coatings

Supplementary Materials: Silica-Supported Assemblage of Cu^{II} Ions with Carbon Dots for Self-Boosting and Glutathione-Induced ROS Generation

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Citation: Bochkova, O.; Dovjenko, A.; Zairov, R.; Kholin, K.; Biktimirova, R.; Fedorenko, S.; Nizameev, I.; Laskin, A.; Voloshina, A.; Lyubina, A.; et al. Silica-Supported Assemblage of Cu^{II} Ions with Carbon Dots for Self-Boosting and Glutathione-Induced ROS Generation. *Coatings* **2022**, *12*, 97. https://doi.org/10.3390/coatings12010097

Academic Editor: Ajay Vikram Singh

Received: 13 December 2021
Accepted: 11 January 2022
Published: 15 January 2022

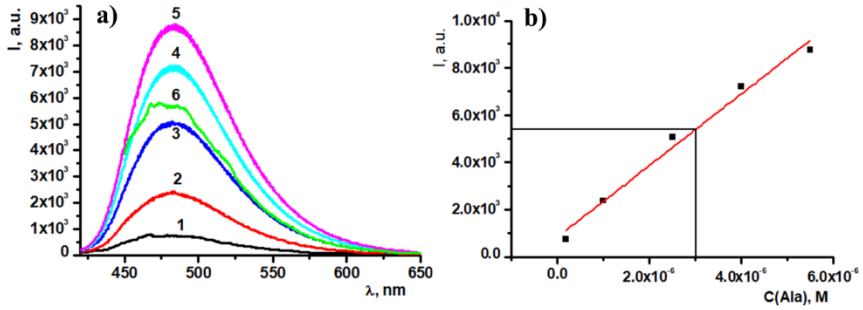

Figure S1. (**a**) The emission spectra of fluorophore, obtained from interaction of fluorescamine (0.55 mM) with various concentrations of alanine (1—1.6×10^{-7}, 2—1×10^{-6}, 3—2.5×10^{-6}, 4—4×10^{-6}, 5–5.5×10^{-2}), $SNs\text{-}NH_2$ (6) (0.05 $g \cdot L^{-1}$), at 0.025 M borate buffer pH = 9, λ_{ex} = 390 nm; (**b**) the calibration graphic.

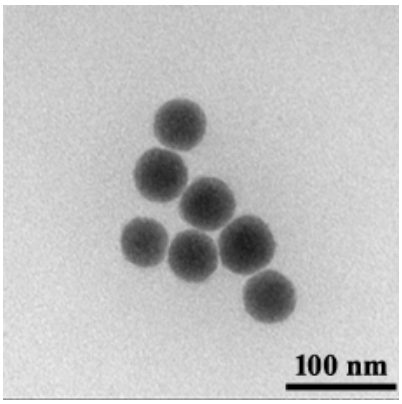

Figure S2. TEM-image of SNs.

