

Photoluminescent polysaccharide-coated germanium (IV) oxide nanoparticles.

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1. The amount of polysaccharide for the synthesis of GeO₂ nanoparticles in aqueous environment was estimated for 10 monolayers on 100 nm GeO₂ particles from the following assumptions: the surface area of 0.1g of germanium oxide, taking every particle as a sphere is 1.41 m². The hydrodynamic diameter of polysaccharide molecules was measured by dynamic light scattering (Figure S1). The area, occupied by polysaccharide molecule is estimated, as a projection of the sphere with hydrodynamic diameter of polysaccharide molecule on a flat surface. The number of polysaccharide molecules in theoretical monolayer was found by division of the total area of particles with the projection area of polysaccharide molecule.

Table S1. Colloidal characteristics and quantities of polysaccharides, used in the synthesis of GeO₂ nanoparticles in aqueous acidic environment.

| polysaccharide | d _h , nm | projection area, m ² | number of moles | Molecular weight | mass for 10 layers, g |
|--------------------------|---------------------|---------------------------------|-----------------------|------------------|-----------------------|
| inulin | 2.50±0.20 | 1.97*10 ⁻¹⁷ | 1.20*10 ⁻⁷ | 3600 | 0.0043 |
| chitosan | 2.00±0.17 | 1.26*10 ⁻¹⁷ | 1.86*10 ⁻⁷ | 5000 | 0.0093 |
| dextrin | 4.00±0.22 | 5.10*10 ⁻¹⁷ | 4.60*10 ⁻⁸ | 10000 | 0.0046 |
| dextran MW 6000 Da | 3.50±0.17 | 3.84*10 ⁻¹⁷ | 6.14*10 ⁻⁸ | 6000 | 0.0037 |
| dextran MW 450-650000 Da | 14.00±0.20 | 6.15*10 ⁻¹⁶ | 3.81*10 ⁻⁹ | 450000 | 0.0175 |

2. Image analysis of GeO₂ nanoparticles, synthesized in aqueous environment.

The particle size range was divided into 16 equal intervals and the relative number of particles within each interval was counted. The cumulative particle size distributions were plotted and differentiated with Origin 9 (Microcal) The differential particle size distribution were fitted as a superposition of 1 to 3 Gaussian functions, $f(L) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(L-L_m)^2}{2\sigma^2}}$ each representing the population of a particles with mean dimension $L_m \pm \sigma$ (Figure S1-S11), where σ is the standard deviation. The average particle dimension L_a was obtained as a weighted ($0 \leq p \leq 1$ is normalized area under Gaussian function) sum of means and used for theoretical prediction of the surface area (m²/g), the standard deviation of L_a was calculated according to: $\sigma =$

$$\sqrt{\sum p_i(\sigma_i^2 + L_i^2) - (\sum p_i L_i)^2}.$$

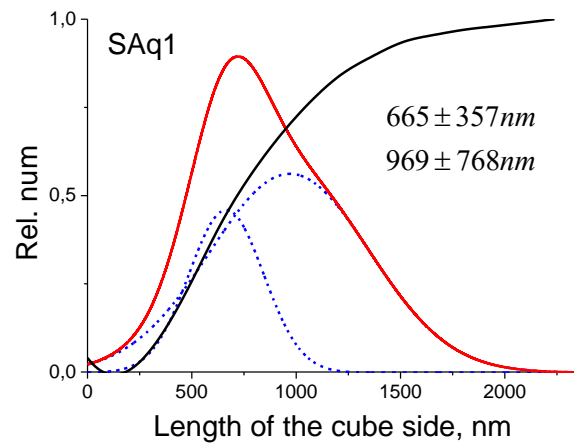
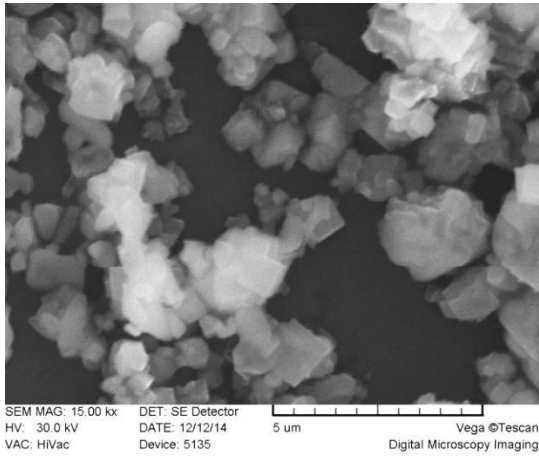


Figure S1 GeO₂ particles without polysaccharide, $L_a = 884 \pm 613$ nm, $A = 1.61 \text{ m}^2/\text{g}$

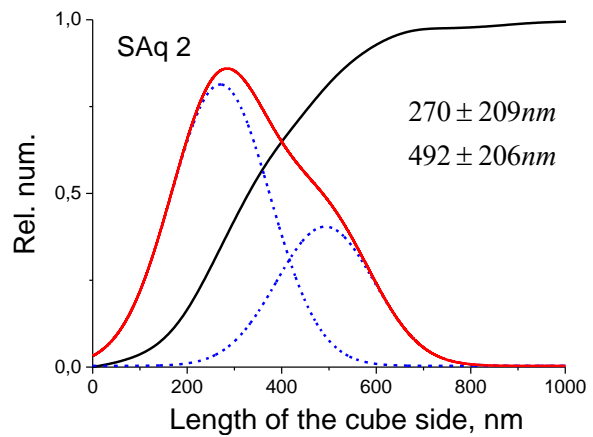
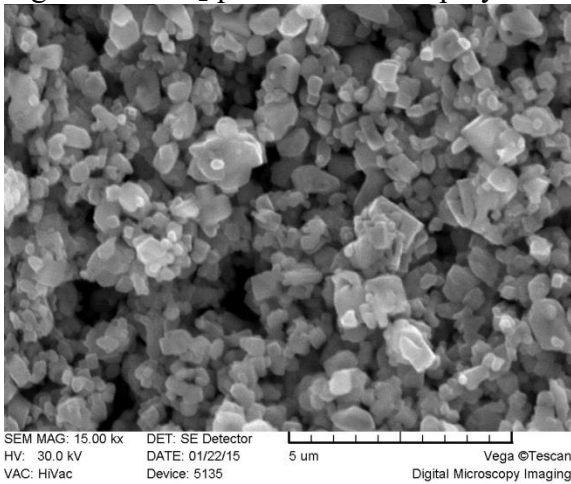


Figure S2 GeO₂ particles with chitosan, 0.0093 g to 0.1g of GeO₂ $L_a = 343 \pm 233$ nm, $A = 4.14 \text{ m}^2/\text{g}$

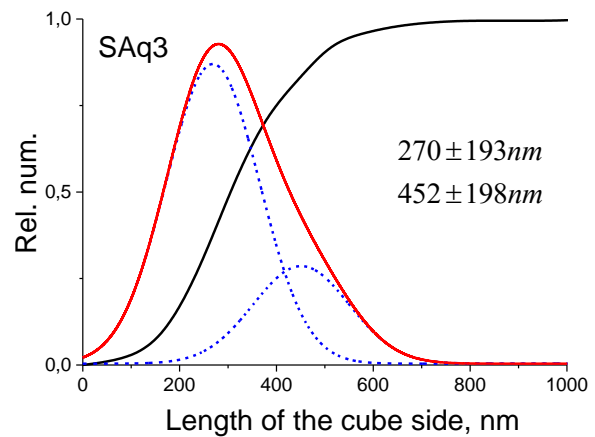
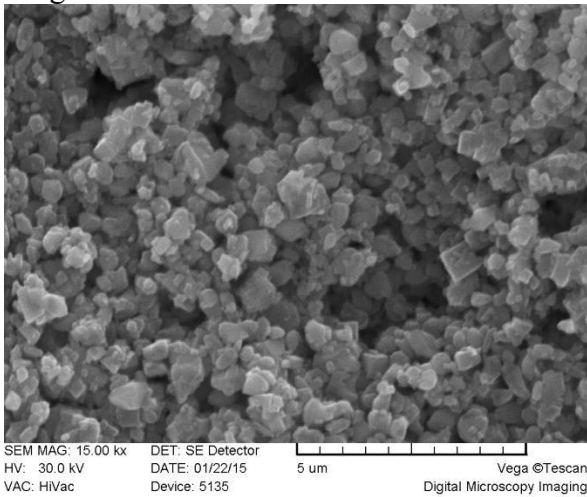


Figure S3 GeO₂ particles with dextrin, 0.0046 g to 0.1g of GeO₂ $L_a = 316 \pm 210$ nm, $A = 4.49 \text{ m}^2/\text{g}$

