

Ag/ α -Ag₂MoO₄/h-MoO₃ nanoparticles based microspheres: the synthesis and photosensitive properties

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Materials

L-cysteine (>99%) and silver acetate (>98.5%) were obtained from Acros. Ammonium heptamolybdate was obtained from Millipore (>99%). All chemicals were used as received. All solutions were prepared on the de-ionized water after their filtration on 0.45 μm filters.

Preparation of microspheres suspension

Microspheres suspension (CSS-3) was obtained by a one-pot synthesis in three stages. Firstly, the cysteine-silver solution (CSS-1) (1 ml.) was prepared using the following scheme^{1,2}: in the vessel filled with 0.325 ml of filtered and de-ionized water 0.3 ml of 0.01 M L-cysteine(L-cys)aqueous solution was added. After slightly mixing 0.375 ml of 0.01 M silver acetate (CH_3COOAg) was added. The ratio of the components L-cys: CH_3COOAg was 1:1.25 respectively. The resulting yellowish-white opalescent mixture was stirred at room temperature (25 °C) for 1 minute and the solution was stayed in dark place for 24 hours. As a result, the yellowish-green transparent solution (CSS-1) was obtained.

Secondly, for obtaining the gel (CSS-2) to 1 ml of CSS-1 0.03 ml (0.02 M) of ammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (AMT) was added.

Finally, to obtain microsphere suspension (CSS-3) CSS-2 was titrated by 0.1 M of alkali (sodium or potassium hydroxide) to values of pH equal to 7 ± 0.5 .

Methods

Viscosity measurements

The viscosity of solutions and hydrogels was measured with a vibratory viscometer SV-10 (A&D, https://www.aandd.jp/products/test_measuring/sv10/sv10.html). The vibration of the sensor plates was carried out with a frequency of 30 Hz and constant amplitude of about 1 mm. For viscosity measurements, 10 ml of CSS-2 solutions were prepared in the special polycarbonate cups (A&D) by addition of AMT into CSS-1 system. After complete gelation, the samples in the cups were transferred to the viscometer and measurements were recorded. All measurements were performed at room temperature (25°C).

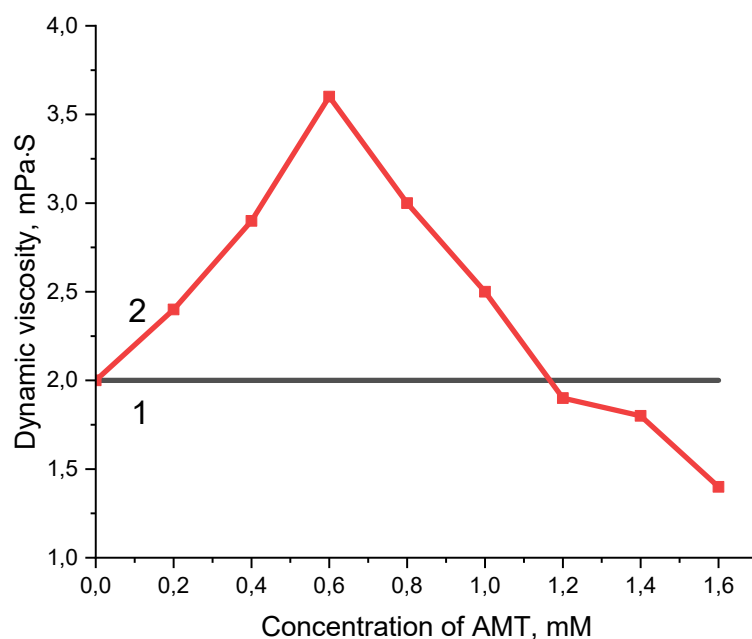


Figure S1. The viscosity curves of the completely formed CSS-1 (1) and CSS-2 (2) with various concentrations of AMT in the system.

XRD analysis

X-ray diffraction analysis of CSS-3 was carried out using a diffractometer ARL X'TRA (Thermo Fisher Scientific) equipped with a parabolic mirror and a pinhole collimator. The sample was centrifuged and the precipitate was washed with the de-ionized water.

