Design, characterization and application of layered double hydroxide-based colloidal systems

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Theses of the PhD work

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1. Introduction and aim of the study

Colloidal dispersions are present in various fields of academic science and in more applied disciplines. For instance in industrial processes, like manufacturing of foods, cosmetics or textiles, colloidal dispersions play an important role. Besides, preparation of pharmaceutical products and wastewater treatment processes also rely on dispersed particle systems. Colloidal stability of these dispersions is of especial importance and thus, control of particle aggregation must be optimized to achieve the desired properties. In the present thesis, both stabilization and destabilization of particle dispersions are utilized in different areas as discussed below.

The first objective was the synthesis of layered double hydroxide (LDH, an anionic clay) particles with various composition and morphology. The preparation processes were optimized to obtain the desired properties for further applications.

The second objective was to functionalize the surface of the LDH particles with synthetic polyelectrolytes. The main goal here was to design LDH-polyelectrolyte composites of remarkable colloidal stability and surface functionalities for later applications.

The third objective was to assess the applicability of the obtained LDH-polyelectrolyte systems as antioxidant agents after immobilization of redox active metal complexes. The main question was their efficiency and selectivity in decomposition of reactive oxygen species.

The fourth objective was to study the effect of sodium dodecyl sulfate (SDS) adsorption on the charge and aggregation features of LDH particles to optimize the dispersion properties for two-step preparation of LDH materials of high specific surface area.

The fifth objective was to apply *in situ* and *ex situ* synthesized LDH compounds in water remediation processes. The tasks to be accomplished included removal of anionic contaminants and to separate the solid LDH-contaminant phase from the systems.

2. Experimental part

The core particles of the LDH-polyelectrolyte hybrids were synthesized by combined flash co-precipitation and hydrothermal treatment. The latter step was not applied during *in situ* syntheses. LDHs of high specific surface area and optimal pore size distribution were prepared via SDS adsorption and subsequent calcination and rehydration processes. To functionalize the LDHs with polyelectrolytes and to immobilize metal complexes in the structures, the sequential adsorption method was applied.

The size and charge of the developed particles and composites were measured with dynamic (DLS) and electrophoretic (ELS) light scattering, respectively. The same techniques were used for the optimization of the loading of each component during surface functionalization and to assess the colloidal stability under different experimental conditions.

Electron paramagnetic resonance (EPR) spectroscopy was used to investigate the coordination geometry around the metal ions in the complexes. The antioxidant activity was measured in colorimetric assays using UV-Vis spectrophotometry, which was also applied to study water purification processes.

Transmission (TEM) and scanning (SEM) electron microscopy measurements were carried out to investigate the size and morphology of the particles. BET measurements were performed to determine the specific surface area and pore size distribution.

The LDH materials obtained in different synthetic processes were extensively characterized in solid state with X-ray diffraction (XRD; information on the lamellar structure) and infrared spectroscopy (IR; information on the composition and structure).

Finally, the antioxidant capacities were tested in enzymatic assays and in reduction of redox active model compounds. Bench-top water treatment experiments were performed to assess adsorption capacities.

3. Novel scientific results

T1. Polyelectrolyte bilayer was successfully built on LDH particles giving rise to the formation of hybrid materials of high colloidal stability.

Two oppositely charged polyelectrolytes, namely poly(styrene sulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC), was adsorbed sequentially on the LDH particles. The outer polyelectrolyte layer provided strong stabilizing forces through electrostatic and steric interactions. The developed composite of remarkable colloidal stability served as an excellent carrier material for further investigation, as discussed later.

T2. Redox active metal complexes, as potential mimics for antioxidant enzymes, were immobilized within the layers of the LDH-PSS-PDADMAC hybrid without sacrificing the high dispersion stability.

The following layers were adsorbed on the LDH substrate: PSS, copper(II)-bipyridine [$Cu(Bpy)_2$], PDADMAC and iron(III)- citrate [$Fe(Cit)_2$] with the sequential adsorption method. The doses of the components were tuned at each step leading to high structural and colloidal stability of the dispersions. Such an LDH-based multilayered hybrid material is reported first time in the literature. Structural investigations revealed that the immobilized complexes interacted on the surface leading to a redox active network in the composite.

T3. The LDH-PSS-[$Cu(Bpy)_2$]-PDADMAC-[$Fe(Cit)_2$] multilayered composite showed excellent activity in dismutation of superoxide radical anions and was highly selective for these radicals.

