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Synthesis and structure of colloidally stable Germanium quantum dots and their application in live cell imaging

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Ali Karatutlu*, [a] Mingying Song, [a] Ann P. Wheeler,[b] Osman Ersoy,[a] William R. Little,[a] Yuanpeng Zhang,[a] Pascal Puech,[c] Filippo S. Boi,[d] Zofia Luklinska [e] and Andrei V. Sapelkin [a]

Electronic Supplementary Material

S1. Experimental Section

S1.1 Laser Power Measurements in Fluorescent Imaging

The laser power, P_L used in taking fluorescent images in Figure 5(c), (d), (e), (f) using spin disk confocal microscopy are shown in Table S1. The values of the laser power at each wavelength such as 647 nm, 561 nm, 488 nm and 405 nm were recorded using an optical power meter (Newport 1916-C). In the measurement of the reflecting light from the sample glass slide, the power meter replaced by the camera and then the corresponding laser power for each wavelength was recorded.

Table S1 Table of the laser power values used in the measurement of wavelength dependent fluorescence images using spin disk confocal microscopy. For each wavelength utilized such as 647 nm, 561 nm, 488 nm and 405 nm, the incident and reflected laser power are represented.

λ_{exc} = 647 nm								
$P_L$excitation mW	0.00	1.00	5.00	10.00	20.00	30.00	40.00	50.00
$P_L$detected nW	0.70	0.70	20.00	72.00	265.00	560.00	900.00	1100.00
λ_{exc} = 561 nm								
$P_L$excitation mW	0.00	1.00	5.00	10.00	20.00	30.00	40.00	50.00
$P_L$detected nW	0.80	0.80	18.00	66.00	260.00	550.00	910.00	1327.00
λ_{exc} = 488 nm								
$P_L$excitation mW	0.00	1.00	5.00	10.00	20.00	30.00	40.00	50.00
$P_L$detected nW	0.90	0.90	10.00	35.00	130.00	271.00	440.00	632.00
λ_{exc} = 405 nm								
$P_L$excitation mW	0.00	1.00	5.00	10.00	20.00	30.00	40.00	50.00
$P_L$detected nW	1.80	1.90	5.00	14.00	48.00	100.00	170.00	250.00

S2 Results

S2.1 EXAFS Fit

EXAFS spectrum of crystalline bulk Ge at the Ge K-edge was recorded between 11 keV and 12 keV in energy space. This was done as a reference measurement in order to determine the amplitude reduction factor, S_0^2 of c-Ge and use it as a set parameter for Ge qdots before conducting any EXAFS measurements of formed nanoparticles.

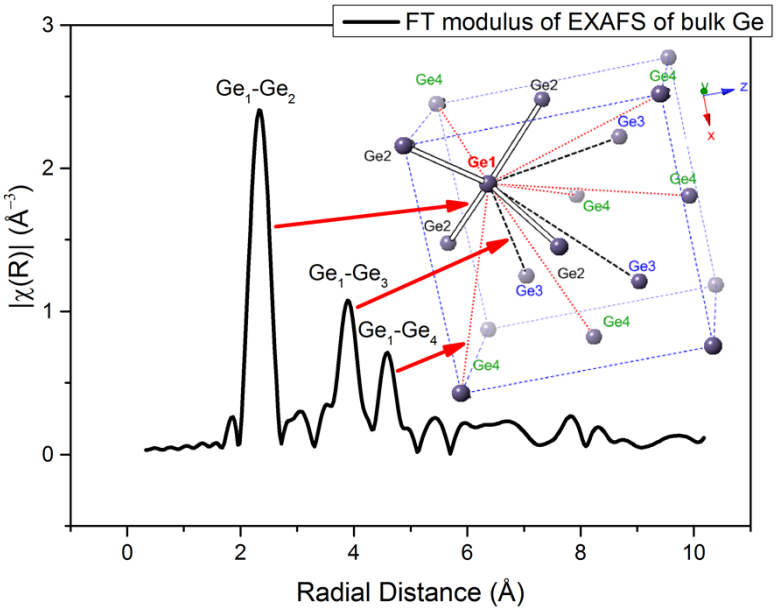

Figure S1 Reference bulk Ge. The three nearest neighbour distances (Ge_1-Ge_2, Ge_1-Ge_3 and Ge_1-Ge_3) were obtained using FT modulus of EXAFS of bulk Ge and are compared with those of the diamond cubic Ge structure (ICDS No. 43422). In the model, Ge1-Ge2 bonds, Ge1-Ge3 bonds and Ge1-Ge4 bonds are shown with white cylinders, black dashed lines and red dotted lines respectively. The values of the interatomic distances measured are shown in Table S2.