TEM, SEM and elemental analysis

The microstructure and elemental mapping analysis of the samples were analyzed using a transmission electron microscope JEM-2100 (JEOL Ltd.), equipped with the energy dispersive X-ray spectrometer X-MAXN OXFORD instruments, with an accelerating voltage of up to 200 kV. The morphology of the samples was also studied using a scanning JEOL 6610 LV electron microscope (JEOL Ltd.) in the high vacuum mode with an accelerating voltage of 15 kV. To get image signals of low-energy secondary electrons were detected, providing topographical contrast, and high-energy back-up scattered (reflected) electrons that determine the composition and phase contrast. Sample preparation consisted of spraying of the samples on the surface of a thin conductive layer of platinum and drying in vacuum (10^{-4} Pa).

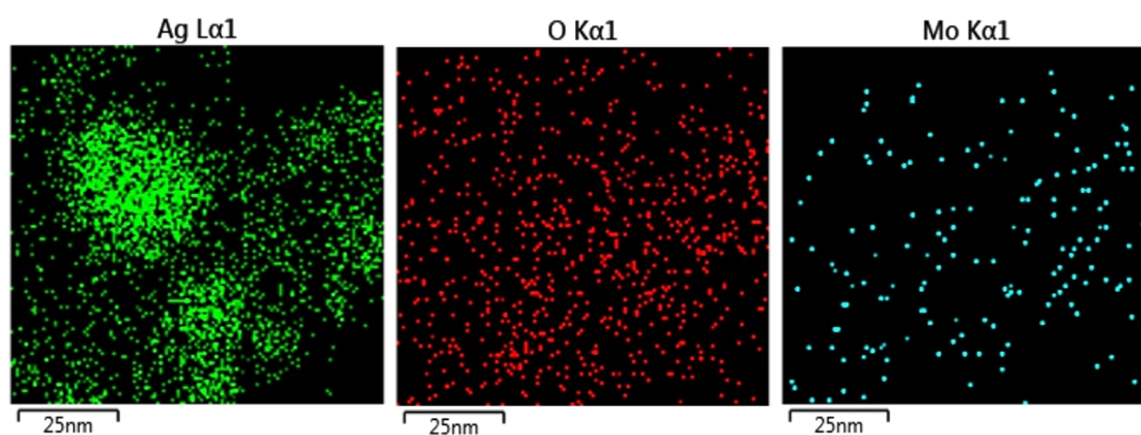


Figure S2. Distribution of elements in the CSS-3 by elemental mapping analysis.

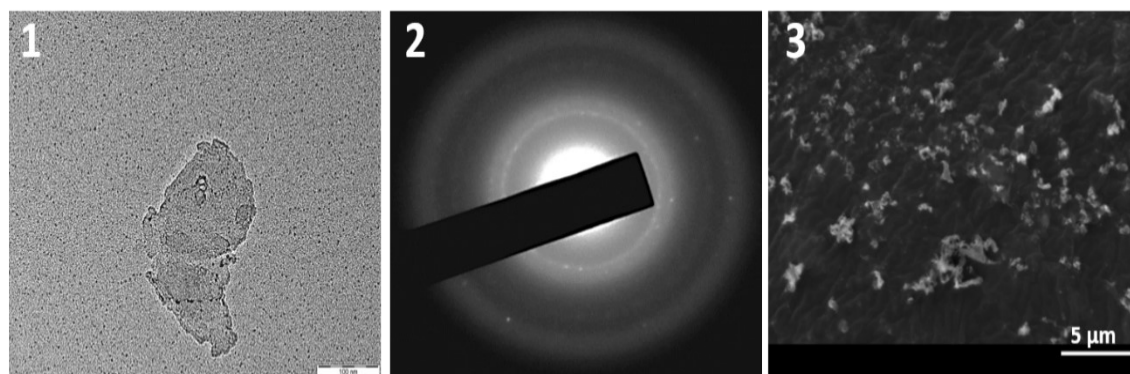


Figure S3. TEM image (1), SAED (2), SEM image (3) of CSS-1.