The immobilized metal complexes were able to operate similarly to the native antioxidant enzymes by mimicking the active centres. Therefore, as demonstrated in biochemical assays, the LDH-PSS-[$Cu(Bpy)_2$]-PDADMAC-[$Fe(Cit)_2$] composite is considered as a highly active antioxidant agent due to the synergistic effect of the metal complexes

upon co-immobilization. Besides, excellent selectivity was achieved since no significant antioxidant activity was observed in other types of antioxidant test reactions.

T4. Charging and aggregation of LDH particles were optimized by varying the dose of SDS molecules in the synthetic process in order to obtain mesoporous LDH materials.

SDS adsorption on oppositely charged LDH particles led to charge neutralization and overcharging and to the formation of unstable and stable colloids, respectively. Based on these findings, LDHs of different morphology were prepared by varying the SDS dose prior to the calcination and rehydration processes during synthesis. A clear correlation was found between the colloidal stability of the precursor materials and the mesoporous structure of the LDH products.

T5. The adsorption capacity of the mesoporous LDHs prepared in T4 was determined in the presence of the nitrate and dichromate ions. For the latter, the obtained values indicated the highest capacity within the literature data reported earlier.

By tuning the SDS dose during preparation, a mesoporous LDH adsorbent of high anion exchange capacity was obtained, which showed great efficiency in removal of water contaminant inorganic anions. Most importantly, such capacity was extremely high for toxic dichromate ions, the largest among the previously published data. The LDH was regenerated in standard processes and recycled several times. Based on these results, the developed material can be recommended as adsorbent in water purification processes.

T6. LDHs were synthesized by co-precipitation in acidic mine waters *in situ* and the optimization of the experimental conditions led to the development of purification processes for efficient removal of sulfate ions.

In cooperation with CSIRO, the leading Australian network for applied research, LDHs were *in situ* prepared in acidic mine waters of high

electrolyte content. Remarkable sulfate removal capacity was achieved by tuning the preparation conditions. The method was recommended for water remediation processes upon contamination by inorganic anions including sulfate, which occurs in considerable concentration in wastewaters of various origin.

T7. For the separation of the LDH adsorbent prepared in T6 from the wastewater samples, a dilution-based method was developed and optimized to avoid the use of traditional flocculants.

The *in situ* formed LDH particles, due to the formation of a gel-like structure, showed great colloidal stability and prevented the efficient separation of the solid material from the samples. Traditional coagulants such as polyelectrolytes and multivalent ions failed in destabilization of the dispersed systems. The results indicated that the samples are made of particle networks due to their high concentrations. The coherent structure was destabilized by dilution. The dilution rates and sedimentation times were determined and hence, an efficient procedure was recommended for water purification using *in situ* prepared solid particles as adsorbents.

4. Applications

The present results are applicable in various fields, as follows. The developed LDH-polyelectrolyte-metal complex composites are of high antioxidant activity as well as remarkable functional and colloidal stability. Therefore, these are promising candidates as antioxidant agents in heterogeneous systems (e.g., in the textile, cosmetic or oil industry), where native antioxidants usually fail. In development of efficient water purification processes, LDHs prepared either *ex situ* or *in situ* may open great opportunities. The former ones can act as adsorbents owing to their high specific surface area and advantageous pore size distribution. The latter ones, which were studied in cooperation with CSIRO, offer solution for remediation of mine wastewaters, which is an important issue worldwide. We hope that our results will contribute to the successful development and application of antioxidant or water purification agents in the near future.

5. List of publications

5.1 Publications serving as the basis of the thesis

[1] Zoltán Somosi, Marko Pavlovic, István Pálinkó, István Szilágyi

Effect of polyelectrolyte mono- and bilayer formation on the colloidal stability of layered double hydroxide nanoparticles

Nanomaterials, volume 986, November 2018, page 986

DOI: 10.3390/nano8120986 SJR Indicator: Q1

IF_{2018}: 4.034 Independent Citation: 8

[2] Zoltán Somosi, Szabolcs Muráth, Péter Nagy, Dániel Sebők, Grant Douglas, István Szilágyi

Contaminant removal by efficient separation of *in-situ* formed layered double hydroxide compounds from mine wastewaters

Environmental Science: Water Research & Technology, volume 5, October 2019, page 2251-2259

DOI: 10.1039/C9EW00808J SJR Indicator: Q1

IF_{2019}: 4.251 Independent Citation: 2

[3] Gábor Varga, Zoltán Somosi, Zoltán Kónya, Ákos Kukovecz, István Pálinkó, István Szilágyi

A colloid chemistry route for the preparation of hierarchically ordered mesoporous layered double hydroxides using surfactants as sacrificial templates

