Electronic supplementary information (ESI)

Layered double hydroxide-based antioxidant dispersions of high colloidal and functional stability

Adél Szerlauth, Szabolcs Muráth, and Istvan Szilagyi*

MTA-SZTE Lendület Biocolloids Research Group, Interdisciplinary Excellence Centre, Department of Physical Chemistry and Materials Science, University of Szeged, 1 Rerrich Béla tér, H-6720 Szeged, Hungary

*Corresponding author. Email: szistvan@chem.u-szeged.hu

†Electronic supplementary information (ESI) available.

Equations used for data evaluation

Equation S1. The Stoke-Einstein equation was applied to calculate hydrodynamic radius (R_h) from the translational diffusion coefficient (D) determined in dynamic light scattering (DLS) measurements.[1]

$$R_h = \frac{k_B T}{6\pi\eta D} \qquad (S1)$$

where k_B is the Boltzmann constant, T is the absolute temperature and η is the dynamic viscosity of the medium.

Equation S2. Stability ratio (W) was used to describe the colloidal behavior of the particle dispersions.[2]

$$W = \frac{\frac{1}{R_h(0)} \frac{dR_h(t)}{dt}|t \rightarrow 0 \,(fast)}{\frac{1}{R_h(0)} \frac{dR_h(t)}{dt}|t \rightarrow 0} \qquad (S2)$$

where t is time, $R_h(0)$ is the hydrodynamic radius of the particles and ($fast$) refers to fast aggregation, which was achieved in 1 M NaCl solutions. Under this experimental condition, only attractive forces are present in the LDH dispersions and thus, the aggregation is controlled solely by the diffusion of the particles.

Equation S3. Lambert-Beer's law was used to determine the remainder percentage of 2,2-diphenyl-1-picrylhydrazyl radicals ($DPPH\%$) after the antioxidant test reaction finished.[3]

$$DPPH\% = \frac{DPPH_T}{DPPH_0} = \frac{\frac{A_T}{\varepsilon_{DPPH}\, l}}{\frac{A_0}{\varepsilon_{DPPH}\, l}} = \frac{A_T}{A_0} \qquad (S3)$$

where $DPPH_T$ and $DPPH_0$ are the final and initial concentration of DPPH radicals, respectively, A_T and A_0 are the corresponding absorbance values, ε_{DPPH} is the molar extinction coefficient of DPPH in methanol and l is the length of the optical path.

Equation S4. The electrophoretic mobilities (u) were converted to zeta potentials (ζ) with Smoluchowski's equation.[4]

$$\zeta = \frac{u\eta}{\varepsilon_0 \varepsilon} \qquad (S4)$$

where ε_0 is the permittivity of the vacuum and ε is the relative permittivity of the medium.

Equation S5. The inverse Debye length (κ) includes the contribution of the ionic species to the electrical double layer formation.[5]

$$\kappa = \sqrt{\frac{2N_A e^2 I}{\varepsilon \varepsilon_0 k_B T}} \qquad (S5)$$

where N_A is Avogadro's constant, e is the elementary charge and I is the ionic strength.

References

1   B. J. Berne and R. Pecora, *Dynamic light scattering*, Robert E. Krieger Publishing, Malabar, 1990.

2   M. Elimelech, J. Gregory, X. Jia and R. A. Williams, *Particle deposition and aggregation: Measurement, modeling, and simulation*, Butterworth-Heinemann Ltd., Oxford, 1995.

3   W. Brand-Williams, M. E. Cuvelier and C. Berset, *Food Sci. Technol.-Lebensm.-Wiss. Technol.*, 1995, **28**, 25-30.

4   A. V. Delgado, E. Gonzalez-Caballero, R. J. Hunter, L. K. Koopal and J. Lyklema, *Pure Appl. Chem.*, 2005, **77**, 1753-1805.

5   W. B. Russel, D. A. Saville and W. R. Schowalter, *Colloidal dispersions*, Cambridge University Press, Cambridge, 1989.