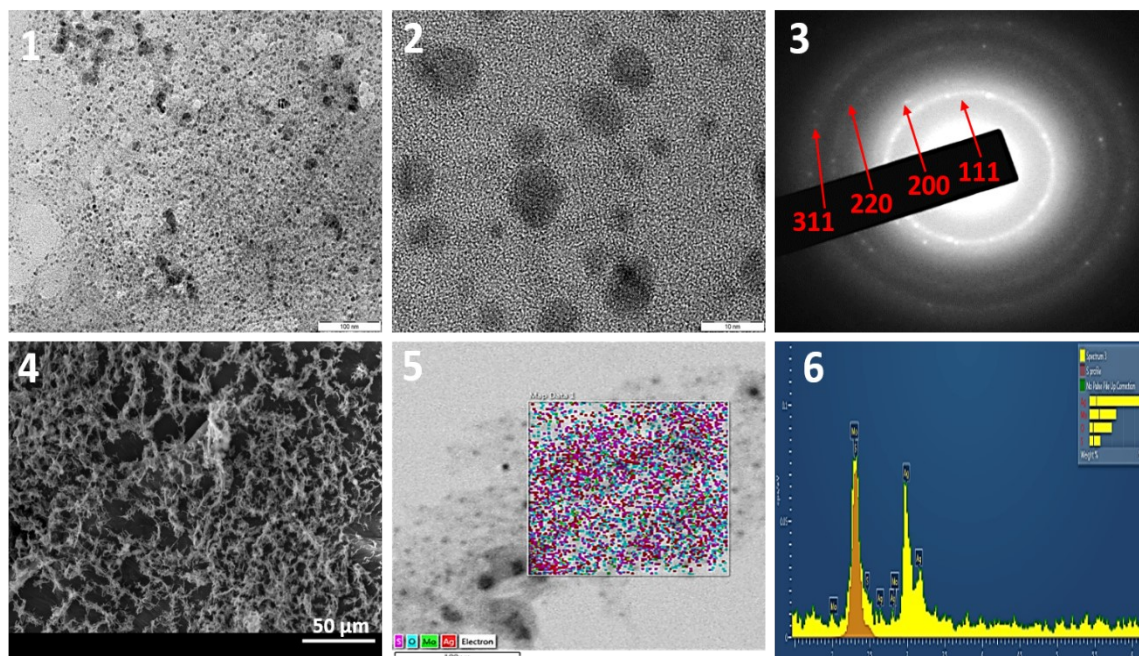


Figure S4. TEM images (1,2), SAED (3), SEM image (4) and elemental mapping analysis (5,6) of CSS-2.

