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Potential Applications of Hybrid Layered Double Hydroxide (LDH) Particles in Pulp and Paper Production

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Functionalization of papermaking pulp fibers using inorganic particles was investigated as a novel approach. Different layered double hydroxide (LDH) particles were used in peroxide bleaching of thermomechanical pulp (TMP) and in oxygen bleaching of eucalyptus kraft pulp. LDH particles were also tested as binding sites for optical brightening agents (OBA) that are commonly used in paper production. The surface chemistry of LDH-treated pulps was examined using X-ray photoelectron spectroscopy (XPS) and apparent contact angle with water. Adsorbed LDH was not detected by XPS on the fiber surfaces after the bleaching trials, but it had a clear impact on the processes. LDH particles modified with terephthalate anions decreased the consumption of hydrogen peroxide and increased opacity by 3 units in TMP. Unmodified LDH particles enhanced the selectivity in oxygen delignification of kraft pulp, leading to 10% gain in ISO brightness and reduction of 2 units in Kappa number in comparison with conventional processes. Paper strength properties were unaffected in the presented system. After bleaching with LDH, the amount of anionic groups on pulp surfaces was increased. Also, the retention of OBA onto TMP fibers was improved with modified LDH particles. LDH proved to have great potential for current and prospective applications in pulp and paper manufacture.

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INTRODUCTION

What if the multitude of chemicals that are currently used in pulp processing, stock preparation, sheet formation, retention, paper coating, and other applications could be replaced with just a few multifunctional environment-friendly additives? In addition to pulp fibers, papermaking consumes notable amounts of different additive chemicals. These include fillers such as calcium carbonate, talc, gypsum, or kaolin to add opacity and lower the production cost but also, simultaneously, working adversely on paper strength; pigments that are also applied as nanoparticles such as TiO_2 or $Al(OH)_3$ to increase whiteness; coatings to improve the paper smoothness, printability, and optical properties; sizing agents such as polyvinyl alcohol to produce surface hydrophobicity and improve fixation of pigments; retention chemicals that affect the fiber flocculation, dewatering, and filler attachment; and wet and dry strength aids that are used to improve the mechanical properties of paper (de Oliveira *et al.* 2009; Rutanen and Toivakka 2012; Gärdlund *et al.* 2002; Chin *et al.* 2012). The impact of these chemicals on the papermaking process and end-product properties has been studied in many publications.

However, multifunctionality has not been considered to such an extent. We decided to test an approach that uses the functionalization of pulp fibers with inorganic-organic hybrid materials, a field that is practically unexplored.

Layered double hydroxides (LDH) belong to a class of inorganic materials that have a layered structure consisting of infinite two-dimensional positively charged hydroxide layers and interlayers of anions and water. The metallic elements within the lamellar lattice are arranged as hexahydroxo complexes that share two hydroxyl groups with each neighbour. The mixed oxidation state of the elements gives rise to an extra cationic charge that is balanced by the inter-lamellar organic anions that LDH are also able to exchange. LDH are therefore referred to as anionic clays (Cavani *et al.* 1991), constituting a group of inorganic-organic hybrid materials (Wang and O'Hare 2012). The importance of using LDH instead of other conventional hydroxides, *e.g.* $Mg(OH)_2$, is that they can be engineered for a specific purpose by intercalating different functional anions into the gallery. LDH have been extensively studied and have attracted interest as environment-friendly catalysts, anion exchangers, and adsorbents. We envisage that LDH could be utilised as a hybrid system in several paper manufacturing processes with multiple functionalities and further in specific applications, including catalysis (Kozhevnikov 1998; Nunan *et al.* 1989), pharmaceutics (Khan *et al.* 2001; Choy *et al.* 2000), composites (Wang *et al.* 2009; Dan *et al.* 2010), separation technology (Ikeda *et al.* 1984; Tarasov *et al.* 2003), optoelectronics (Yan *et al.* 2009; Giannelis *et al.* 1987), and sensor technology (Frey *et al.* 2001; de Melo *et al.* 2002). At the present stage LDH has proven its industrial importance and has been sold *e.g.* as a precursor for alkaline catalyst, as a halogen scavenger for polyolefins, for heat stabilisation in PVC resin, and as an anionic trash removal agent for water treatment through several manufactures under commercial names such as L-55RII, Hycite 713, Pural MG 61 HT, Hysafe 510, and Baeropol MC 6280 to mention but a few.