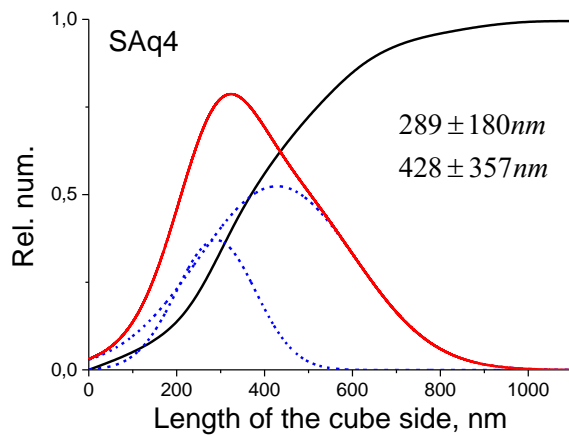
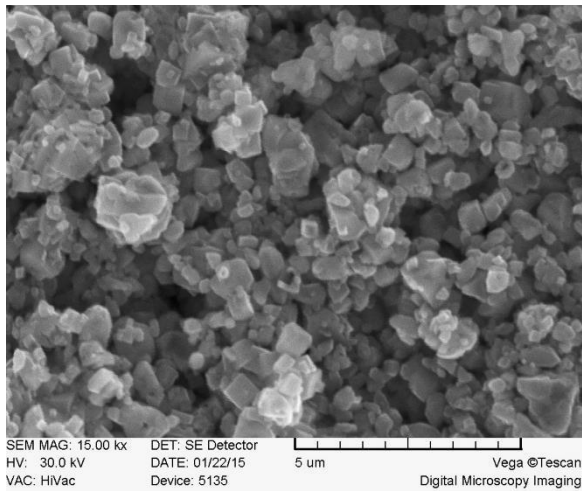


Figure S4 GeO₂ particles dextran 6000 Da, 0.0037 g to 0.1g of GeO₂ $L_a = 392 \pm 265 \text{ nm}$, $A = 3.62 \text{ m}^2/\text{g}$

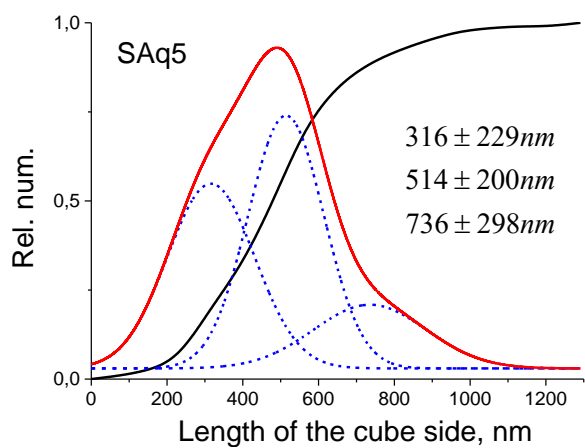
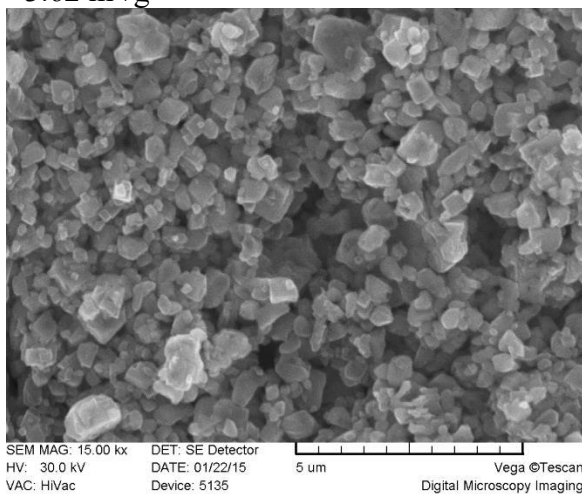


Figure S5 GeO₂ particles with dextran 450 000 Da, 0.0175 g to 0.1g of GeO₂ $L_a = 474 \pm 274 \text{ nm}$, $A = 2.99 \text{ m}^2/\text{g}$

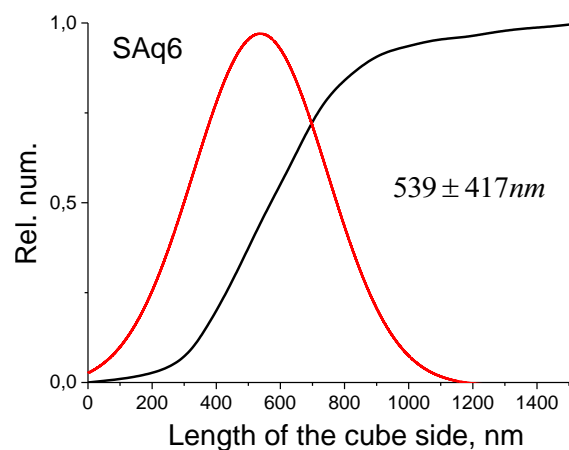
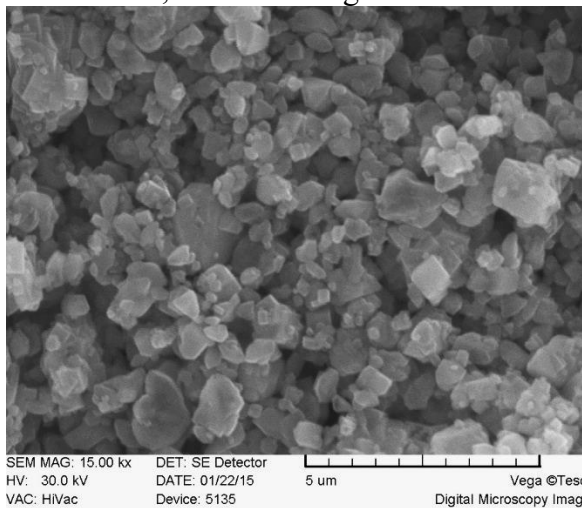


Figure S6 GeO₂ particles with inulin, 0.0043 g to 0.1g of GeO₂, $L_a = 539 \pm 417 \text{ nm}$, $A = 2.63 \text{ m}^2/\text{g}$

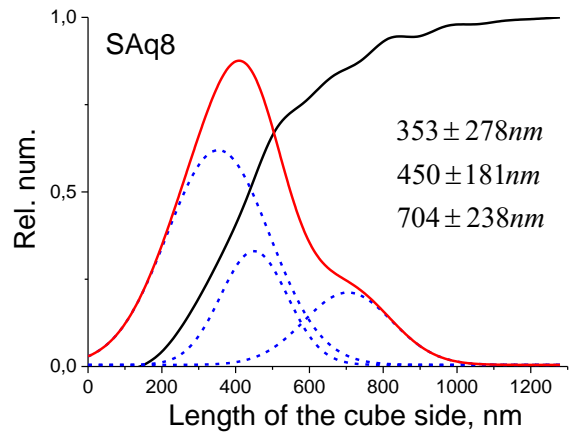
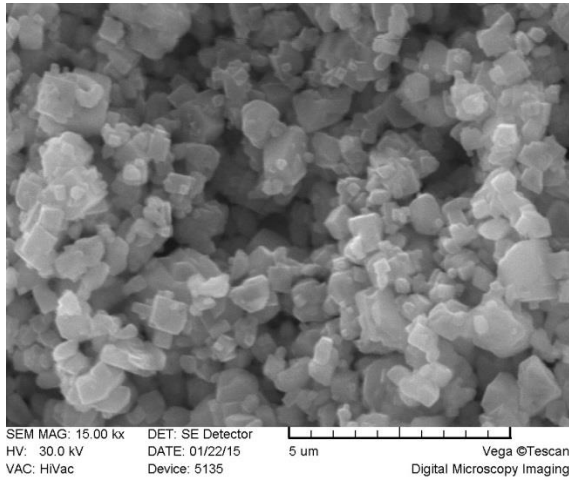


Figure S7 GeO₂ particles with inulin, 0.1 g to 0.1g of GeO₂ $L_a = 437 \pm 293 \text{ nm}$, $A = 3.25 \text{ m}^2/\text{g}$

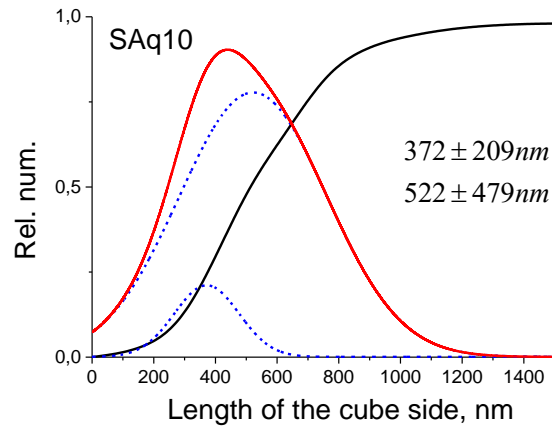
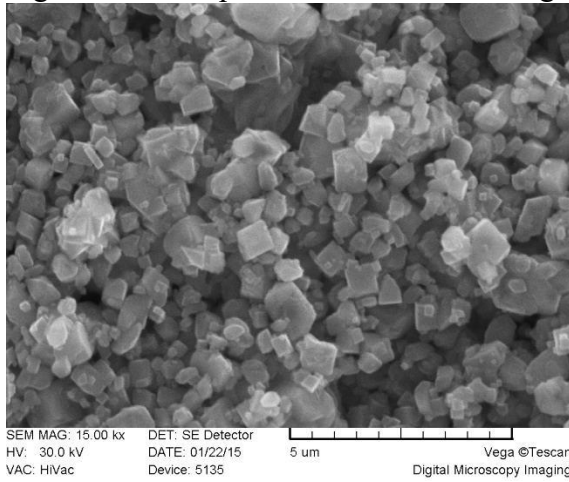