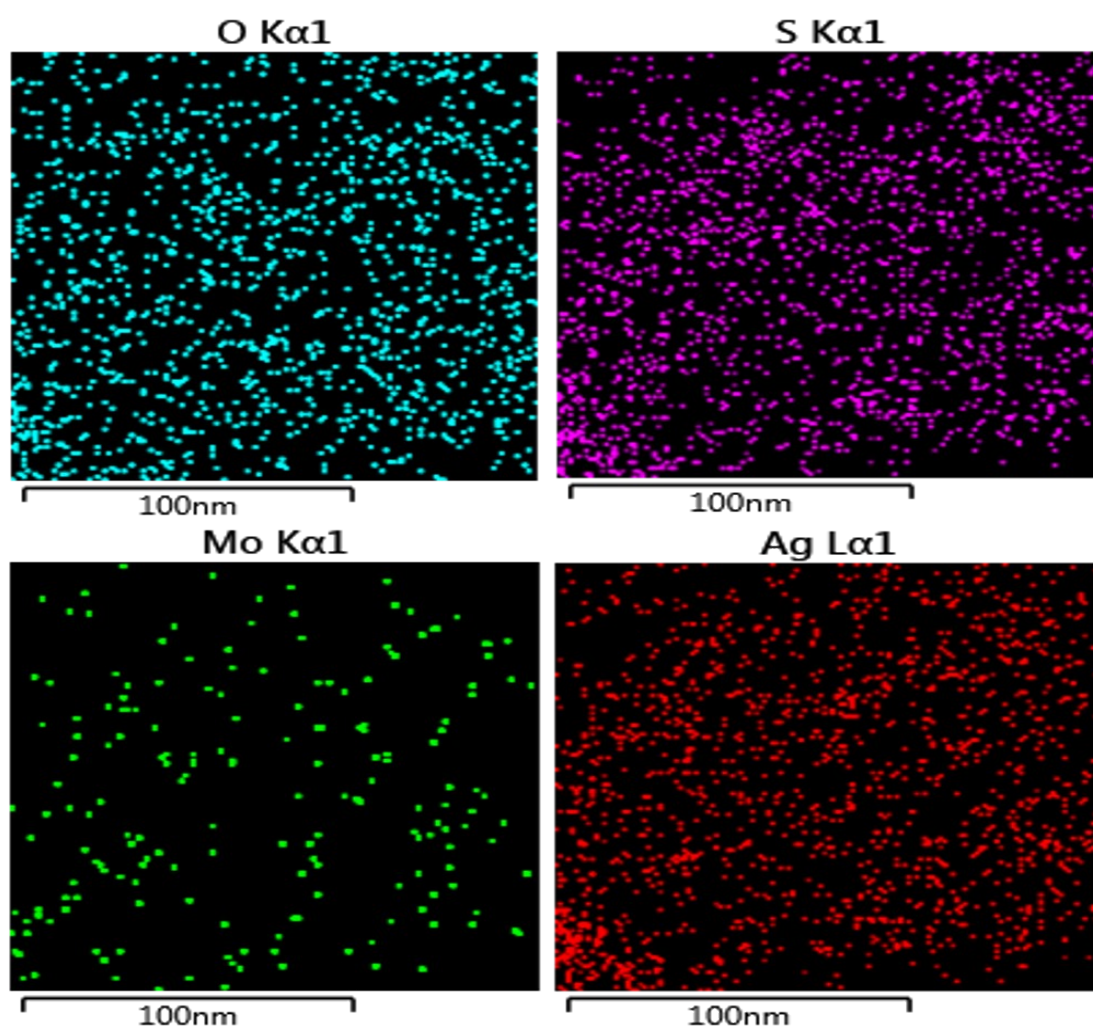


Figure S5. Distribution of elements in the CSS-2 by elemental mapping analysis.

UV analysis

Electronic spectra of the samples were recorded on the UV spectrophotometer Evolution Array (Thermo Scientific) in a quartz cell with a 1 mm path length.

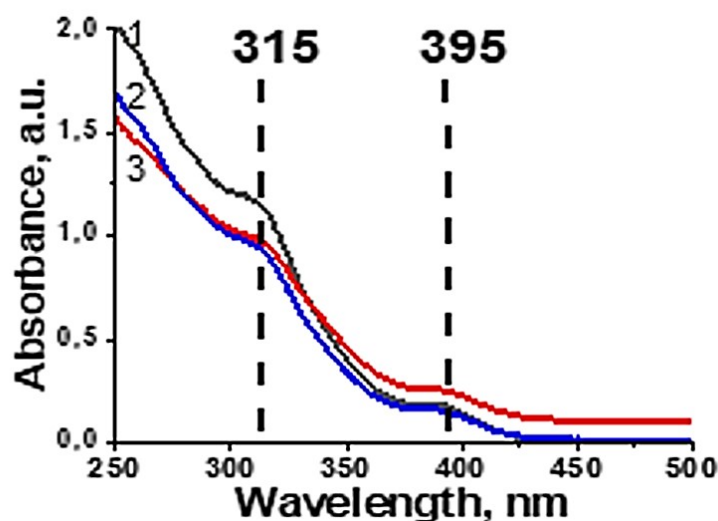


Figure S6. UV-spectra of the systems: 1 – CSS-1, 2 – CSS-2 at $C(\text{AMT}) = 0.01 \text{ mM}$, 3 – CSS-2 at $C(\text{AMT}) = 0.03 \text{ mM}$.

pH measurements

The pH of the solutions was measured using a Seven Multi S70 (Mettler Toledo) pH meter.