Recently LDH was applied, for example, in flame retardant paper production (Wang *et al.* 2012) and in coating composition (Talma *et al* 2009). However the cross-scientific research of LDH in pulp production is still in its infancy, and only a handful of publications can be found via SciFinder (in February 2014). Other nanoparticles that have gained interest especially in paper production from wood fibres, and to a lesser degree in pulp production, are *e.g.* Al_2O_3, ZnO, SiO_2, $CaCO_3$, and silanes. These have been applied for pulp production formulation, for paper and board with microfibrillated cellulose, in research for wear resistance and wet strength, and on paper surface among others (Haakana *et al.* 2013; Heiskanen *et al.* 2013; Luna *et al* 2013; Stepien *et al.* 2013; Tyurin *et al.* 2013). Methods for applying these particles range from flame spray and laser ablation to more convenient solvothermal synthesis and self-assembly. In this regard, the aim of our research is to investigate the possibilities of LDH as a functional platform especially for pulp but also for paper production to add value of these products by using the existing manufacturing processes.

We have previously described how the surface of natural fibers can be made hydrophobic with LDH particles in low supersaturation conditions that resemble the wet end chemistry in pulp production (Lange *et al.* 2012). We have also investigated the properties of functionalised pulp fibers in injection moulding of a thermoplastic composite (Lange *et al.* 2013). Bleaching trials were carried out with different per-activators. In this study, we investigated the possibility of using LDH in the pulp manufacturing process, specifically in bleaching, by exploiting the LDH's reconstruction property to capture organic acids into the lamellar gallery. To the best of our knowledge,

this is the first attempt to utilise a single inorganic-organic engineered hybrid material as a multi-functional process aid in pulp and paper manufacturing.

EXPERIMENTAL

Materials

Synthetic hydrotalcite $[Mg_6Al_2(OH)_{16}]^{2+}CO^{2-}_3 \cdot 4H_2O$ (St. Louis, MO, USA), benzoic acid (99.5%, Sigma-Aldrich, Netherlands), terephthalic acid (98%, Steinheim, Germany), and NaOH (97%, France) were all purchased from Sigma-Aldrich. Sodium silicate with a SiO_2 content of 25.5 to 28.5% and hydrogen peroxide (30%) were both purchased from Merck (Darmstad, Germany). The optical brightening agent (sometimes called a fluorescent whitening agent) Tinopal ABP-Z liquid (solid content 21%) was kindly provided by BASF. All chemicals were used without further purification. Unbleached TMP pulp from spruce (*P. abies*), which was previously refined in a double disc refiner at 1700 kWh/ton (air dry) to approximately 170 mL CSF (Canadian freeness), was provided by Stora Enso, Sweden. Unbleached eucalyptus (*E. grandis*) was provided by Veracel Cellulose, Brazil.

LDH Modification

Hydrotalcite was modified with different anions *via* the rehydration method explained by He *et al.* (2006). In short, hydrotalcite was calcinated at 525 °C for 4 h and was then dispersed with anion modifier into 100 mL of de-carbonated aqueous suspension. The molar fraction of modifier in the suspension with respect to aluminium was 2:1. The aqueous anion solutions used were benzoate (BA), terephthalate (TA), sodium xylene sulphonate (SXS), and per-benzoate (pBA).

Unmodified hydrotalcite is denoted LDH in this paper, and the modified hydrotalcites are denoted LDH-BA, LDH-TA, LDH-SXS, and LDH-pBA, using the abbreviations given above. All suspensions were purged with nitrogen (N_2) for 10 min prior to vigorous stirring, and the gas was allowed to flow on the solution surface during the adsorption and intercalation processes (24 h). The modified LDH particles were then collected by centrifugation (45 min at 3000 g) and were dried in an oven at 60 °C until the weight was constant.

Modification of pulp fibres with LDH for testing adsorption of OBA

Two automatic titrators were utilized in particle synthesis. The pH in the reaction medium was kept close to 10.2 with NaOH solution (2.0 M), while the metal salt solution (0.5 M) was dispensed with the rate of 1.0 mL min from another titrator. The concentrations of metal salts in the reaction medium were calculated from the final volume (1500 mL) and kept at 100 mM.

The ageing was allowed to proceed hydrothermally in 1000 mL digestion bombs at 135 °C for 24 h. To remove all the loosely bound LDH particles from the fibre surface before the functionalization step, the pulp was washed with distilled water at 1% consistency at least ten times. Filtration was performed through 125 mesh size wire cloth and subsequently through a filter paper with average retention capacity of 12 to 25 μm. All filtrations were carried out in reduced pressure