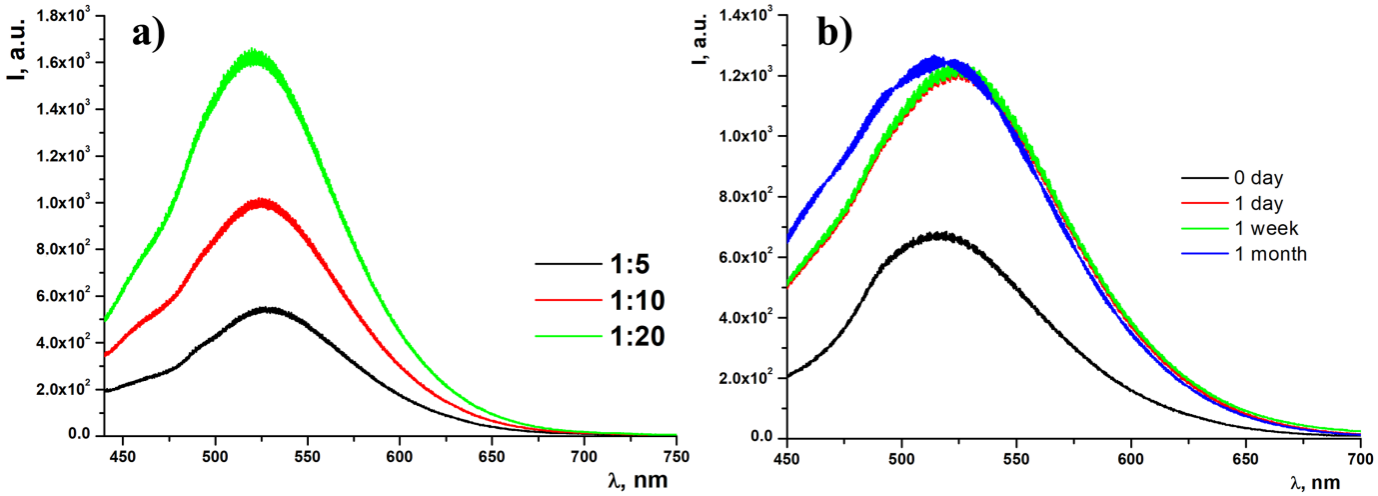

Figure S3. The emission spectra of water dispersion of SNs-NH_2-Cu^{II}-CDs (0.5 gL^{-1}): (**a**) prepared by mixing of water dispersions of SNs-NH_2-Cu^{II} and CDs at different concentration ratios (SNs:CDs) designated on the graphic, after 1 day of storage; (**b**) SNs-NH_2-Cu^{II}-CDs prepared at SNs:CDs=1:20 after various period of time of this system storage (also designated on the graphic). λ_{ex} = 420 nm, slit = 5 nm, voltage = 500 mV.

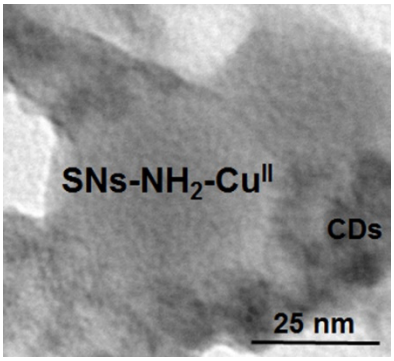

Figure S4. TEM-image of SNs-NH_2-Cu^{II}-CDs, where SNs are manifested by the larger silica spheres, while the CDs as black dots on their surface.

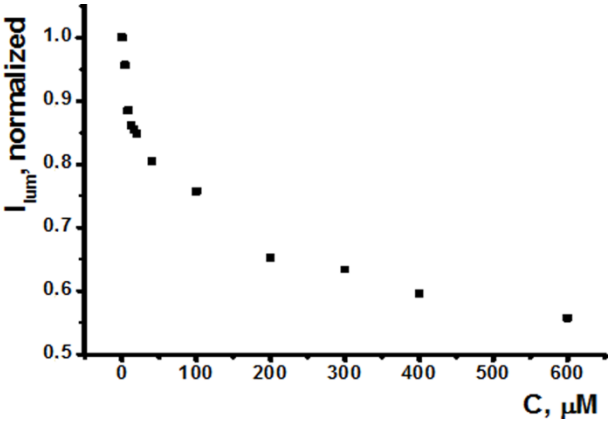

Figure S5. The dependence of the emission intensity of CDs (0.005 gL^{-1}) on the concentration of $CuCl_2$ in water; λ_{ex} = 420 nm, slit = 5 nm, voltage = 700 mV. The emission intensity was normalized to initial luminescent intensity of CDs before addition of water solution of $CuCl_2$.

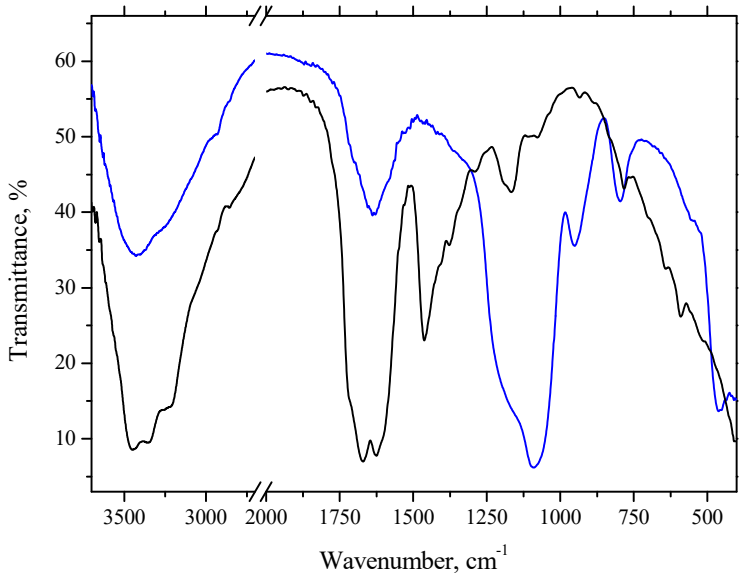

Figure S6. The Infrared spectrum of CDs (black) and SNs-NH_2-Cu^{II}-CDs (blue).

Infrared spectrum of CDs (black) contains bands at the region 3200–3500 cm^{-1}, most probably associated with stretching vibrations of OH and NH_2 groups, weak bands at 2865 and 2931 cm^{-1} correspond to stretching vibrations of aliphatic CH groups. Complex band at 1600–1750 cm^{-1} suggests the presence of amide group in the sample. Bands at 1462 cm^{-1} and 1377 cm^{-1} are tentatively interpreted as CH_2 and CH_3 deformations.