Figure S8 GeO₂ particles with dextran 450 000 Da, 0.1 g to 0.1g of GeO₂ $L_a = 506 \pm 460 \text{ nm}$, $A = 2.80 \text{ m}^2/\text{g}$

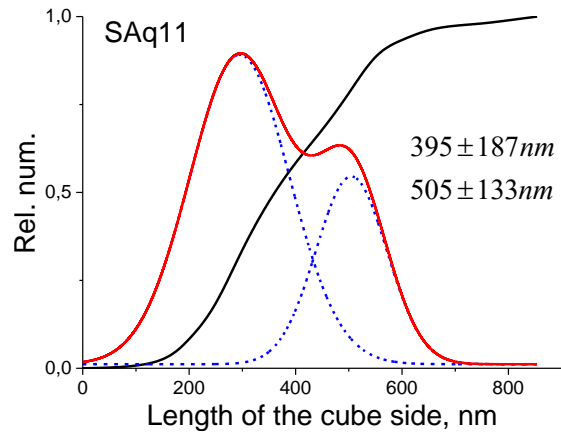
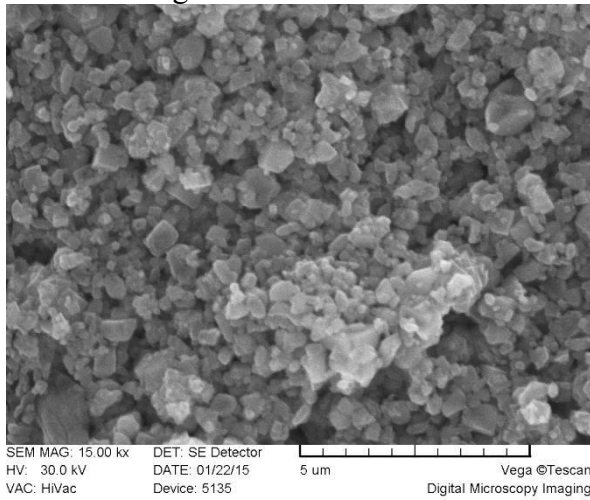
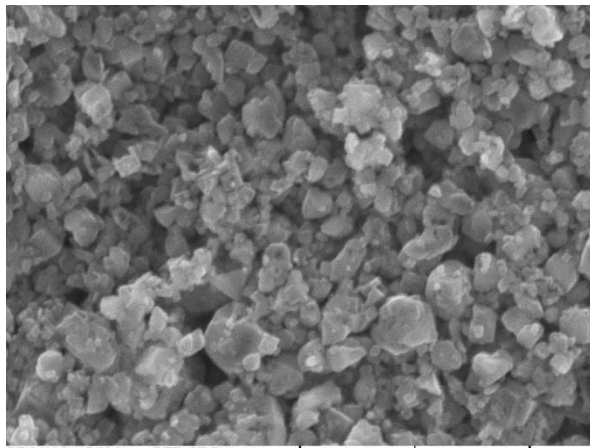


Figure S9 GeO₂ particles with dextran 0.1 g to 0.1g of GeO₂ $L_a = 429 \pm 180 \text{ nm}$, $A = 3.31 \text{ m}^2/\text{g}$



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 HV: 30.0 kV DATE: 01/22/15
 VAC: HiVac Device: 5135 Vega ©Tescan
 Digital Microscopy Imaging

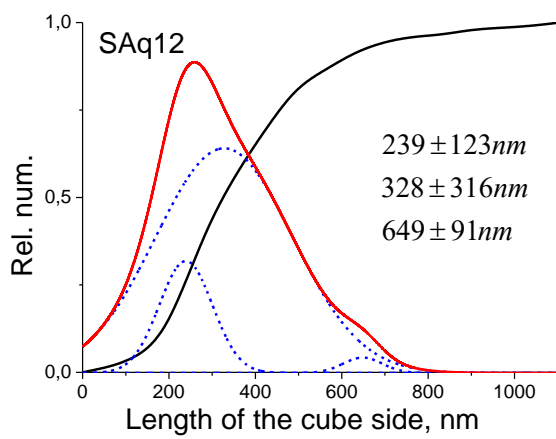
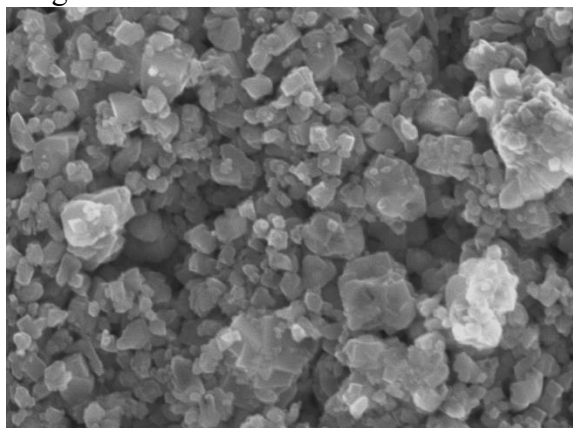


Figure S10 GeO₂ particles with chitosan, 0.1 g to 0.1g of GeO₂ $L_a = 317 \pm 242$ nm, $A = 4.48$ m²/g



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 VAC: HiVac Device: 5135 Vega ©Tescan
 Digital Microscopy Imaging

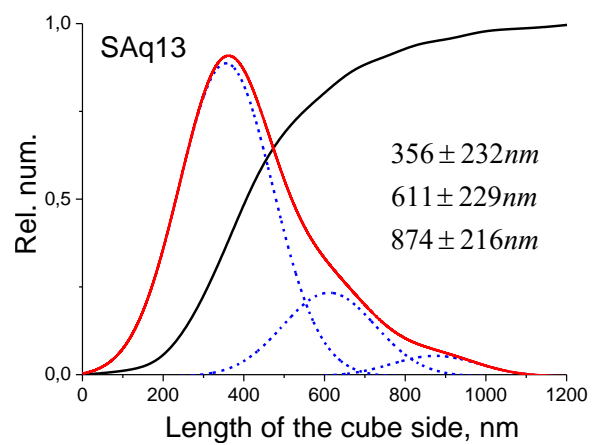


Figure S11 GeO₂ particles with dextran 6000 Da, 0.1 g to 0.1g of GeO₂ $L_a = 433 \pm 271$ nm, $A = 3.28$ m²/g

Table S2 Colloidal properties of GeO₂ nanoparticles, synthesized in aqueous solutions of polysaccharides

| Poly-saccharide | Carbon content in poly-sacch. (theor.) % | Amount of poly-sacch. per 1g of GeO ₂ | Number - average dimension (SEM), nm | Number-average dimension (Gaussian fits), nm | | Surface area (BET) m ² /g | Carbon content in GeO ₂ , % | Adsorption | | | Surface area per molecule | | ζ potential mV | Weight loss 280-400°C % |
|-----------------|--|--|--------------------------------------|--|----------------------|--------------------------------------|--|------------|-------------------------|--------------------------------------|---------------------------|---------------------------------------|----------------------|-------------------------|
| | | | | 1 st mode | 2 nd mode | | | %, weight | mg/m ² (BET) | mole/m ² *10 ⁷ | exp., nm ² | theor. ¹ , nm ² | | |
| | | | | | | | | | | | | | | |
| - | - | - | 884 | 665±357 | 969±768 | - | n/a | | | | | ~0 | 0.34 | |
| chitosan | 41 | 0.0093 | 343 | 270±209 | 492±206 | - | 0.58±0.30 | 1,41±0.73 | 3.45 ² | 4.16 | 24 | 13 | +18.1 | 0.30 |
| | | 1 | 317 | 239±123 | 328±316 | 6.62 | 0.76±0.30 | 1,85±0.73 | 2,85 | 5,69 | 29 | | +26.4 | 0.58 |
| dextrin | 44 | 0.0046 | 316 | 270±193 | 452±158 | 4.18 | 0.55±0.30 | 1,25±0,68 | 3,03 | 3,03 | 55 | 51 | -30.5 | 0.40 |
| | | 1 | 429 | 395±187 | 505±135 | 3.42 | 0.63±0.30 | 1,43±0,68 | 4,24 | 4,24 | 39 | | -30.7 | 0.42 |
| inulin | 41 | 0.0043 | 539 | 539±417 | | 1.82 | 0.44±0.30 | 1,07±0.73 | 5,94 | 16,51 | 10 | 20 | -38.3 | 0.35 |
| | | 1 | 437 | 353±278 | 450±181 | 1.50 | 0.47±0.30 | 1,15±0.73 | 7,76 | 21,54 | 8 | | -29.7 | 0.47 |
| dextran 450 000 | 44 | 0.0175 | 506 | 316±229 | 514±200 | 3.40 | 0.71±0.30 | 1,61±0,68 | 4,81 | 0,11 | 1553 | 615 | -37.9 | 0.31 |
| | | 1 | 474 | 372±209 | 577±479 | 2.54 | 0.44±0.30 | 1,00±0,68 | 3,98 | 0,09 | 1880 | | -31.7 | 0.61 |
| dextran 6000 | 44 | 0.0037 | 392 | 289±180 | 428±357 | 1.97 | 0.56±0.30 | 1,27±0,68 | 6,53 | 10,88 | 15 | 38 | -22.6 | 0.30 |
| | | 1 | 433 | 356±232 | 611±229 | 3.12 | 0.47±0.30 | 1,07±0,68 | 3,47 | 5,78 | 29 | | -35.3 | 0.16 |