Scheme S1. The scheme of DPPH reaction to estimate the antioxidant capacity of the materials. DPPH radicals react with the antioxidant (RH) compound with reactive hydrogen to produce the saturated DPPH-H substance and a less reactive radical (R˙).
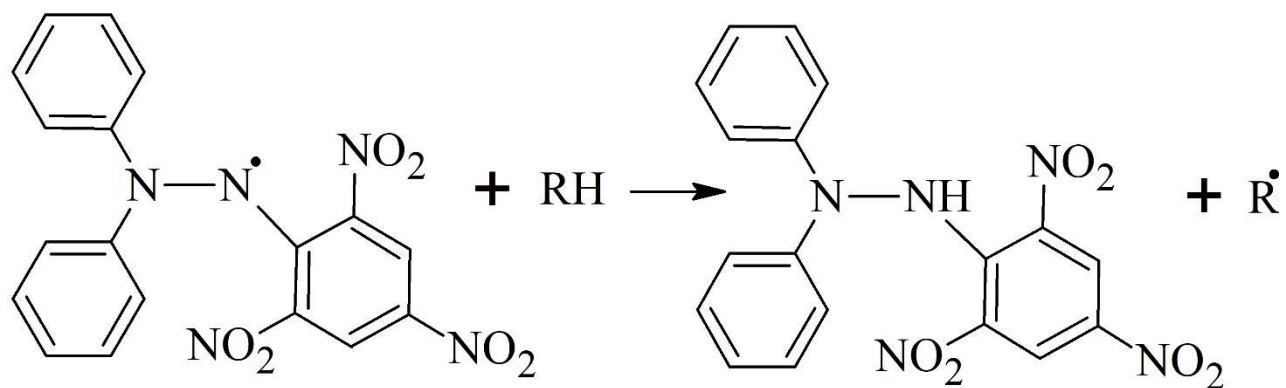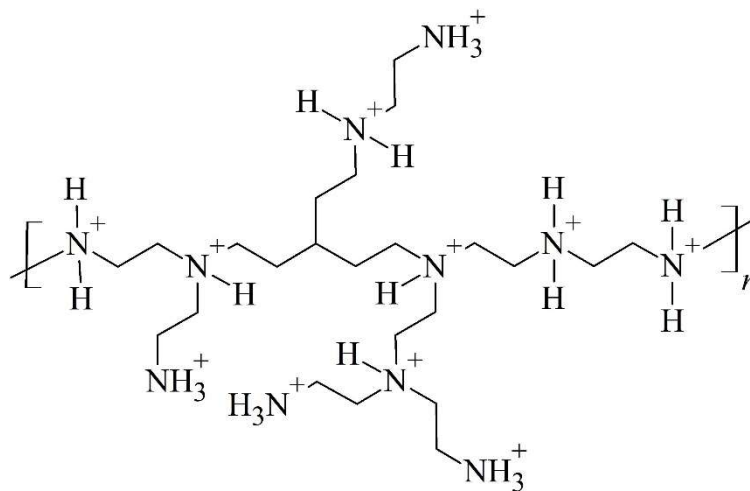
Fig. S1. The molecular structure of the polyelectrolytes used in this study. The structure is shown in the fully ionized mode. Protamine sulfate (PS) is not shown, since it is a mixture of various polypeptides with arginine amino acids and an approximate nitrogen content of 22%.

Polyethyleneimine (PEI)

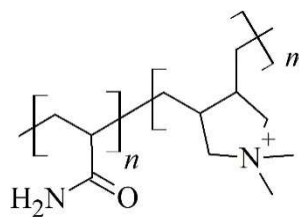Poly(acrylamide-*co*-diallyl dimethyl ammonium chloride) (PAAm-*co*-DADMAC)