Table S2 The fit quality and the parameters obtained at the end of multiple shell fit of the FT modulus of the k^2-weighted EXAFS spectrum of crystalline bulk Ge.

The fitting quality and Parameters	**Bulk Ge**
R-factor	0.023
N (Ge_1-Ge_2) (set)	4
S_0^2	0.843 ± 0.054
ΔE_0	2.095 ± 0.619
σ^2	0.0020 ± 0.0003
ΔR	-0.007 ± 0.002
N (Ge_1-Ge_3) (set)	12
σ^2	0.0035 ± 0.0004
ΔR	-0.010 ± 0.005
N (Ge_1-Ge_4) (set)	12
σ^2	0.0038 ± 0.0005
ΔR	-0.016 ± 0.006

Table S3 shows the R-factor and fitting parameters obtained after the fit of FT modulus of EXAFS of CS_1 using the first coordination shell of the diamond cubic structure of Ge. The fitting parameters includes the amplitude reduction factor, S_0^2, the energy shift, ΔE_0, the debye-waller factor, σ^2 and the shift between the theoretical structural model and the experimental measurement, ΔR are shown.

Table S3 The fit quality and the parameters obtained at the end of fit of the FT modulus of the k^2-weighted EXAFS spectrum of Ge qdots (CS_1).

The fitting quality and parameters	CS_1
R-factor	0.029
N (Ge_1-Ge_2) (set)	4
S_0^2 (set)	0.843
ΔE_0	2.175 ± 2.427
σ^2	0.0062 ± 0.0005
ΔR	-0.013 ± 0.012

S2.2 Raman Spectroscopy Results

Raman of a-Ge [1] were compared with the bulk Ge (the diamond cubic structure) in Figure S1. In a-Ge (black square), there is one peak at 275 cm^{-1} which is very broad and asymmetric. Crystalline bulk Ge has a symmetric peak at 300 cm^{-1}.

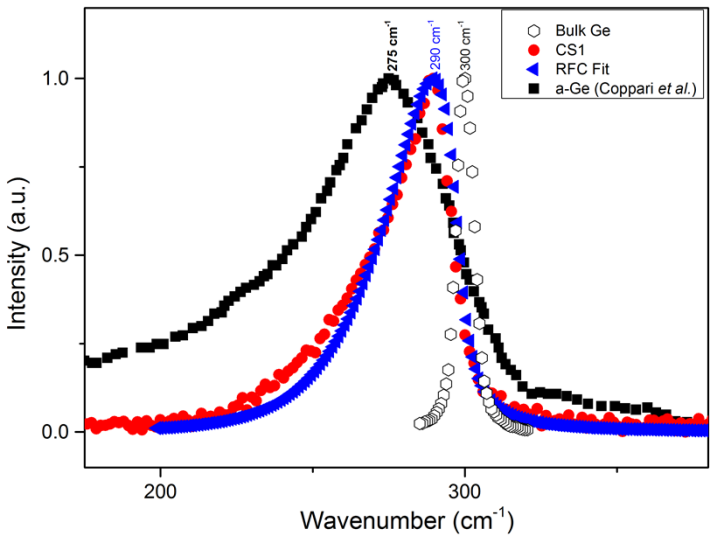

Figure S1. Raman shift of CS1 and RFC fit to CS1 are shown for comparison with Raman of crystalline bulk Ge (black sphere) and that of a-Ge (black square). Raman shift of bulk Ge is shown to have a peak position at 300 cm^{-1}. In a-Ge, there is one but a very broad and asymmetric peak at 275 cm^{-1} (reproduced from reference [1]).

The particle size of CS1 by Raman, TEM and XRD is shown in Table S1.

Table S1. Particle Size by Raman, TEM and XRD

Method	Particle size (nm)
Raman	3.2±0.3

TEM	3.68 ± 0.62
XRD	1.54

In order to test long-term stability of CS_1 in water, CS_1 was stored in water for 35 days. Then, photoluminescence spectrum was collected and is given in Figure S3.

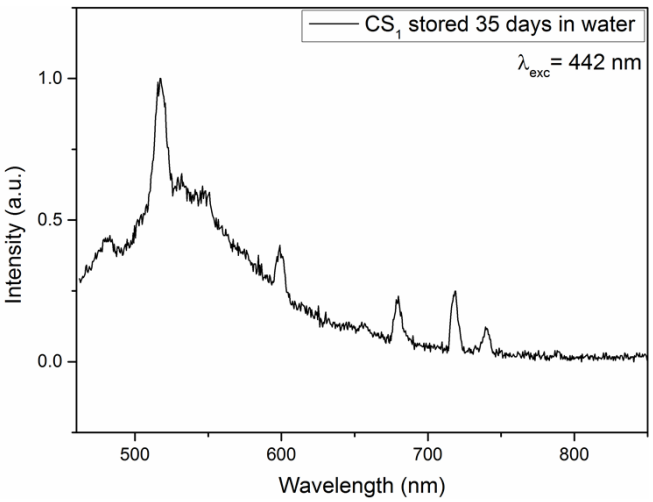

Figure S3. Photoluminescence spectrum of CS_1 stored 35 days in water. The excitation wavelength is 442 nm.