Bleaching with Added LDH

To remove the peroxide bleaching encumbering metal ions, TMP was soaked in 0.2% aqueous solution of ethylenediaminetetraacetic acid (EDTA) at 50 to 70 °C for 30 min. The pulp was then washed with water and centrifuged to 30% consistency. Peroxide bleaching of TMP was conducted in polyethylene bags in a water bath at 60 °C. The bags were kneaded every 15 min to ensure appropriate homogeneous dispersion of chemicals. The hydrogen peroxide charge was 20 kg/t, the alkali (NaOH) charge was 20 kg/t, and the sodium silicate charge was 30 kg/t. LDH or modified LDH was added at 30 kg/t (3%) or 60 kg/t (6%). The reaction was terminated after 60 min by adjusting the pH to approximately 6 with 1.0 M HCl. The pulp was then filtered, and the filtrate was analysed for residual peroxide. Bleached fibers were washed several times with distilled water and centrifuged to 30% consistency. Residual peroxide was determined by iodometric titration, where 4.0 mL of 1.0 M sulphuric acid and 10.0 mL of 10% potassium iodide solution along with a small amount of ammonium molybdate were added to 5.0 mL of pulp filtrate and the equivalence point was detected using thiosulphate solution (20 mM) with a starch indicator.

Oxygen bleaching of eucalyptus kraft pulp was performed in a Quantum mixer (Quantum Mark IV, Quantum Technologies Inc., Twinsburg, OH, USA) for 60 min at 100 °C with a 10/10 s/min mixing sequence. The mixing chamber and pulp were both pre-heated prior to the experiments. The oxygen pressure was 6 bar, and the pulp consistency was 10%. The alkali (NaOH) charge was 20 kg/t, and the LDH or modified LDH addition was 60 kg/t (6%). A reference bleaching was done similarly but without added LDH, where magnesium silicate (3 kg/t) was added to prevent carbohydrate degradation. Bleached kraft pulps were subsequently washed with distilled water until a clear filtrate was obtained. Kappa (K_a) analysis was performed according to the standard SCAN-C 1:00.

Characterisation of Pulps Modified with LDH

The limiting viscosity number that relates to the degree of polymerisation of cellulose chains in the reference pulp and bleached pulp fibers was analysed with a capillary viscometer according to the standard SCAN-CM 15:99.

The amount of anionic groups in the pulp was detected by methylene blue adsorption method according to Fardim and Holmbom (2003). In short, different volumes of 400 µM methylene blue solution were mixed with 50 mg of pulp and were reacted for 15 min with stirring to reach the adsorption equilibrium. A buffer solution with 0.60 mM diethyl barbituric acid was used. The pulp filtrate was diluted and analysed with a UV-Vis spectrophotometer (PerkinElmer, Lambda 40, USA) at a wavelength of 664 nm, and the free methylene blue was plotted against the specific absorption. The monolayer adsorption saturation level (occurring at approximately 100 µM free methylene blue in the filtrate) is reported as the amount of anionic groups in the pulp (Fardim and Holmbom 2005). The amount of anionic groups on the pulp surface was detected on the pulp filter cake after air drying by measuring the relative amount of sulphur on the surface by X-ray photoelectron spectrophotometer (XPS). Because methylene blue is adsorbed to the anionic sites on the pulp in a 1:1 ratio, and each methylene blue molecule contains one S atom, the amount of S detected by XPS can be converted to the amount of anionic groups on the pulp surface (Orblin *et al.* 2012).

XPS was also used to quantify the surface coverage on the fibers of carbohydrates, lignin, and extractives. The instrument (Physical Electronics, PHI

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Quantum 2000 ESCA, Eden Prairie, MN, USA) was equipped with a monochromatic Al Kα X-ray source combined with an electron flood gun and ion bombarding and operated at 25 W with a 45° take-off angle. Pulps were analysed before and after extraction with an acetone:water mixture of 9:1 in the Soxhlet apparatus for 4 h. An internal standard of pure cellulose was analysed together with the extracted samples, and four spots per sample were measured. The pass energy in the low-resolution scanning was 187 eV, and the scan was acquired in 3 min, while the high-resolution C1s scanning was done with a pass energy of 23 eV in 10 min. Software provided by the instrument manufacturer was used for data treatment, including the C1s curve deconvolution into the four partial curves C1, C2, C3, and C4, representing different carbon chemical states (Dorris and Gray 1978). C1 denotes aliphatic carbon with the binding energy 284 eV. When carbon has bonds with more electronegative elements, in this case oxygen, higher binding energies are detected by XPS. C2 is the proportion of carbon atoms having one bond with oxygen (C-O), C3 is that having two bonds (O-C-O or C=O), and C4 is that having three bonds (O-C=O). In pulps, the C1 signal is obtained from extractives but includes the contribution from lignin as well. Carbohydrates, hemicelluloses, pectins, and extractives (sterols and hemicelluloses) contribute to C2 and C3 signals, while C4 comes solely from carboxylic acids (esterified and un-esterified); hydrogen cannot be detected by XPS. For example, theoretical values for pure cellulose are easily calculated based on its polymeric structure. Out of six carbons, one is hemiacetal and the rest are hydroxylic. Oxygen-to-carbon (O/C) ratios were obtained from the low-resolution spectra. The surface coverage by extractives in kraft pulp was calculated based on the difference in the O/C ratios of the unextracted and extracted samples, compared to the O/C ratio of extractives (the theoretical value of oleic acid was used) (Laine *et al.* 1994). The surface coverage by lignin in kraft pulp was calculated for the extracted samples, comparing the O/C ratio to those of lignin (Ström and Carlsson 1992) and cellulose (internal reference). The surface coverage by carbohydrates was reported as the lignin coverage subtracted from 100%. Thus, the surface extractives are assumed to be located on top of the lignin and carbohydrates, and the sum of the reported surface coverage values is more than 100%.