1 – theoretical area per one polysaccharide molecule is estimated as a projection of a sphere with hydrodynamic diameter of polysaccharide molecule on a flat surface (Table S1)

2 - calculated from the average dimension, obtained by SEM

3 Size distributions (DLS) and TEM images of GeO₂ nanoparticles.

Table S3 Concentrations of Ge(IV) in samples, synthesized in ethanol and size of GeO₂ nanoparticles

| Synt. N | Volume of the reaction mixture, ml | Number of moles of Ge(IV) | Conc. of Ge(IV) in reaction mixture | Volume of the purified sample, ml | Conc. of Ge(IV) in purified sample, M ¹ | Diameter of GeO ₂ particles (DLS), nm |
|-----------------|------------------------------------|---------------------------|-------------------------------------|-----------------------------------|--|--|
| 1 | 4.0 | 0.0024 | 0.60 | 1.5 | 1.6 | 74±18 |
| 2 | | | | | | 78±18 |
| 3 | | | | | | 74±18 |
| 4 ² | | | | | | aggregated |
| 6 | | | | | | 498±151 ⁵ |
| 7 | | | | | | 97±23 |
| 8 | | | | | | 0.0017 |
| 9 | 0.0006 | 67±15 | | | | |
| 10 ³ | | dissolved | | | | |
| 11 ⁴ | | 227±51 | | | | |

- 1 - theoretical for 100% yield
- 2 - synthesized in acetonitrile
- 3 - with 0.03g polyvinylpyrrolidone
- 4 - with 0.03g poly(ethylene glycol)
- 5 – aggregation

Particle size distributions (PSD), measured by DLS, were fitted with unimodal lognormal function $f(x) = \frac{1}{x\sigma\sqrt{2\pi}} e^{-\frac{(\ln x - \mu)^2}{2\sigma^2}}$ and the number average particle diameter was represented by median value $d \pm SD_v$, where $d = e^\mu$, and standard deviation $SD_v = \sqrt{e^{2\mu + \sigma^2} (e^{\sigma^2} - 1)}$: Figure S12-S25

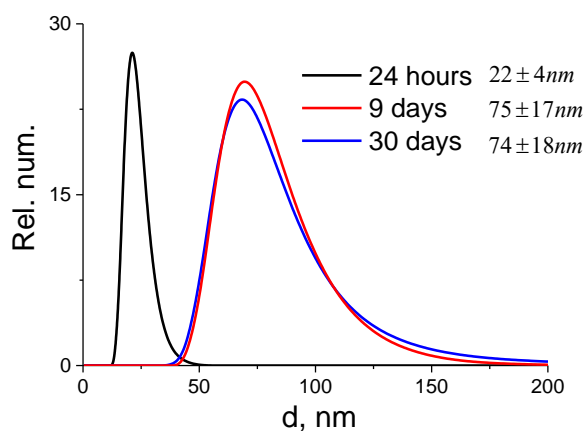
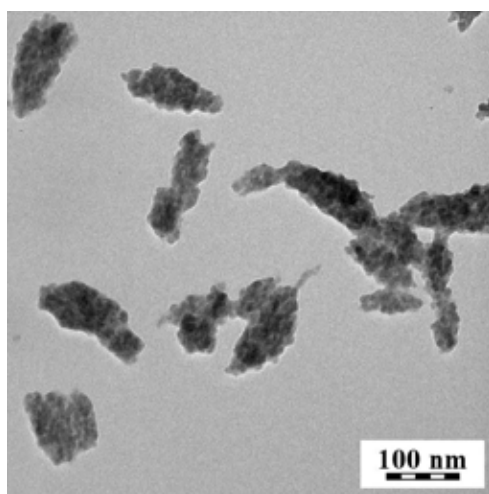


Figure S12 Synthesis N1, TEM image of particles, aged for 30 days

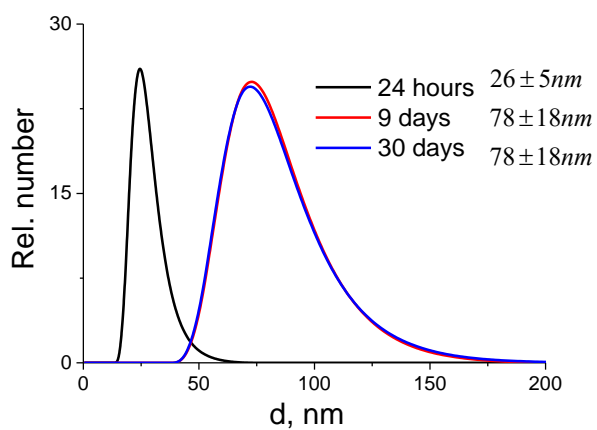
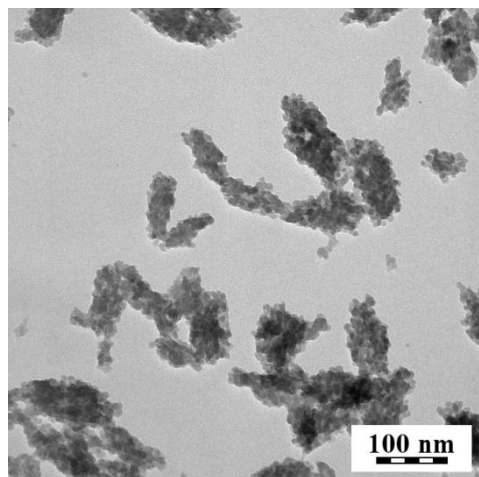


Figure S13 Synthesis N2. TEM image of particles, aged for 30 days

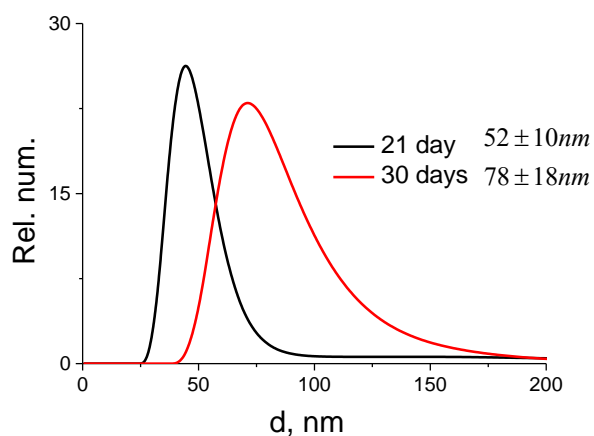
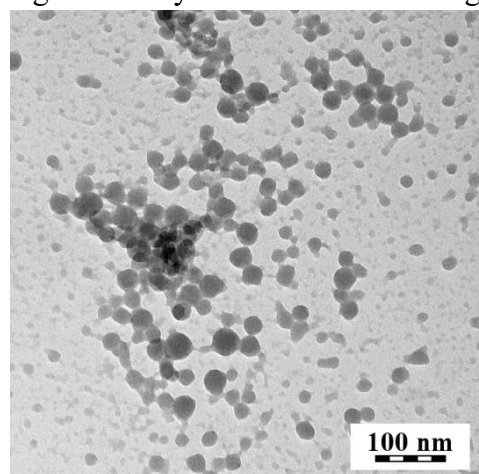


Figure S14 Synthesis N3. TEM image of particles, aged for 1 hour.

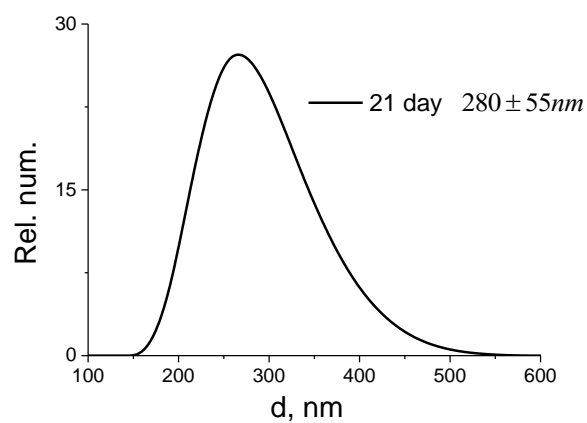
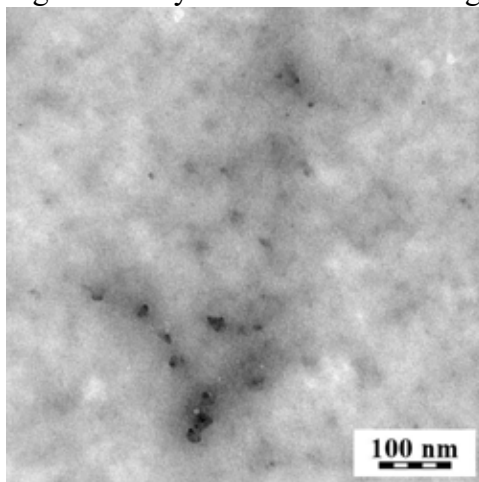


Figure S15 Synthesis N4, in acetonitrile. TEM image of particles, aged for 1 hour.