Concentrations dependent viability results of CS_1 and the carboxyl coated CdSe/ZnS qdots are shown in Figure S4. In very small concentrations such as 10 nmole, the CdSe qdots can also be considered to be viable.

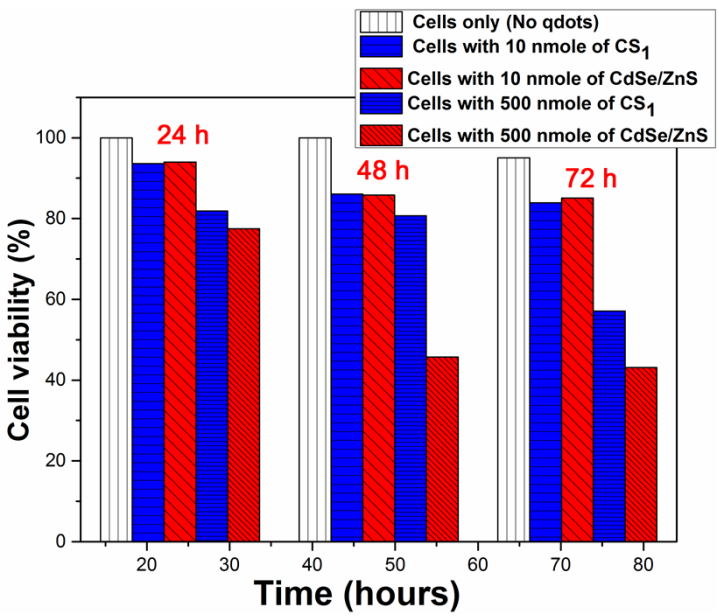

Figure S4. Cell viability of CS_1 and the commercial carboxyl coated CdSe/ZnS qdots when cultured with various concentrations of CS_1 at the end of 24 h, 48 h and 72 h.

The energy dispersive X-ray spectroscopy (EDS) measurement of the Ge qdots stored in ethanol prior to the measurement is shown in Figure S5. The EDS data of Ge qdots results the elemental composition with 31.3 % of Ge and 68.7 % of O respectively. The O peak are considered to be due to storing the sample in ethanol.

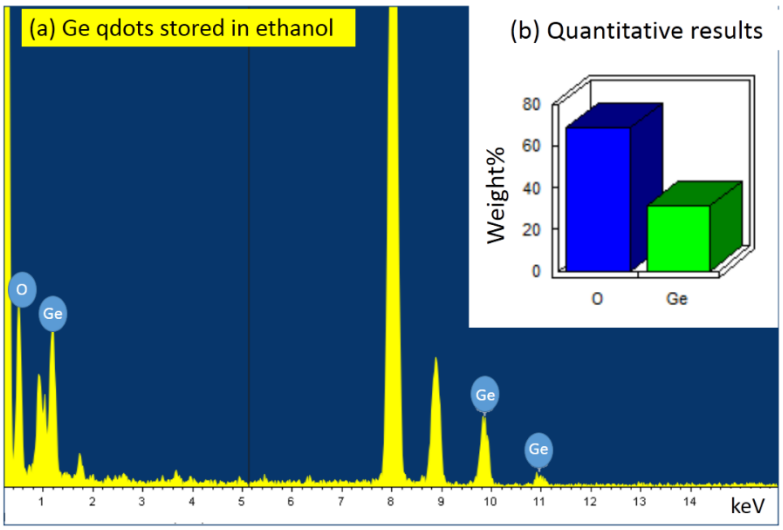

Figure S5. (a) EDS data of Ge qdots stored in ethanol shows the traces of elemental composition of Ge and O. The peaks omitted at 1.756 keV, refer to C and peaks at 3.701 keV, 8.035 keV and 8.896 keV refer to Cu result from C coated Cu TEM grid. C peak at 1.756 keV. (b) Quantitative results shows the elemental weight of Ge and O to be 31.3 % and 68.7 % respectively.

References

1. F. Coppari, a. Di Cicco, a. Congeduti, J. C. Chervin, F. Baudelet, and a. Polian, *High Press. Res.*, 2009, **29**, 103–107.