DLS and zeta-potential measurements

Measurement of intensity of light scattering in the studied samples was carried out using analyzer Zetasizer Nano ZS (Malvern) with a He-Ne laser (633 nm), power of 4 mW. For the correct analysis of the particle sizes and zeta-potential CSS-1 and CSS-2 systems diluted in 4 times were used. Concentration of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in CSS-2 system was also reduced in 4 times to the point of 0.4 mM. This concentration does not initiate gelation in the diluted system, but there are observed changes in the structure of aggregates of CSS-1. All measurements were carried out at 25°C in the backscattering configuration (173°), providing the highest sensitivity of the device. Mathematical processing of the results of the obtained cross-correlation functions of the diffuse light intensity fluctuations g_2 was carried out in the program Zetasizer Software, where the solution of the obtained equation of the g_2 dependence on the diffusion coefficient was performed by the cumulant method. The result of the solution was the function $z(D)$. The hydrodynamic radius of the scattering particles were calculated from the diffusion coefficients by the Stokes-Einstein formula: $D = kT/6\pi\eta R$, where D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the medium, R is the radius of the scattering particles. Measurements of the electrophoretic mobility of aggregates in the samples were carried out in aU-shaped capillary cuvettes. Zeta potential distributions were calculated using the Henry equation: $UE = 2ezf(Ka)/3Z$, where UE – electrophoretic mobility, z – zeta potential, e – dielectric constant, Z – viscosity, and $f(Ka)$ – Henry's function, $f(Ka) = 1.0$ for systems with hydrodynamic diameter of particles less than 200 nm.

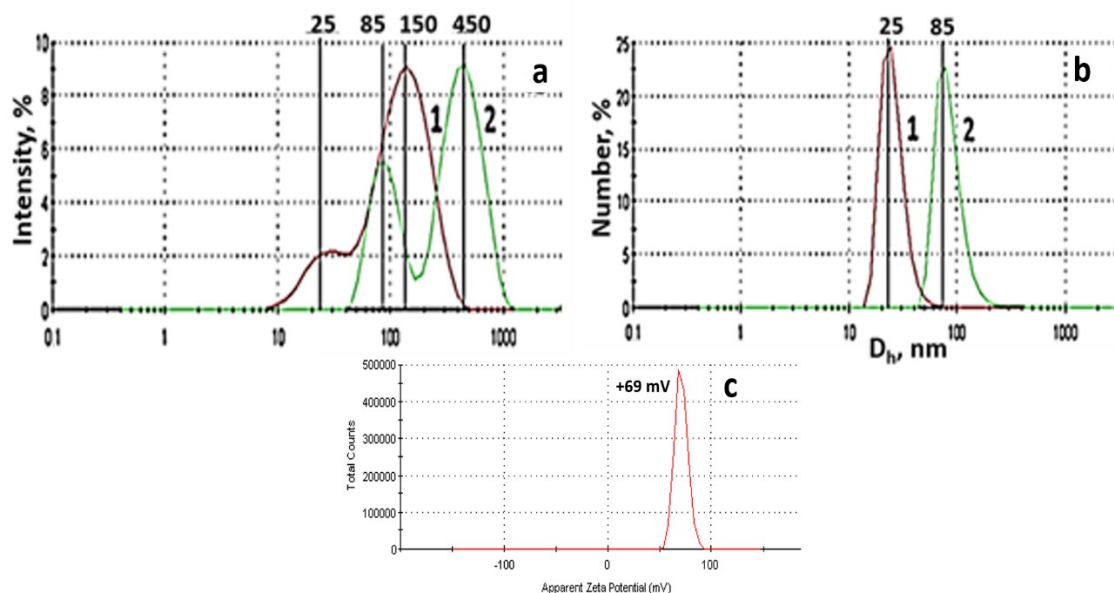


Figure S7. DLS: distribution by intensity (a) and distribution by number (b), 1 – CSS-1, 2 – CSS-2, C(AMT) = 0.01 mM; zeta-potential measurements of CSS-1 (c).

FTIR analysis

FTIR spectra of the samples were recorded on a Vertex 70 spectrometer (Bruker) in the range of 7000–400 cm^{-1} at a resolution of 4 cm^{-1} . The number of scans was 32. CSS-1, CSS-2 and CSS-3 samples were preliminarily frozen in liquid nitrogen. The obtained precipitates were carefully washed with de-ionized water and vacuum dried at 25°C. The methylene blue (MB), CSS-3 with MB before and after UV exposure were centrifugated and precipitates were carefully washed with de-ionized water and vacuum dried at 25°C. The 22 mg of the precipitate was mixed with 700 mg of potassium bromide and pressed into a pellet.