Fig. S2. The time-dependent aggregation of EtOH-EA-LDH functionalized with (A) PEI, (B) PS and (C) PAAm-*co*-DADMAC. Three different doses are shown. Stable dispersions were obtained at the lowest and highest doses, while the intermediate doses resulted in particles with close to neutral charge leading to rapid aggregation.
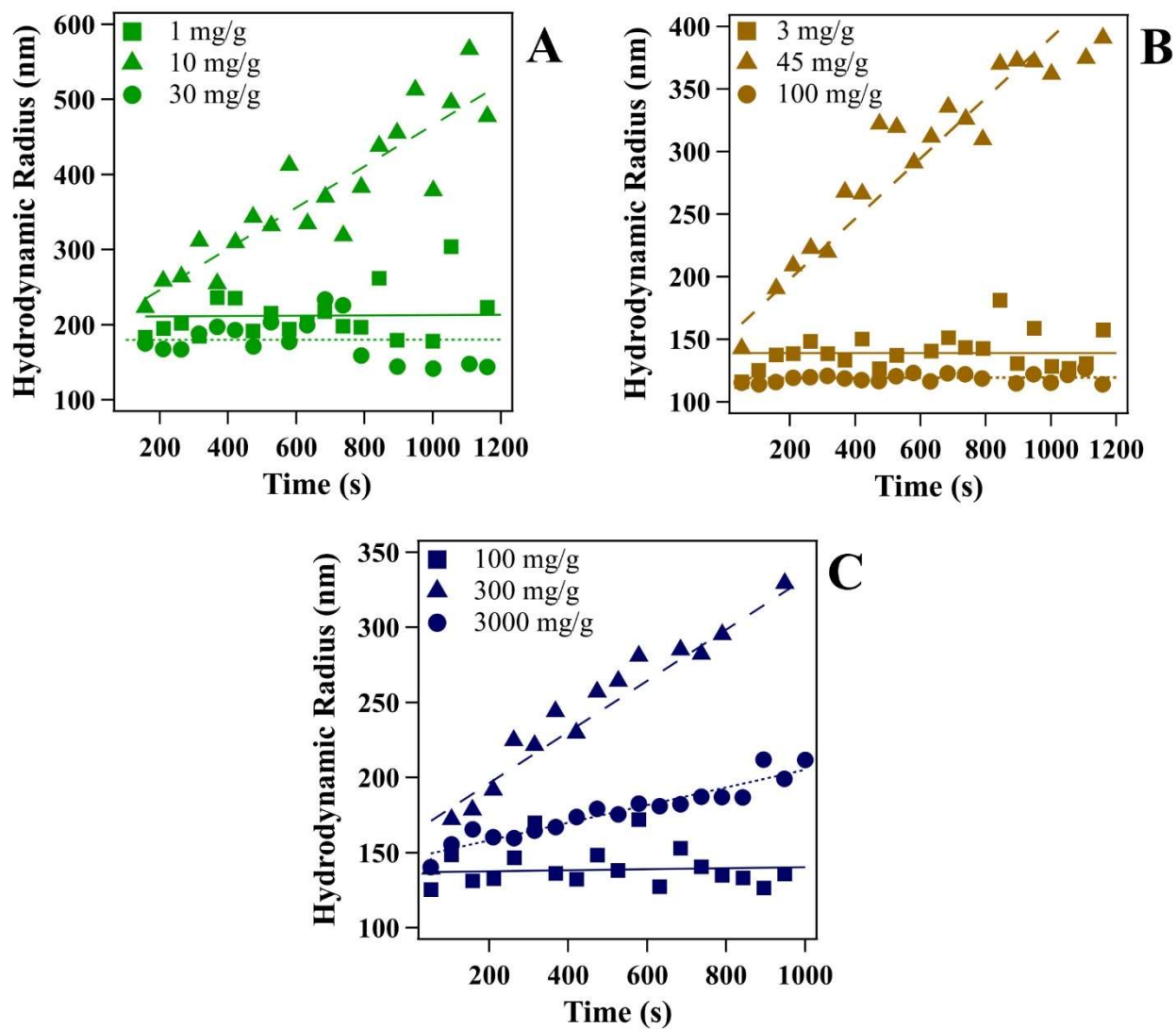
Fig. S3. The TEM micrographs of the LDHs investigated. (A) Bare and untreated EA-LDH consisted of plate-like crystalline particles with round edges. (B) EA-LDHs treated with ethanol (EtOH-EA-LDH) consisted of irregular, aggregated particles on the TEM sample grid. Very similar morphology was observed for (C) PEI, (D) PS and (E) PAAm-*co*-DADMAC-coated particles. Scale bars represent 100 nm.
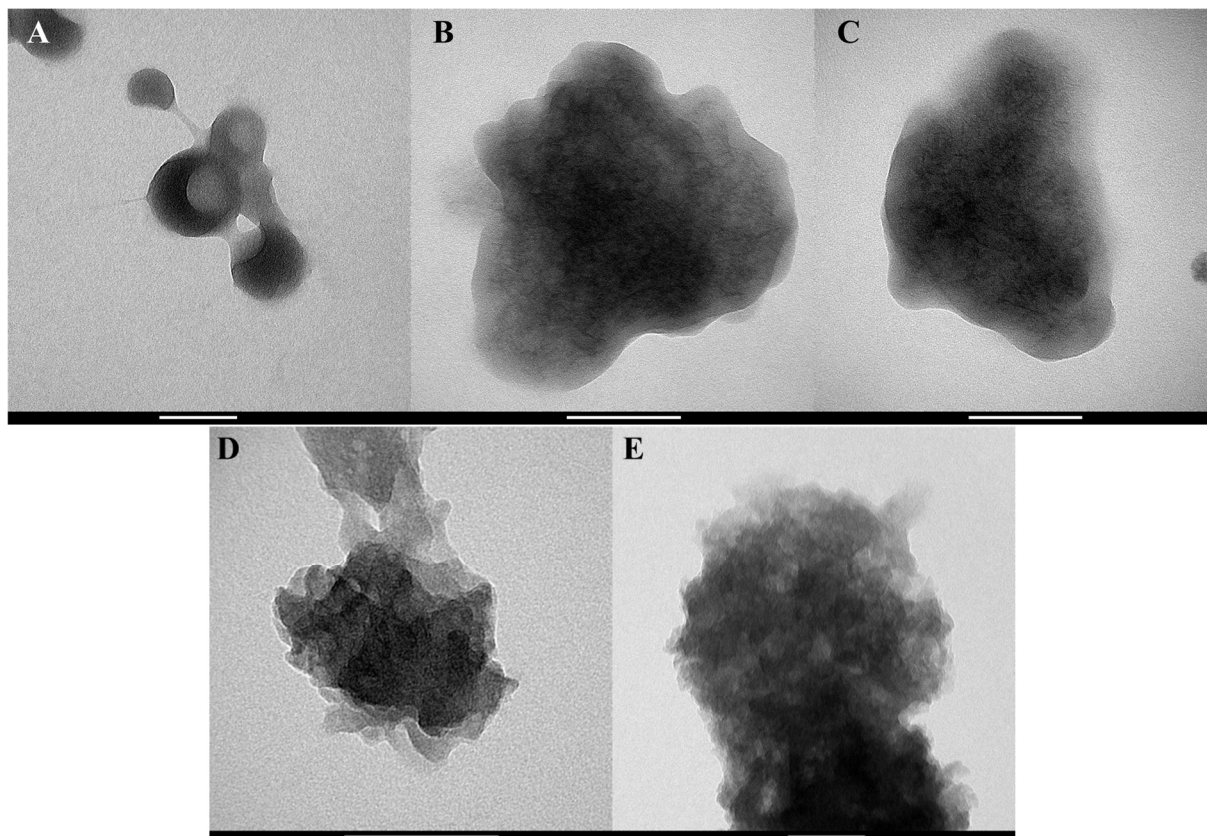
Fig. S4. Changes in absorbances at 517 nm (corresponding to the DPPH level) in the presence of EtOH-EA-LDH (A) and EtOH-EA-LDH/PEI (B) at different EA concentrations. Remaining DPPH concentration as a function of time in the presence of the polyelectrolytes applied at concentrations corresponding to the ASP doses.