Contact angle measurements were performed with an optical Contact Angle Meter, CAM 200 (KSV Instruments Ltd, Finland), with ion-exchanged water. The contact angle values were collected at the beginning of 30-ms intervals and subsequently with 1- and 2-s intervals until the droplet was absorbed or until no changes from the wetting occurred. The droplet size was 1.6 ± 0.2 µL. The results were analysed with Attention Theta software (Biolin Scientific, Sweden) based on the Young-Laplace function for iterative contact angle calculation. A minimum of five measurements were taken, so that the obtained deviation was $\leq 7°$; the average is reported.

TMP handsheets were prepared in a conventional sheet former according to the standard SCAN-CM 64:00, and the mechanical properties were determined according to the standard SCAN-C 28:76. Kraft handsheets for optical measurements were prepared according to SCAN-CM 11:95. An Elrepho spectrophotometer (Elrepho SE070R, Lorentzen & Wettre, Kista, Sweden) was applied for the optical measurements of the handsheets. This method is applicable to ISO 2470 and 2471-1977 standards.

SEM imaging was performed with a Leo Gemini 1530 field emission scanning electron microscope, equipped with In Lens detector (LEO Electron Microscopy Ltd., Oberkochen, Germany). The pulp fibre was coated with carbon in Temcarb TB500 sputter coater (Emscope Laboratories, Ashford, U.K.) Optimum accelerating voltage was 2.70 kV at 6.0 mm working distance.

RESULTS AND DISCUSSION

Surface Chemistry and Charge of the LDH-modified Bleached Pulps

As measured by XPS, the elemental surface composition of the pulp samples that were bleached with 6% LDH consisted of only carbon and oxygen in the cases of kraft pulp and TMP (Table 1). The technique did not detect the presence of the LDH constituents Mg or Al. The origin of the Si traces detected in some cases is unknown contamination, possibly from sodium silicate used in the pulping process. Further, the O/C ratio was not significantly increased with the LDH addition. After acetone extraction, a barely detectable signal of Mg was seen in the kraft pulps (the detection limit of XPS is 0.1%), but not in TMP. The results confirm that the given concentration range of LDH is only present in pulp fibers in very small amounts, and it is probably covered by some acetone-extractable material during the process. The measured O/C ratios were slightly higher in the pulps treated with LDH-BA and LDH-TA than in those with unmodified LDH. The relative amount of hydroxyl-containing carbons (C2) was slightly higher in the LDH modified pulps. Because of lignin oxidation, a simultaneous decrease in hemiacetal, ketone, or aldehyde carbons (C3) could be estimated.

Table 1. Elemental Data Obtained from XPS and the Boundary States of Carbon Deconvoluted from the C1s Curve for Bleached Pulps with 6% LDH or Modified LDH