DOI: 10.1016/j.jcis.2020.08.118 SJR Indicator: D1

Journal of Colloid and Interface Science, volume 581, January 2021, page 928-938

IF_{2020}: 7.489 Independent Citation: 2

[4] Zoltán Somosi, Nóra V. May, Dániel Sebők, István Pálinkó, István Szilágyi

Catalytic antioxidant nanocomposites based on sequential adsorption of redox active metal complexes and polyelectrolytes on nanoclay particles

Dalton Transactions, volume 50, January 2021, page 2426-2435

DOI: 10.1039/D0DT04186F SJR Indicator: Q1

IF_{2020}: 4.390 Independent Citation: 0

5.2 Conference participations connected to the thesis

[1] Zoltán Somosi, István Szilágyi, István Pálinkó: Synthesis and polyelectrolyte functionalization of layered double hydroxide nanoparticles

35th International Conference on Solution Chemistry, Szeged, Hungary, 2018, Poster

[2] Zoltán Somosi, István Szilágyi, István Pálinkó: Influence of Polyelectrolyte Mono- and Bilayer Formation on the Charging and Aggregation of Layered Double Hydroxide Nanoparticles

Euroclay, Paris, France, 2019, Oral Presentation

[3] Zoltán Somosi, István Szilágyi: Layered double hydroxides for remediation of mining wastewaters

XLII. Kémiai Előadói Napok, Szeged, Hungary, 2019, Oral Presentation

[4] Zoltán Somosi, István Szilágyi, István Pálinkó: Sequential adsorption of polyelectolyte layers and guest molecules on layered double hydroxide nanoparticles

Okinawa Colloids, Nago, Japan, 2019, Oral Presentation

5.3 Publications not connected to the thesis

[1] Szabolcs Muráth, Zoltán Somosi, Ildikó Tóth, Etelka Tombácz, Pál Sipos, István Pálinkó

Delaminating and restacking MgAl-layered double hydroxide monitored and characterized by a range of instrumental methods

Journal of Molecular Structure, volume 1140, July 2017, page 77-82

DOI: 10.1016/j.molstruc.2016.10.056 Quality of paper: Q3

IF_{2017}: 2.011 Independent Citation: 4

[2] Marko Pavlovic, Paul Rouster, Zoltán Somosi, István Szilágyi

Horseradish peroxidase-nanoclay hybrid particles of high functional and colloidal stability

Journal of Colloid and Interface Science, volume 524, April 2018, pages 114-121

DOI: j.jcis.2018.04.007 Quality of paper: D1

IF_{2018}: 6.361 Independent Citation: 12

[3] Szabolcs Muráth, Zoltán Somosi, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó

Novel route to synthesize CaAl- and MgAl-layered double hydroxides with highly regular morphology

Journal of Sol-Gel Science and Technology, volume 89, December 2018, page 844-851

DOI: 10.1007/s10971-018-4903-8 Quality of paper: Q2

IF_{2018}: 1.986 Independent Citation: 2

[4] Szabolcs Muráth, Szilárd Sáringer, Zoltán Somosi, István Szilágyi

Effect of ionic compounds of different valences on the stability of titanium oxide colloids

Colloids and Interfaces, volume 2, August 2018, page 32

DOI: 10.3390/colloids2030032 Quality of paper: -

IF: ESCI Independent Citation: 14

[5] Szabolcs Muráth, Nizar Alsharif, Szilárd Sáringer, Bojana Katana, Zoltán Somosi, István Szilágyi

Antioxidant materials based on 2D nanostructures: A review on recent progresses

Crystals, volume 10, March 2020, page 148

DOI: 10.3390/cryst10030148 Quality of paper: Q2

IF_{2020}: 2.53 Independent Citation: 6

5.4 Conference participations not connected to the thesis

[1] Szabolcs Muráth, Zoltán Somosi, ldikó Tóth,Etelka Tombácz, Pál Sipos, István Pálinkó: Delaminating and restacking MgAlLayered double hydroxide monitored and characterized by a range of instrumental methods

33rd European Congress on Molecular Spectroscopy, Szeged,

Hungary, 2016, Poster

[2] Zoltán Somosi, István Szilágyi, István Pálinkó: Anion specific effects on the size and charge of monodisperse layered double hydroxide particles

11th Conference on Colloid Chemistry, Eger, Hungary, 2018,

Poster

∑ **Publications:**

Connected to dissertation: 4 Total: 9

∑ **Impact factor:**

Connected to dissertation: 20.164 Total: 33.052

∑ **Independent citations:**

Connected to dissertation: 12 Total: 50