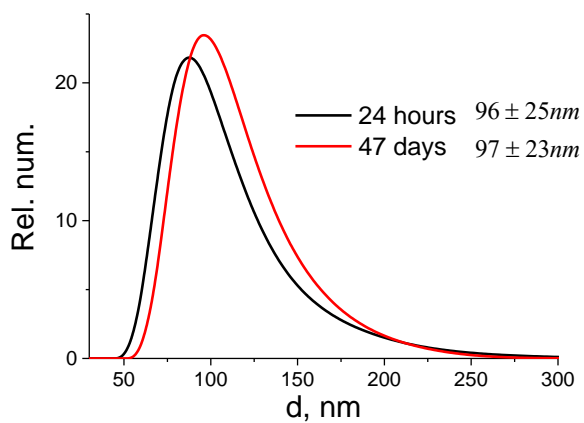
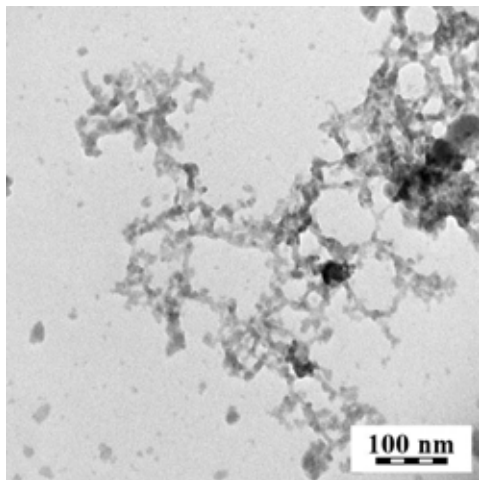


Figure S16 Synthesis N7. TEM image of particles, aged for 10 days

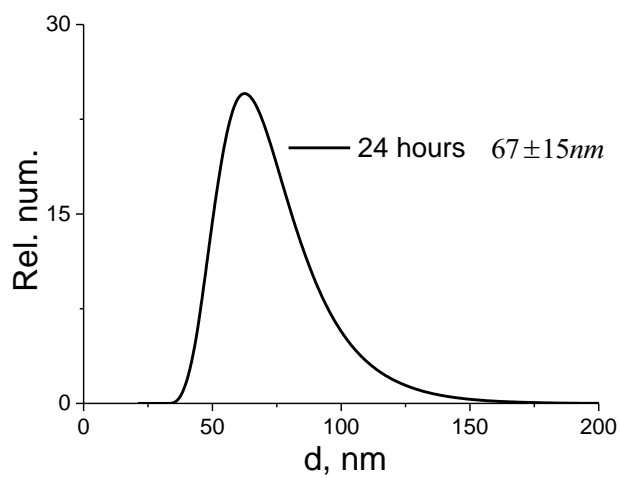
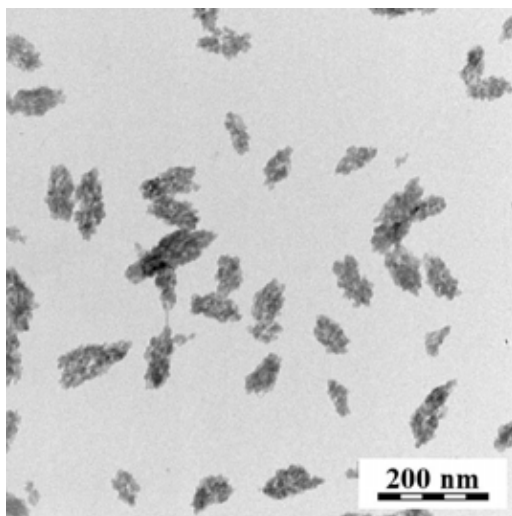


Figure S17 Synthesis N9. TEM image of particles, aged for 3 days.

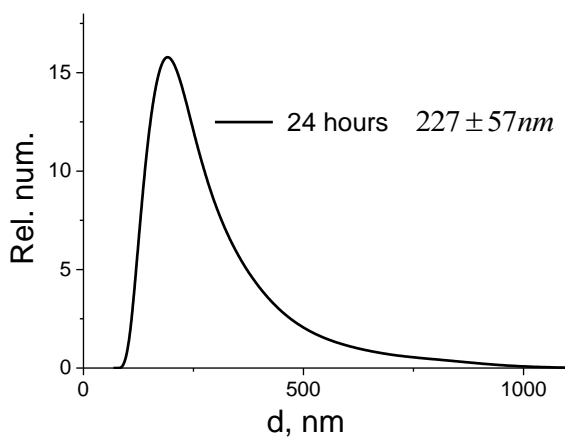
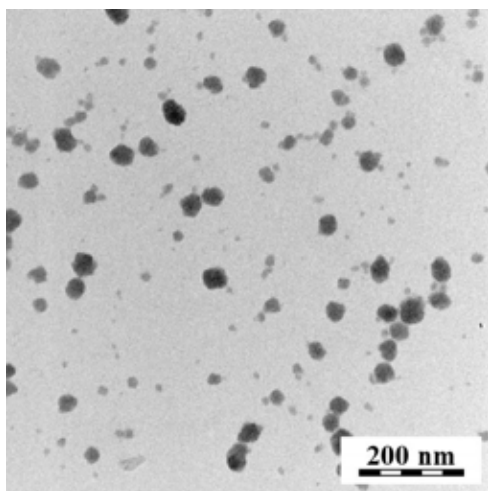


Figure S18 Synthesis N11. TEM image of particles, aged for 3 days.

Table S4. Concentrations of Ge(IV) and Si(IV) in coating of the GeO₂ nanoparticles with SiO₂ shell. Colloidal properties of GeO₂ and GeO₂@SiO₂ nanoparticles

| Synt. N* | Volume of reaction mixture, ml | Aliquot of purified GeO ₂ , ml | Number of moles of Ge(IV), | Number of moles of TEOS, | Volume of ammonium hydroxide, 0.5M, ml | Volume of the purified sample, ml | Conc. of Ge(IV) in purified sample, M | Size of initial GeO ₂ (DLS), nm | Diameter of coated GeO ₂ @SiO ₂ , (DLS), nm |
|------------------|--------------------------------|---|----------------------------|--------------------------|--|-----------------------------------|---------------------------------------|--|---|
| 1-1 | 0.052 | 0.05 | 8*10 ⁻⁵ | 4.48*10 ⁻⁷ | 0.002 ¹ | 0.5 | 0.16 | 74±18 | aggregated |
| 1-2 | 0.059 | | | 8.96*10 ⁻⁷ | 0.005 | | | | 65±15 |
| 1-3 | 0.066 | | | 1.34*10 ⁻⁶ | 0.010 | | | | 80±20 |
| 1-4 | 0.073 | | | 1.79*10 ⁻⁶ | 0.015 | | | | 75±18 |
| 3-2 | 0.059 | | | 8.96*10 ⁻⁷ | 0.005 | | | 78±18 | 79±19 |
| 3-3 | 0.066 | | | 1.34*10 ⁻⁶ | 0.010 | | | | 90±23 |
| 3-4 | 0.073 | | | 1.79*10 ⁻⁶ | 0.015 | | | | 93±24 |
| 6-1 ² | 0.713 | | | 0.5 | 8*10 ⁻⁴ | | | | 1.40*10 ⁻⁵ |
| 7-1 ² | 0.66 | 2.24*10 ⁻⁴ | 0.1 | | | 97±23 | 115±16 | | |
| 7-2 | 0.6 | 1.6*10 ⁻³ | 0.2 | | | | 122±31 | | |
| 7-3 ² | 1.4 | | 0.5 | | | | 151±41 | | |
| 7-4 ³ | 1.7 | 0.5 | 5.7*10 ⁻⁴ | 8.96*10 ⁻⁴ | 0.3 ⁴ | 0.57 | 498±99 | aggregated | |
| 8-1 ³ | 1.5 | | | | aggregated | | | | |
| 8-2 ² | 1.25 | | | | aggregated | | | | |
| 8-3 | 1.25 | | | | aggregated | | | | |
| 8-4 ² | | 0.2 | 1,2*10 ⁻⁴ | 2.24*10 ⁻⁴ | 0.05 ⁵ | 0.12 | 67±15 | 336±82 | |
| 9-1 | 1 | | | | | | | 211±81 | |
| 9-2 | | | | | | | | 112±32 | |
| 9-3 | | | | | | | | 356±130 | |

1 - of pure water; 2 - dosage of ammonium hydroxide with 10 equal aliquots during 120 min; 3 - dosage of ammonium hydroxide with increasing aliquots (10; 20; 40; 80; 150; 200 microliters); 4 - 1.3 M ammonium hydroxide; 5 - 6.5 M ammonium hydroxide.

*The numbering of the syntheses X-Y, where X – number of GeO₂ sample (Table S3), Y - the sequence number of coating reaction.