Sample	O/C	Trace elements	C1	C2	C3	C4
BEFORE EXTRACTION						
Kraft reference	0.75 (0.03)	Si (Mg)	16 (2)	52 (2)	23 (3)	6 (1)
Kraft with LDH	0.67 (0.02)		23 (1)	51 (2)	21 (2)	5 (1)
Kraft with LDH-BA	0.73 (0.01)		19 (2)	56 (1)	20 (2)	5 (1)
Kraft with LDH-pBA	0.74 (0.01)		18 (1)	59 (1)	18 (1)	5 (1)
TMP with LDH	0.53 (0.01)		37 (4)	47 (2)	13 (4)	3 (1)
TMP with LDH-BA	0.56 (0.02)		33 (1)	54 (1)	10 (1)	3 (1)
TMP with LDH-TA	0.59 (0.01)		32 (2)	54 (1)	12 (2)	2 (1)
TMP with LDH-SXS	0.57 (0.01)		35 (1)	53 (1)	10 (1)	2 (1)
EXTRACTED						
Kraft reference	0.80 (0.02)	Si, Mg, (Al)	14 (3)	45 (1)	30 (3)	7 (1)
Kraft with LDH	0.79 (0.01)	(Mg)	17 (2)	55 (6)	23 (4)	5 (1)
Kraft with LDH-BA	0.77 (0.02)	(Mg)	17 (2)	57 (2)	21 (3)	5 (1)
Kraft with LDH-pBA	0.69 (0.05)	Si, (Mg)	27 (3)	54 (5)	16 (2)	3 (1)
TMP with LDH	0.60 (0.04)		30 (2)	55 (3)	13 (1)	2 (1)
TMP with LDH-BA	0.63 (0.01)		24 (2)	57 (2)	16 (2)	3 (1)
TMP with LDH-TA	0.66 (0.02)		26 (2)	61 (2)	12 (1)	1 (1)
TMP with LDH-SXS	0.63 (0.01)	Si	29 (3)	55 (2)	13 (3)	3 (1)
Internal reference	0.81 (0.02)		18 (2)	57 (2)	20 (3)	5 (1)
Cellulose[a]	0.83		0	83	17	0
Extractives (oleic acid)[b]	0.11		94	0	0	6
AraGluXyl[c]	0.81		0	78	19	3
Lignin[d]	0.33		49	49	2	0

[a] Calculated from the molecular formula
[b] Laine *et al*. (1994)
[c] Arabinoglucuronoxylan (Mjöberg 1981)
[d] Freudenberg and Neish (1968)

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The calculated values of the surface coverage by carbohydrates, lignin, and extractives on the pulps are presented in Table 2 (standard deviations in parentheses). In kraft pulp, the carbohydrate content is naturally very high. The measured values for surface coverage by lignin and by carbohydrates were in the range of previously reported values for oxygen bleached kraft eucalyptus pulp (Orblin *et al.* 2012), or even lower than reported for some other bleached hardwood kraft pulps (Orblin *et al.* 2011; Fardim *et al.* 2006), but the differences between the bleaching trials with or without LDH were small. Some re-deposition of lignin and extractives during the process can be suspected in the case of the addition of LDH and LDH-BA in the oxygen bleaching. In the case of kraft bleached with the addition of LDH-pBA, contamination was suspected on the extracted sample (Table 1); thus, no useful surface coverage result was obtained with this method. In the peroxide bleaching of TMP, LDH addition seemed to enhance surface lignin removal, particularly with LDH-BA. A relatively large amount of surface extractives were found in all bleached pulp samples, which were possibly redistributed during the process.

Table 2. Surface Coverage by Carbohydrates, Lignin, and Extractives in Oxygen-bleached Eucalyptus Kraft Pulp and Peroxide-bleached TMP without LDH and with 6% LDH, and Results from Contact Angle with Water

Bleached pulp	Sample	Carbohydrates (%)	Lignin (%)	Extractives (%)	Ψ_{ini}	t_0
Kraft	Reference	98 (2)	2 (2)	7 (5)	-	-
	LDH	96 (2)	4 (2)	18 (3)	20-25°	≤ 1 s
	LDH-BA	93 (4)	7 (4)	6 (3)	20-25°	≤ 1 s
TMP	Reference[a]	66	34	17	-	-
	LDH	57 (7)	43 (7)	14 (7)	63°	13 s
	LDH-BA	63 (1)	37 (1)	14 (4)	50°	14 s
	LDH-TA	68 (3)	32 (3)	12 (3)	40°	12 s
	LDH-SXS	61 (1)	39 (1)	9 (2)	48°	20 s
[a] Values reported by Koljonen *et al.* (2003)						

Table 2 also lists the results for pseudo-equilibrium contact angles after initial spreading of the sessile water droplet, *i.e.*, after 1 s of initial wetting. The values have been linearly extrapolated from the measured data. An example of evaluating the contact angle from the paper surface is explained and discussed in our previous work (Lange *et al.* 2013). The initial pseudo-equilibrium contact angle (Ψ_{ini}) was extrapolated to 0 s, while time of absorption (t_0) was extrapolated to $\Psi = 0$. The Ψ_{ini} of sessile water droplets in all kraft pulp samples was between 20° and 25°, while the droplet absorption was complete in less than a second. It was therefore impossible to detect any chemical changes in the surfaces of bleached chemical pulp fibers with this method. The contact angle of TMP fibers, on the other hand, correlated well with the results from XPS. The t_0 and Ψ_{ini} values decreased with increasing surface coverage by lignin, as expected. The LDH-BA and LDH-SXS samples had initial contact angles rather similar to those previously reported for TMP and model lignin (Liukkonen 1997). Indeed, LDH is a highly hydrophilic material, but XPS verified that it was not attached to the fiber surfaces. Thus, the fact that unmodified LDH gave a higher initial contact angle is most probably due to its lower efficiency in surface lignin oxidation (compared to modified LDH), combined with statistical issues related to sheet roughness.