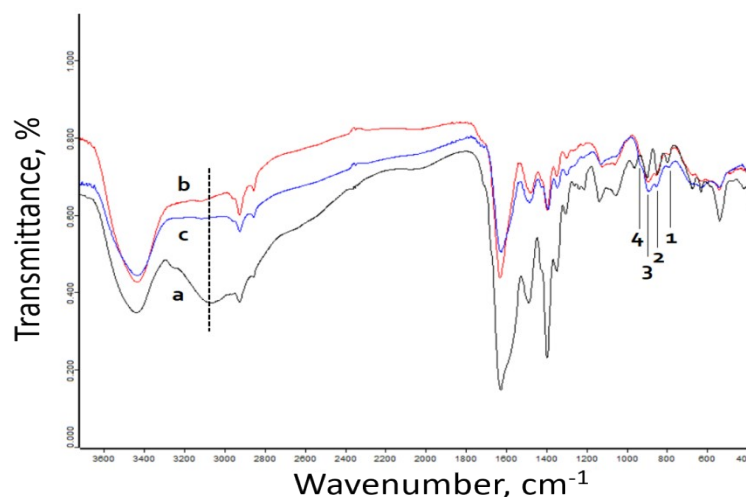


Figure S8. FTIR spectra of CSS-1 (a), CSS-2 (b) and CSS-3 (c). 1,2–785 cm^{-1} and 875 cm^{-1} - characteristic bands of the h-MoO_3 ,³ 3,4 – 914 cm^{-1} and 971 cm^{-1} - characteristic bands of symmetric valence vibrations $\nu_1(\text{A}_1)$ of MoO_4^{2-} .⁴

Photodegradation of methylene blue dye

Transmittances of the UV-light of the samples were recorded on the UV photometer KFK-3 (ZOMZ) in a polystyrene cell with a path length of 1cm. The photosensitivity was determined by the change in the percentage of transmission (τ) of 0,1 ml (2,5%) water solution of the methylene blue dye at adding of 1 ml (0,01%) CSS systems to it at wavelengths of 635-685 nm on a KFK-3 photometer. The transmission at a wavelength of 395 nm was additionally measured for the purpose of qualitative control of the presence of AgNPs. Photodegradation experiments were carried out using natural light irradiation by standing at room light for 12 hours and by irradiating with a 250 W UV generator for 30 minutes. The samples were placed in a polystyrene cell, after which it was irradiated using one of the described methods. After irradiation, the samples were placed in a photometer, where the transmission was recorded on each wavelength from the 635-685 nm with the step of 5 nm.

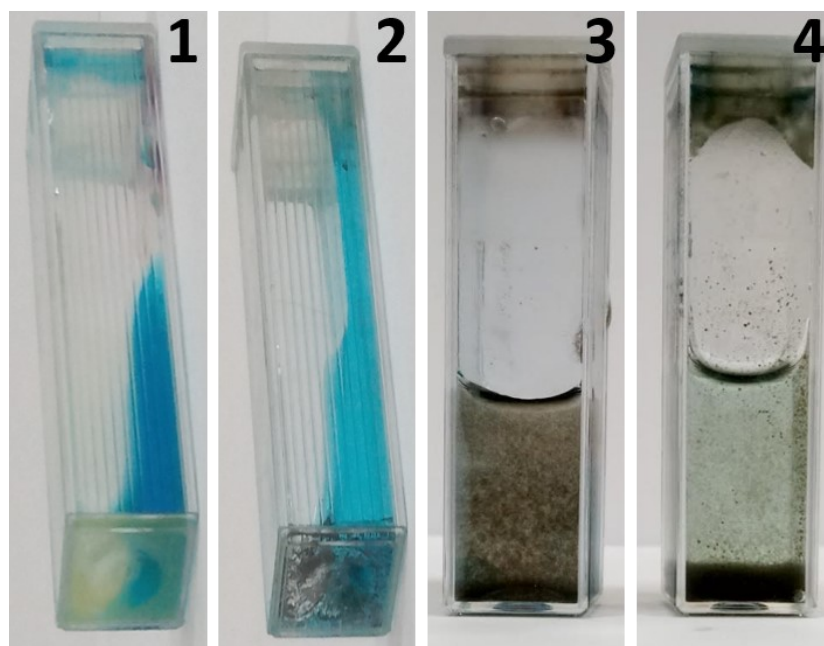


Figure S9. The images of the MB with CSS systems after the UV exposure: 1 – CSS-1 at natural light irradiation, 2 – CSS-1 at UV lamp irradiation, 3 – CSS-2 at UV lamp irradiation, 4 – CSS-3 at UV lamp irradiation.

References:

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