The spectrum of SNs-NH_2-Cu^{II}-CDs (blue) contains very strong bands of –Si–O–Si– deformations at 1100–1200 cm^{-1}. The characteristic bands of C-dots are whether weak compared to silica NP (1460–1370 cm^{-1}) or masked by absorption of water molecules at 3200–3600 and ~ 1650 cm^{-1}. However detailed analysis of the latter allows to find a weal shoulder at ~1720 cm^{-1}. The maximum at 1655 cm^{-1} can be associated with amide group and its shift compared to 1670 cm^{-1} in CDs spectrum may point to some changes in structure, related with this group.

Thus, the analysis of infrared spectra allows tentatively assume some changes in the CDs structures in the samples with silica nanoparticles, most probably affecting amide groups.

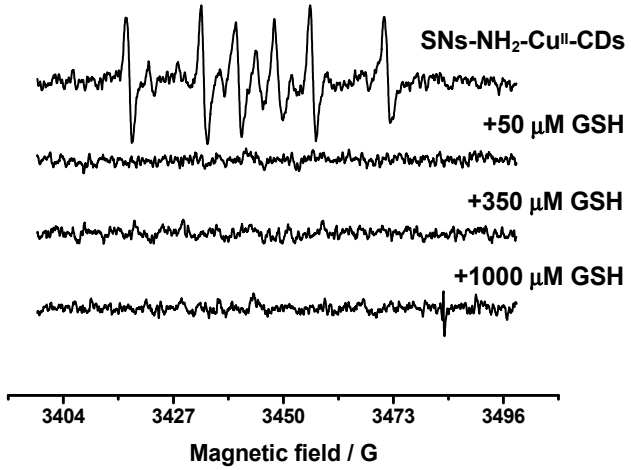

Figure S7. The ESR spectra of SNs-NH_2-Cu^{II}-CDs (0.5 gL^{-1}; 10 μM of Cu^{II}) in the presence of GSH at 50, 350 and 1000μM with DMPO spin trap (0.1 M) at 22 °C.

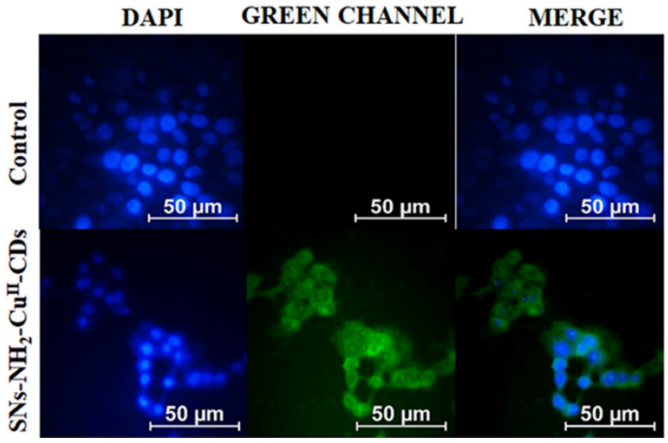

Figure S8. Fluorescent microscopy images of M-HeLa cells incubated with SNs-NH_2-Cu^{II}-CDs at 0.5 gL^{-1} (Nikon eclipse Ci, ×1000 oil).

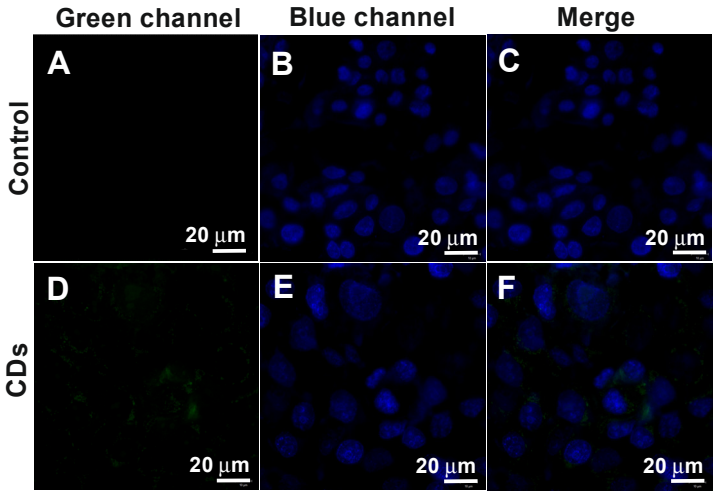

Figure S9. Confocal laser microscopy images of the control M-HeLa cell lines (**A**–**C**) and cells, incubated with CDs (**D**–**F**) at 0.5 gL^{-1} stained with DAPI.