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Table 3. Amount of Anionic Groups (AG) in Total and on the Surface of Pulp Fibers

Pulp	AG (tot) mmol/g	AG (surf) mmol/g	AG (surf) / AG (tot)
Unbleached eucalyptus kraft	0.11 (0.01)	0.18	1.6
Oxygen-bleached euc. Kraft	0.20	0.22 (0.00)	1.1
Oxygen-bleached euc. kraft with LDH	0.18	0.22 (0.00)	1.2
Oxygen-bleached euc. kraft with LDH-BA	0.19	0.24 (0.04)	1.3
Oxygen-bleached euc. kraft with LDH-pBA	0.19	0.20 (0.04)	1.0
Unbleached TMP[a]	0.10 (0.01)	0.10	1.0
Peroxide-bleached TMP[a]	0.18 (0.01)	0.15	0.8
Peroxide-bleached TMP with LDH	0.21	0.26 (0.04)	1.2
Peroxide-bleached TMP with LDH-BA	0.21	0.24 (0.04)	1.1
Peroxide-bleached TMP with LDH-TA	0.22	0.15 (0.01)	0.7
Peroxide-bleached TMP with LDH-SXS	0.23	0.27 (0.04)	1.2
[a] Results of Fardim and Holmbom (2005) recalculated with the equation of Orblin *et al.* (2012)			

The amount of anionic groups in total and on the fiber surface is displayed in Table 3 (standard deviations in parentheses). In the alkaline peroxide bleaching of TMP, the amount of anionic groups increased *via* creation of galacturonic acids and carboxyl groups in lignin as well as demethylation of pectins (Pranovich *et al.* 2003). Addition of LDH enhanced the formation of anionic groups during the peroxide bleaching process. Unmodified LDH promoted an increase in the surface charge (260% greater than the unbleached reference), whereas LDH-BA and LDH-TA directed the charge formation below the imminent surface (the detection depth of XPS is less than 10 nm). The highest anionic group content was measured on the LDH-SXS-treated pulp; however, the result could not be explained by surface carbohydrate content based on XPS and contact angle measurements and remains without clarification. Oxidative bleaching of chemical pulp can produce carboxyl groups in lignin (Buchert *et al.* 1995), but is in general charge-reducing because of the degradation of carbohydrates. In our experiments, LDH did not significantly affect the amount of anionic groups in oxygen bleaching of kraft pulp, although slightly lower numbers were measured in the LDH pulps. However, a charge increase was observed on the fiber surface in oxygen-bleached kraft pulp with added LDH, and particularly with LDH-BA, which may be due to re-deposited oxidised lignin. The detected amount of anionic groups on the surface correlated rather well in both pulps with C4 values, as indicated in Table 1. The carboxylic acid content increased in all TMP samples bleached with LDH. Anionic groups in fibers are important in papermaking, as they participate in electrostatic interactions with various chemicals and affect the retention and final sheet properties (Fardim and Holmbom 2005).

LDH in Peroxide Bleaching of TMP

The content of residual peroxide after peroxide bleaching with and without added LDH was measured. A higher amount of residual peroxide was detected from the bleaching trials with modified and unmodified LDH, meaning that the addition of LDH lowered the peroxide consumption. The maximum increase (77%) in residual peroxide was observed for LDH-TA, and the unmodified particles were responsible for approximately 10% of the increase in the value. With 3% addition of the different LDH species, similar trends were seen, but in slightly smaller quantities than with the 6% dosage. In hydrogen peroxide bleaching, the active component is consumed in