4. Size distributions (DLS) and TEM images of GeO₂@SiO₂ nanoparticles.

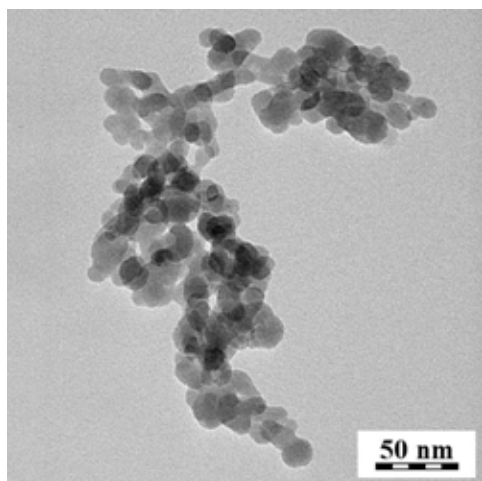


Figure S19 Synthesis 1-2

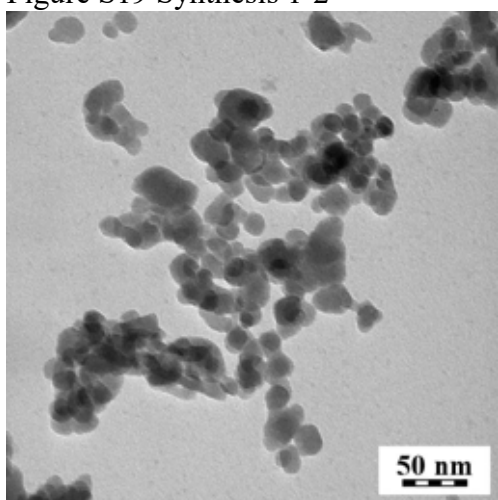
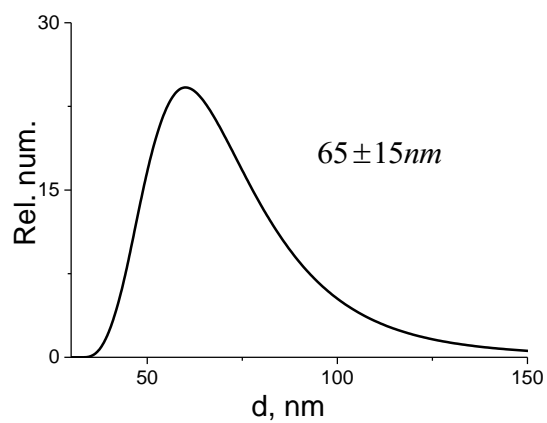


Figure S20 Synthesis 1-3

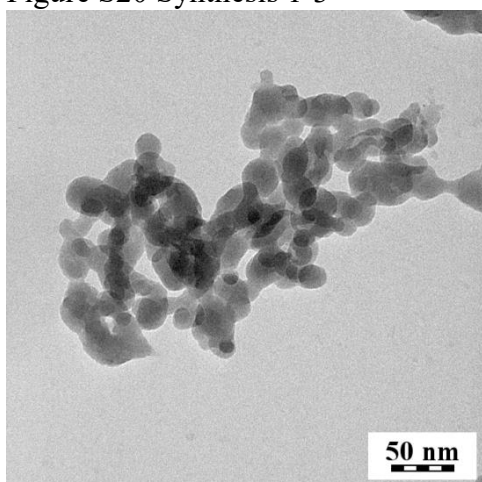
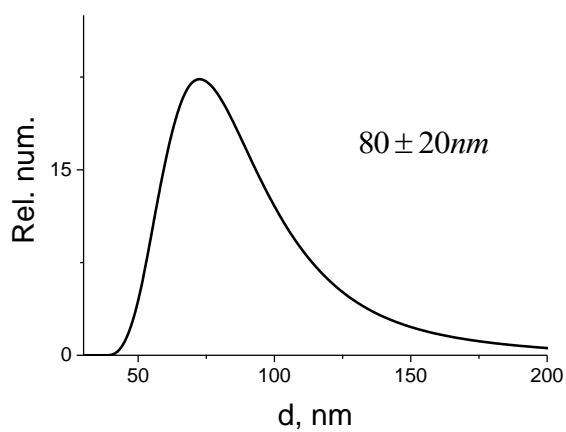
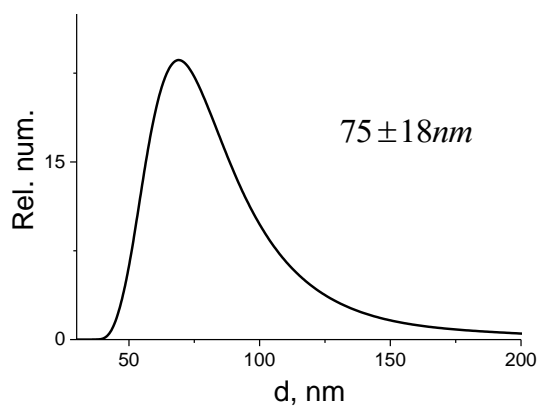


Figure S21 Synthesis 1-4



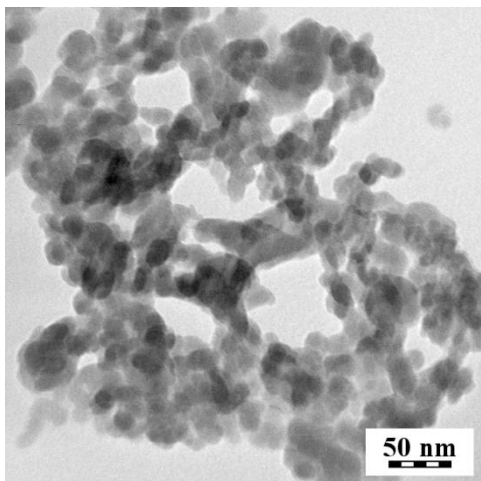


Figure S22 Synthesis 3-2

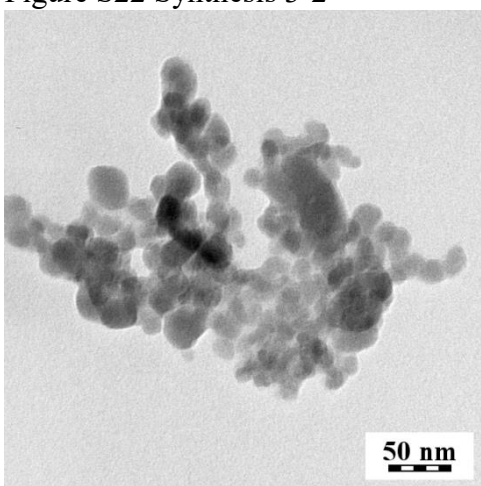
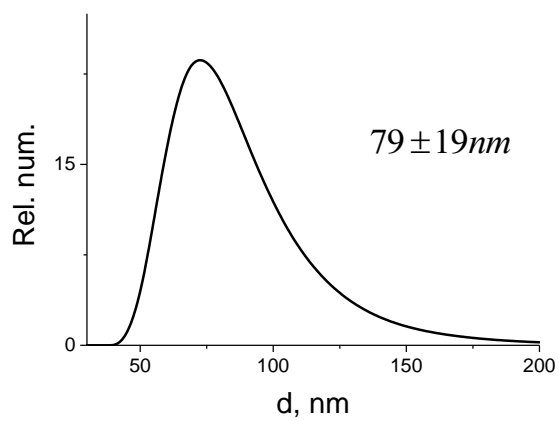


Figure S23 Synthesis 3-3

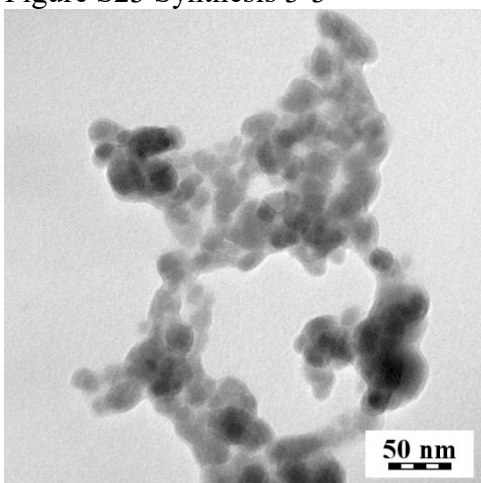
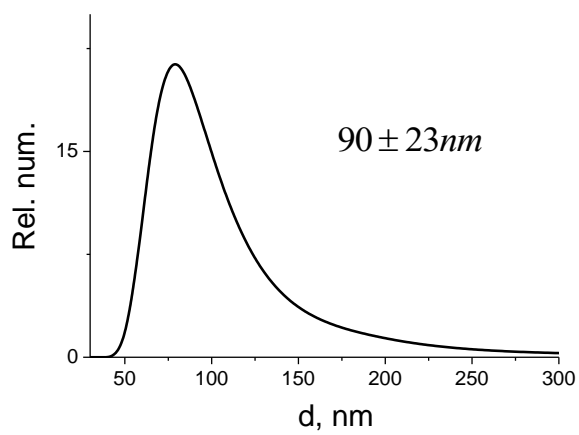
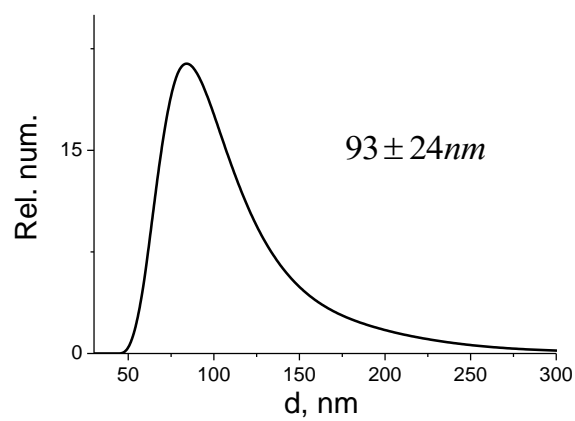


