green, yellow, orange and red hydrophilic QDs, respectively (Fig. S2a). Larger dots were more susceptible towards agglomeration during *in situ* ligand exchange. The original hydrophobic dots differed in size only slightly (Fig. S2b), which can be explained by the lower reactivity of large nanoparticles with the zinc precursor and hence a thinner ZnS shell being deposited. Thus the hydrodynamic diameters of orange (9 nm) and red (33 nm) QD pertain to agglomerates and not individual QDs. The results are comparative rather than quantitative because of relatively weak DLS sensitivity in the 1-10 nm regime. Due to the presence of organic capping ligands, the actual inorganic nanocrystals are slightly smaller than measured by DLS, especially in the case of OA ligands (ligand chain length *ca.* 1.8 nm).

#### 4. Stability plot of bare QD/silica composites



**Fig. S3** Decrease in the integrated PL intensity of a dry green QD/silica monolith during illumination with a blue LED operated at 20 mA.

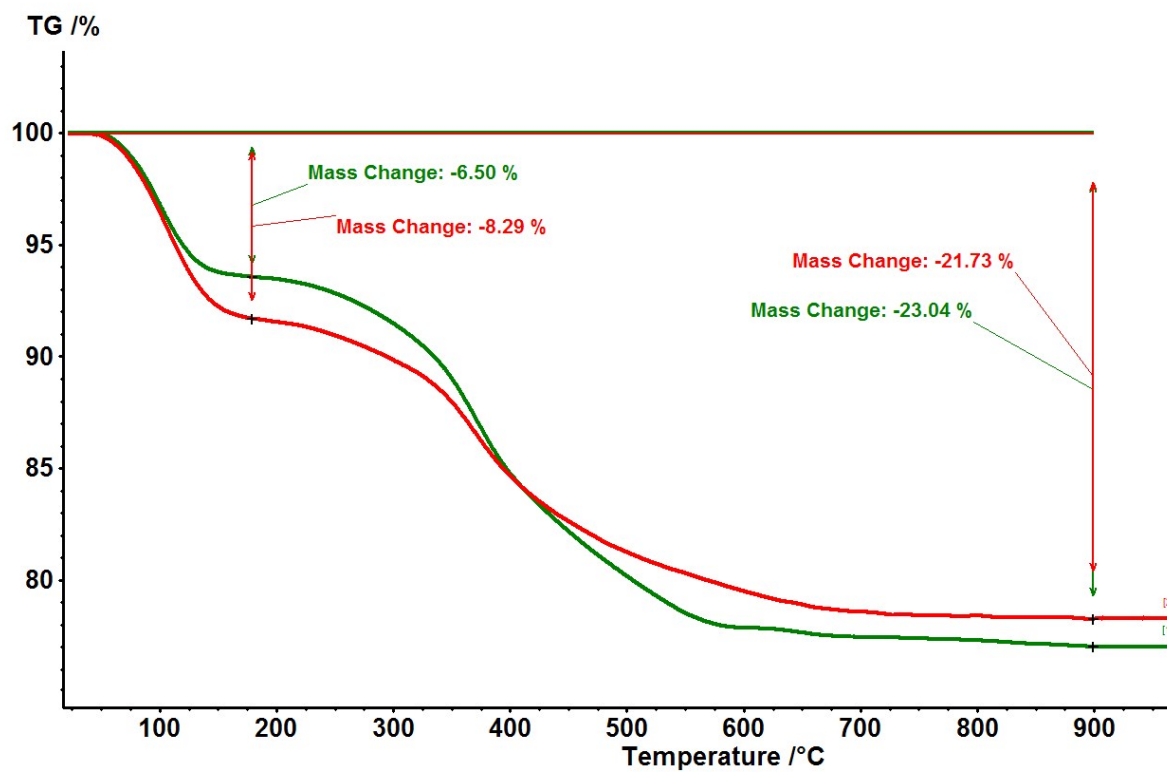
## 5. BET adsorption/desorption isotherms



**Fig. S4** Volume of adsorbed/desorbed nitrogen vs relative pressure for a composite dried over an extended period of time (slow drying) and one dried at 100 °C for a short time (fast drying).

The slowly dried monolithic samples showed a very high porosity of 592  $\text{m}^2/\text{g}$ , a pore diameter of 4 nm according to the BET theory. Fast dried composites were mesoporous with small specific surface areas (BET theory could not be applied for quantitative evaluation).