complicated ways that involve various bleaching and non-bleaching reactions. In our experiments, a good level of effective reactions was obtained in all trials with LDH addition, resulting in brightness values of 67 to 71% ISO (the unbleached TMP had 60% ISO). Reference bleaching gave values on the same level. Because an increase in brightness was accompanied with a considerable increase in the residual peroxide level compared to reference bleaching, it is clear that the modified LDH promoted better process efficiency (Fig. 1). LDH possibly stabilised the active bleaching components and acted as a catalyst. The overall best performance was seen with LDH-TA at the 6% dosage. The brightness was 2 units higher than in the reference, which is notable considering the low peroxide consumption. The intercalated and surface bound terephthalate anions could have functioned as precursors for the formation of peracid, which is an efficient and selective bleaching species in the process.
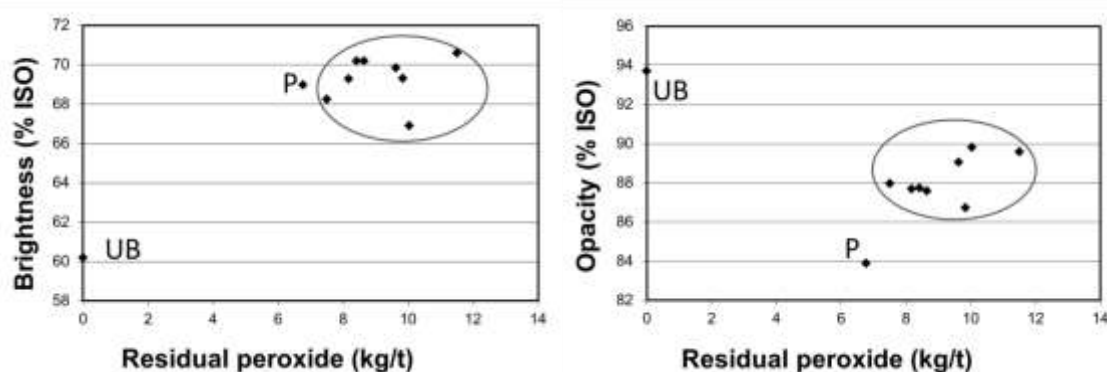

Fig. 1. The correlation between the residual peroxide and optical properties in the bleaching modified with LDH. Results obtained by the LDH modified bleaching trials are circled; the type of LDH or the dosage are not specified. UB = unbleached TMP, P = peroxide-bleached TMP without added LDH.

The bleaching process is always detrimental to the opacity values of a particular paper because fewer functional groups remain in fibers, such as conjugated double bonds in lignin and other chromophores that are responsible for light absorption. However, after the bleaching process with added LDH, the opacity was rather high in all experiments (Fig. 1). While the reference bleaching was responsible for 10-unit decrease in opacity, the addition of LDH resulted in a decrease of only 4 to 8 units. The 3% dosage resulted in slightly lower opacity than the 6% dosage in the modified LDH (LDH-BA, LDH-TA, and LDH-SXS), but the dosage did not affect the result in the unmodified LDH.

One possible reason for the detected good opacity is the chance that LDH made the fibers more rigid. This would have a negative effect on the mechanical sheet properties. The tensile stiffness index, tensile index, tear index, and bulk were measured for TMP handsheets with the LDH modified fibers (details not shown). All results were on the same level with the reference pulp that was bleached without added LDH. Modification of the LDH anion did not bring changes to the LDH performance in this regard, except for a slightly higher bulk (dm^3/kg). The difference in LDH dosage (3% or 6%) did not significantly affect the results. In general, LDH had no deteriorating influence on the mechanical properties of pulp. Conventional fillers that are used in papermaking to increase opacity have the drawback of lowered paper strength. LDH seems to have the potential to replace at least part of the fillers and possibly to optimise the triangle of optical and mechanical paper properties and cost.

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LDH in Oxygen Bleaching of Kraft Pulp

The impact of LDH on the oxygen bleaching of kraft pulp was estimated from the resulting pulp properties (Table 4). The intrinsic viscosity results obtained with a capillary viscometer indicate the level of carbohydrate degradation during the bleaching process as the bleached samples were compared to the unbleached pulp. In the bleaching experiments with LDH, the viscosity drop was only slightly higher than in the reference bleaching (with added $MgSO_4$), alluding to the fact that LDH did not promote degradation. Further, the Mg in LDH could have functioned in a similar manner to $MgSO_4$, protecting carbohydrates from severe degradation during the process. In that sense, LDH could substitute for $MgSO_4$ in oxygen bleaching, and LDH-BA worked even better than LDH.

Table 4. Pulp Properties of Oxygen-bleached Kraft Pulps Modified with LDH

Sample	Dosage (%)	Viscosity (mL/g)	Kappa (K_α) index	Brightness (ISO %)
Unbleached kraft pulp	-	1325	16.68	38
Oxygen-bleached pulp	-	1220	11.36	42
Oxygen-bleached pulp with LDH	3	1160	9.88	53
	6	1125	9.59	54
Oxygen-bleached pulp with LDH-BA	3	1115	9.96	54
	6	1140	9.76	54
Oxygen-bleached pulp with LDH-pBA	3	1130	10.26	54
	6	1160	10.59	52

The pulp had an initial K_α of 16.7, but the reference bleaching stage reduced it by 5 units down to 11.4. This was a clear indication of lignin removal, even though the ISO brightness was not affected as much as was anticipated. Application of LDH was beneficial, as K_α decreased more than it did in the reference bleaching. The reduction in K_α and the simultaneous increase in the surface coverage by lignin, as estimated by XPS, confirms the assumption that lignin was re-adsorbed on the fiber surface after it was dissolved during the bleaching stage, and that LDH seemed to promote this reaction. The ISO brightness results correlated with K_α, and higher brightness was measured in the pulps bleached in the presence of LDH compared to the reference bleaching. The dosage did not affect the brightness, and modification of LDH with BA or pBA did not contribute to further improvement in the pulp properties. It is possible that organic functionalities on the LDH surface and its lamellar gallery consume active oxygen, thus preventing or slowing down the bleaching kinetics. On the other hand, the achieved brightness gain with bare LDH calls for further experiments.