Figure S24 Synthesis 3-4



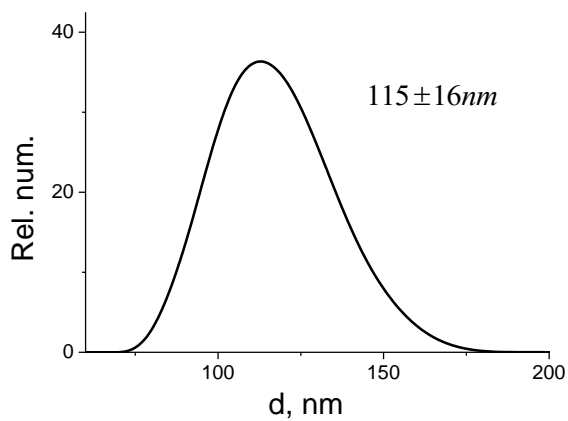
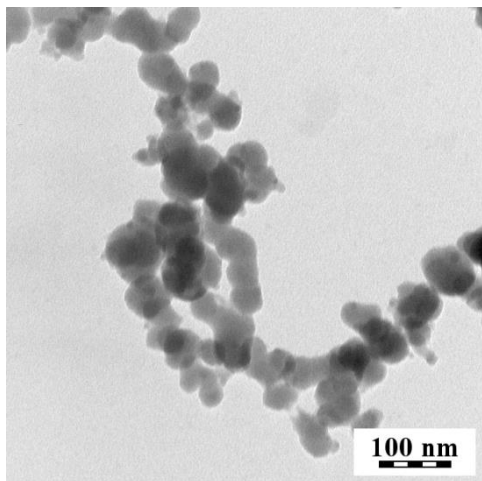


Figure S25 Synthesis 7-1

5. FTIR and FT-Raman spectroscopy

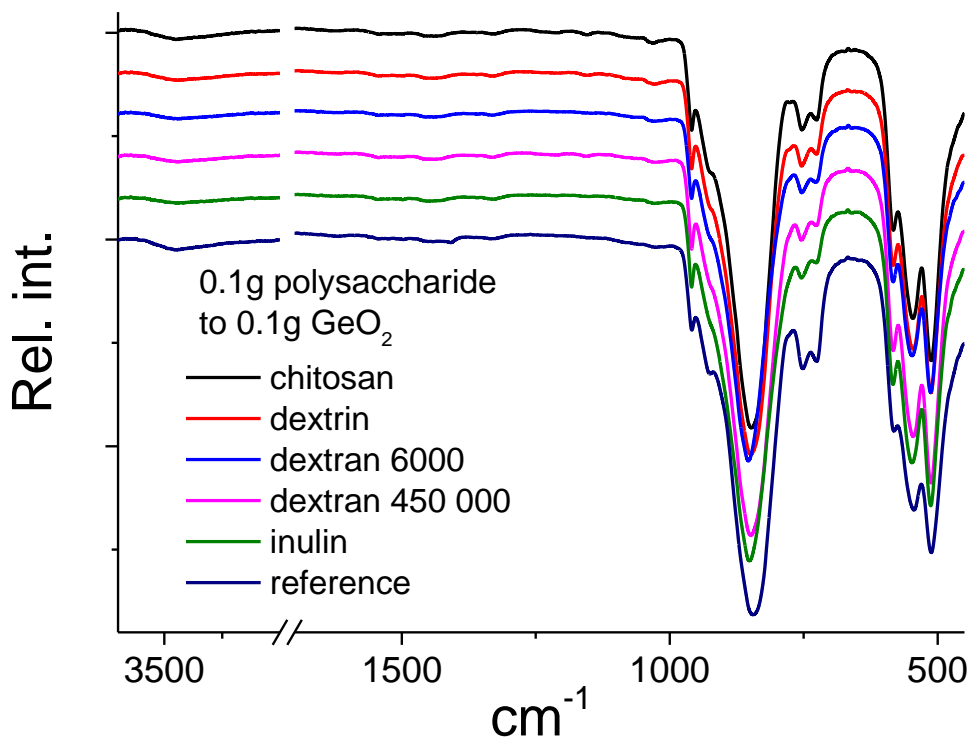


Figure S26 FTIR spectra of GeO₂ nanoparticles, synthesized in the aqueous solutions of polysaccharides

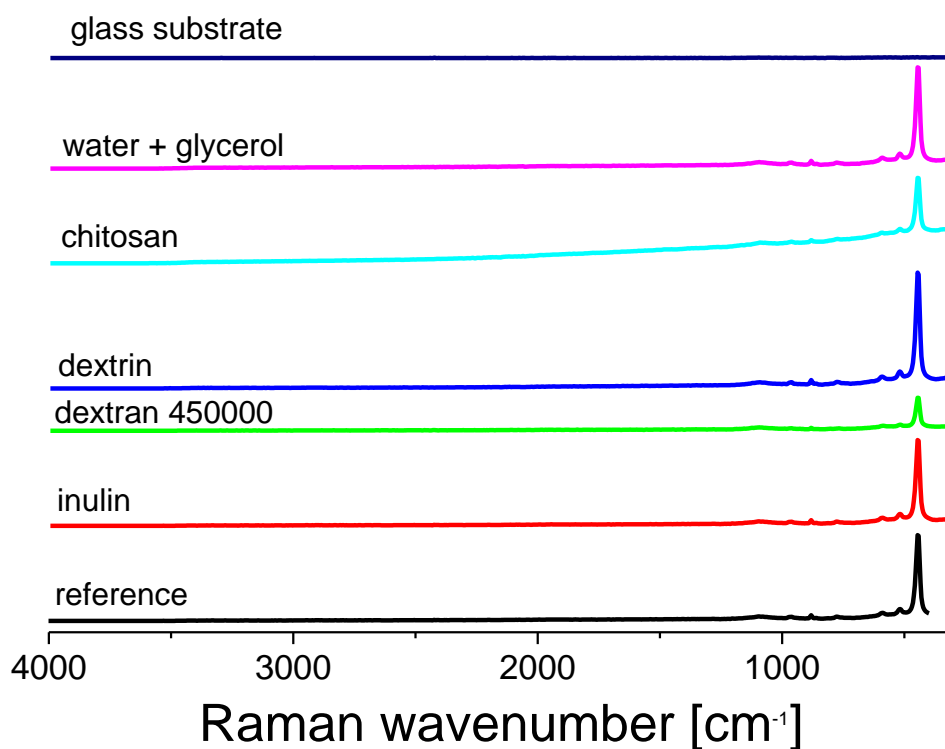


Figure S27 FT-Raman spectra of GeO_2 synthesized in the aqueous solutions of polysaccharides

The FTIR spectra of coated $\text{GeO}_2@\text{SiO}_2$ nanoparticles (Figure 5 c) were plotted in wavelength range $650\text{-}1200\text{ cm}^{-1}$ and fitted as a superposition of five Gaussian lines, having two of them fixed at 850 cm^{-1} and 1045 cm^{-1} . From the fits the ratio of the areas under the peak at 850 and 1045 cm^{-1} was calculated and used for estimation of the composition of coated $\text{GeO}_2@\text{SiO}_2$ nanoparticles. Black solid line – experimental spectrum; dashed lines - Gaussian fits; yellow solid line – sum of fitted peaks.

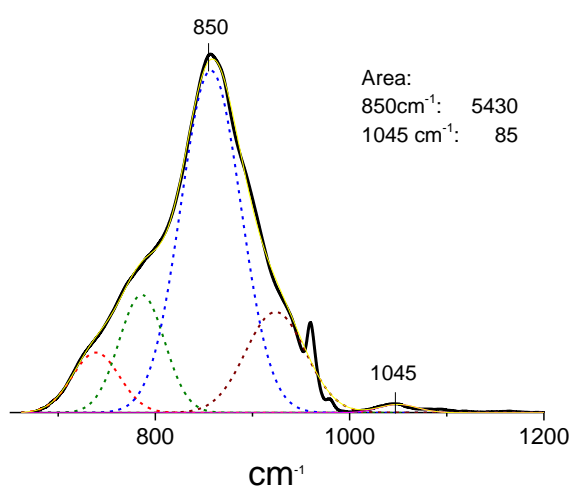


Figure S28 FTIR spectrum. Initial molar ratio GeO_2/TEOS - $1/0.0168$. Ratio from Gaussian fit $1/0.0156$

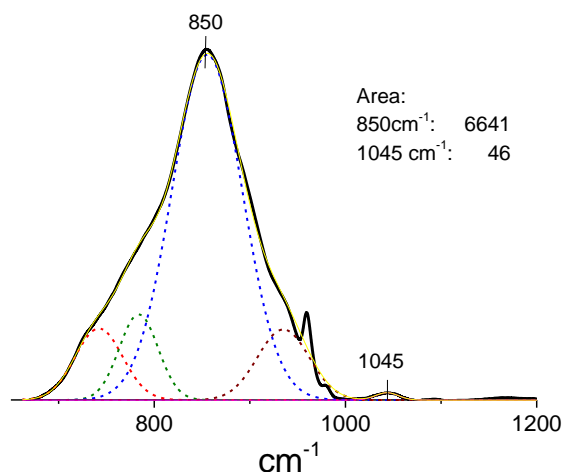


Figure S29 FTIR spectrum. Initial molar ratio GeO₂/TEOS – 1/0.0224. Ratio from Gaussian fit: 1/0.0069