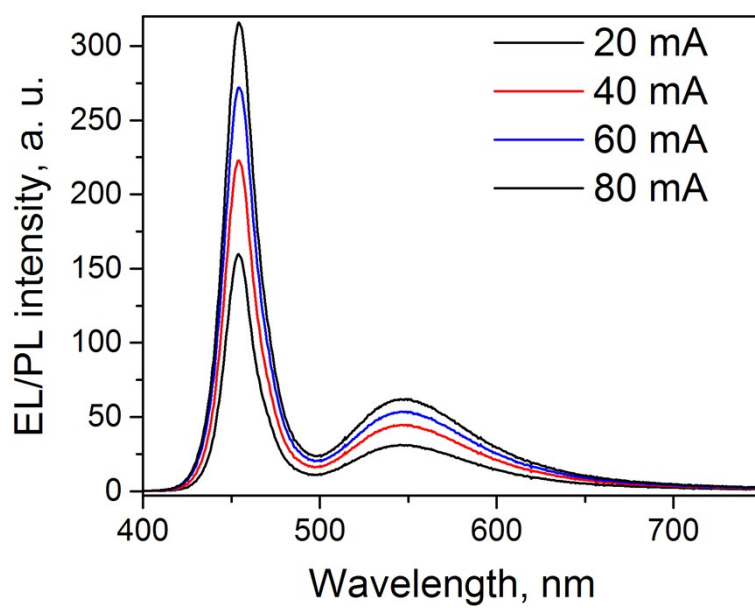
## 6. Thermogravimetric measurements



**Fig. S5** TG curves of a silica composite at 10 % solid loading (green curve) and 15 % loading (red curve).

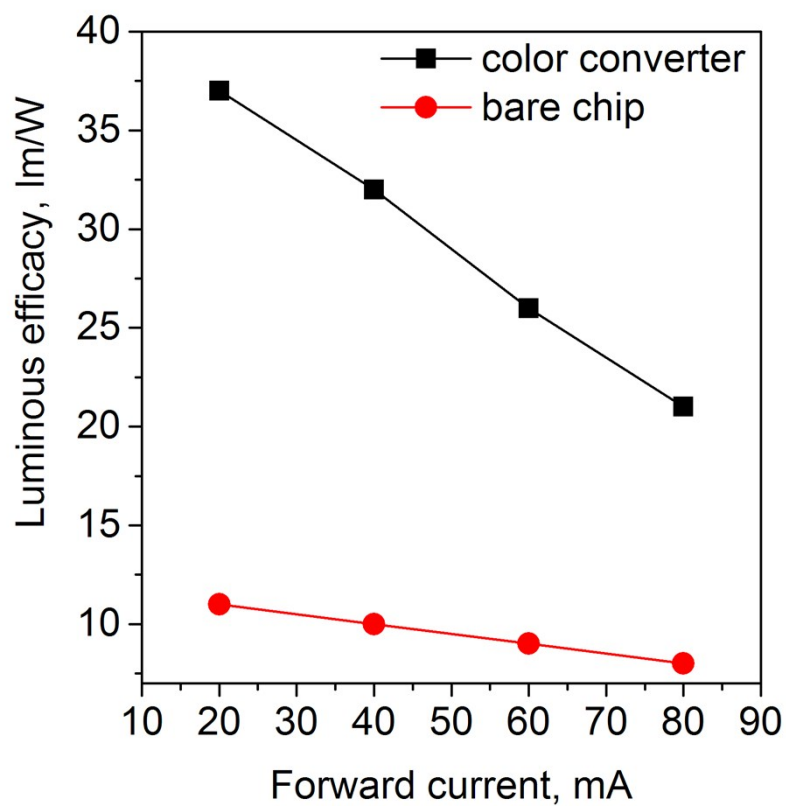


## 7. EL/PL spectra of the QD/silica/PVC composite



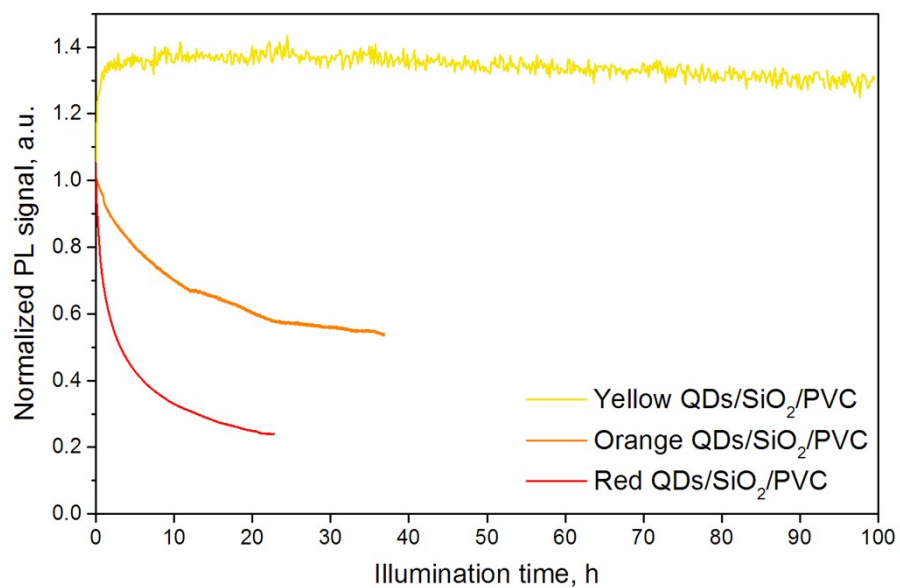
**Fig. S6** LED spectra with the ultrastable green-QD/silica/PVC composite after prolonged illumination at different driving currents.

## 8. Luminous efficacy of the ultrastable QD/silica/PVC composite



**Fig. S7** Efficiency droop of the bare chip and LE of the ultrastable composite at different forward currents.

## 9. Stability of the yellow, orange and red QDs in PVC-infused silica.



**Fig. S8.** Stability measurement results for the yellow, orange and red QDs embedded in silica/PVC composites under blue LED illumination (20 mA). Yellow QDs were measured with a USB650 and orange and red QDs with an Avantes ULS2048XL spectrometer.