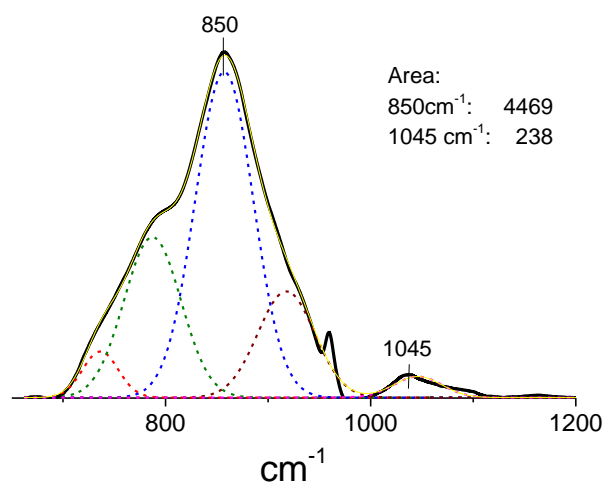


Figure S30 FTIR spectrum. Initial molar ratio GeO₂/TEOS – 1/1.54. Ratio from Gaussian fit: 1/0.0533

6. Calculation of the crystalline size

Table S. X-ray diffraction characterization of GeO₂ nanoparticles

| Sample | Cryst. plane | (100) | (101) | (110) | (102) | (111) | (200) | (112) |
|---------|--------------------|--------|--------|--------|--------|--------|--------|--------|
| water | q, Å ⁻¹ | 1,45 | 1,84 | 2,53 | 2,67 | 2,77 | 2,93 | 3,37 |
| | 2θ | 21 | 27 | 37 | 39 | 41 | 43 | 50 |
| | FWHM, rad | 0,0015 | 0,0016 | 0,0020 | 0,0022 | 0,0027 | 0,0024 | 0,0038 |
| | sinθ | 0,181 | 0,230 | 0,317 | 0,334 | 0,346 | 0,366 | 0,421 |
| | d, nm | 504 | 379 | 220 | 186 | 147 | 158 | 87 |
| ethanol | q, Å ⁻¹ | - | 1,83 | 2,53 | 2,66 | 2,75 | 2,91 | 3,37 |
| | 2θ | - | 26 | 37 | 39 | 40 | 43 | 50 |
| | FWHM | - | 0,229 | 0,317 | 0,332 | 0,344 | 0,364 | 0,421 |
| | sinθ | - | 0,0839 | 0,1533 | 0,0879 | 0,1226 | 0,1185 | 0,0833 |
| | d, nm | - | 59 | 23 | 39 | 27 | 26 | 32 |

7. Thermogravimetry:

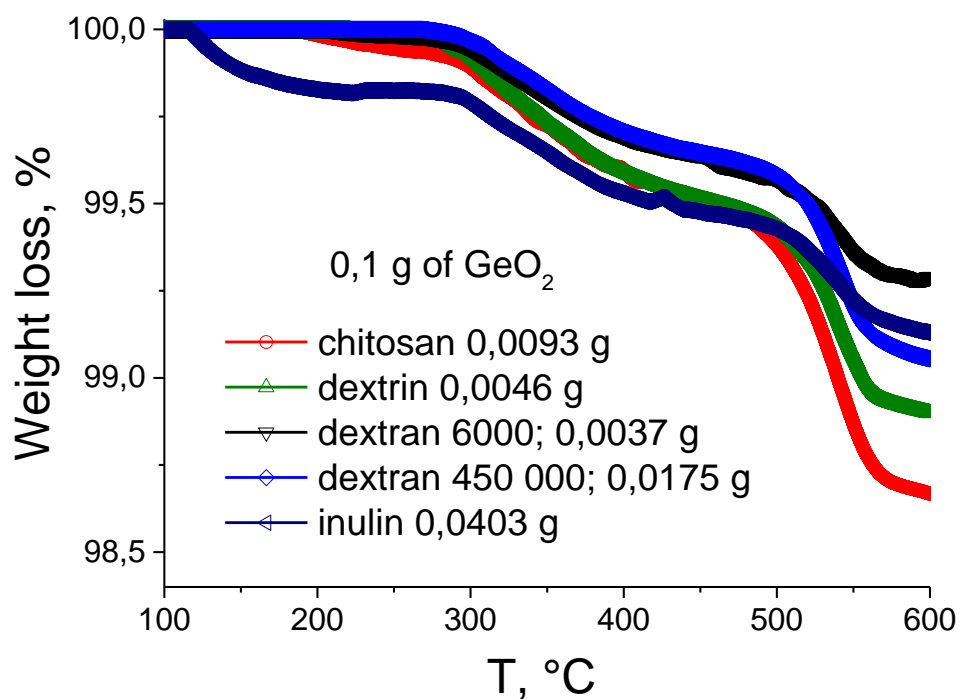


Figure S31 Thermogravimetry of GeO_2 nanoparticles, synthesized in aqueous solutions of polysaccharides

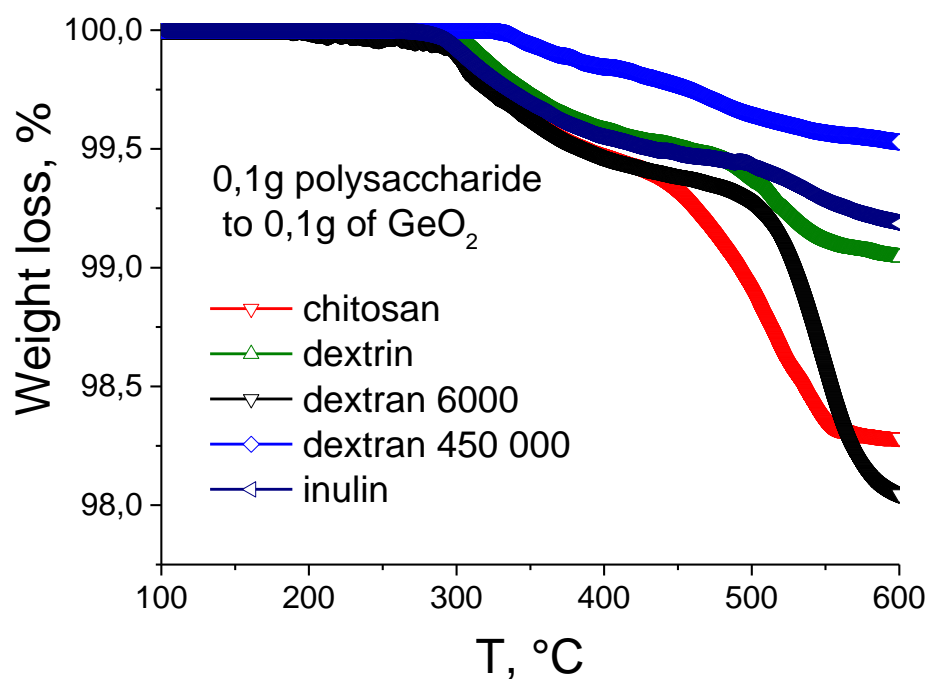


Figure S32 Thermogravimetry of GeO_2 nanoparticles, synthesized in aqueous solutions of polysaccharides

The amount of grafted polysaccharides was calculated from the sharp weight loss in temperature range 250-350°C.

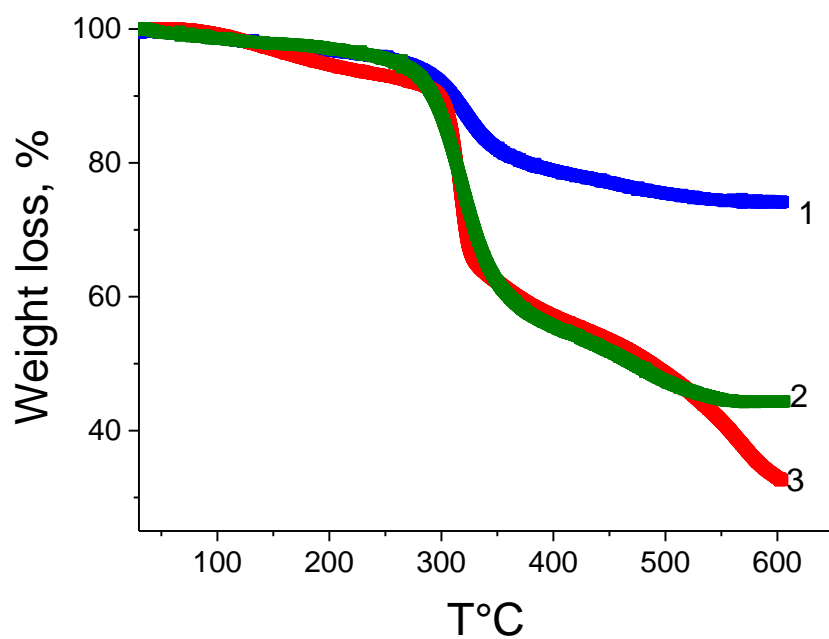


Figure S 33 TGA of GeO₂@SiO₂ particles with labelled polysaccharides: Dy-615-GG (1); FITC-GG (2); TRITC-dextran (3)