As LDH was not attached on the pulp surfaces (according to XPS results) yet affected the bleaching, it can be assumed that LDH may have a role as a carrier for intercalated anions or as a radical- or metal-trapping system, enhancing the selectivity of the bleaching reactions. LDH dosage did not affect the results significantly. One of our hypotheses had been that the anions in LDH would have similar functions as the anion species have separately, for example, SXS as a lignin dissolution agent (Korpinen and Fardim 2009) and BA as a precursor for peracids (Plesnicar 1978), but the results did not give any clear evidence on this. Again, unmodified LDH had more positive impacts on the oxygen bleaching processes.

LDH as a Carrier of Fluorescence Whitening Agents in Papermaking

To test the absorption of a common optical brightening agent (OBA) that is used in the paper making industry, pulp fibers were modified with LDH through co-precipitation method in aqueous solution as described in more detailed in our previous work (Lange *et al.* 2012). The amount of LDH was approximately 4.5% (w/w), according to the elemental analysis. The modified pulp was subjected to different OBA loadings and was allowed to mix at room temperature for approximately 30 min before filtration. The filtrate was examined with UV-Vis spectrometry at the wavelength (λ) = 348 nm to quantify the amount of OBA retained by pulp fibers. The results are presented in Fig. 2.
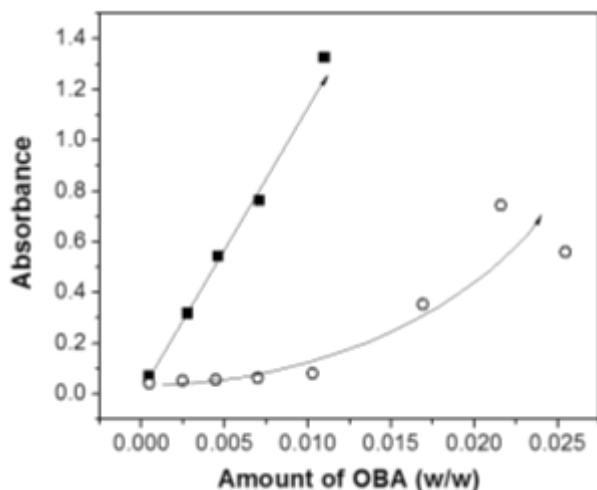
Fig. 2. The amount of optical brightening agent (OBA) applied to a pulp slurry plotted against the absorbance (λ = 348 nm) measured from the pulp filtrate. The lines are drawn to guide the eye. Filled squares correspond to TMP pulp filtrate obtained without modification, and open circles correspond to TMP pulp filtrate obtained with LDH (4.5% (w/w))-modified fibers.

The benefit of LDH application on TMP fiber surfaces was clearly observed. It was possible to load the modified TMP pulp up to 1.0% (w/w) with OBA before any appreciable leaching occurred. The reference filtrate instead showed a steep linear response with added substances. By introducing 0.05% (w/w) OBA into the pulp slurry, the absorbance level with reference pulp was 0.07. In comparison, the level was 0.04 with modified pulp. As the amount was increased up to 20 fold, the absorbance doubled to 0.08 with modified pulp but increased up to 1.33 (a 19-fold increase) with the reference sample. Therefore, approximately 90% of the added OBA was retained up to a 1.0% (w/w) addition level with respect to modified pulp, whereas only about 5% was retained without modification. An example of the fibre morphology upon LDH addition is shown in Fig. 3. The OBA was applied to similar fibres. The reader is referred to (Lange 2012) for further information on particle morphology on pulp fibre surface.

Inorganic particles are known to have adverse effect on fluorescent whitening and optical brightening agents through electrostatic repulsion and quenching of quantum yield. Also, the electrostatic repulsion with negatively charged fibre surfaces prevent efficient adsorption as indicated with the straight slope in Fig. 2. Typically the sulphonate-containing anionic OBAs are applied with *e.g.* calcium ions for better retention. LDH are naturally anion exchangers, and they provide a strong retention for quaternary sulphonated OBA as indicated with open circles in Fig. 2. We did not,

however, optimize the LDH content on wood fibre surface for the best possible dosage to address the maximum obtainable quantum yield, which calls for further research.
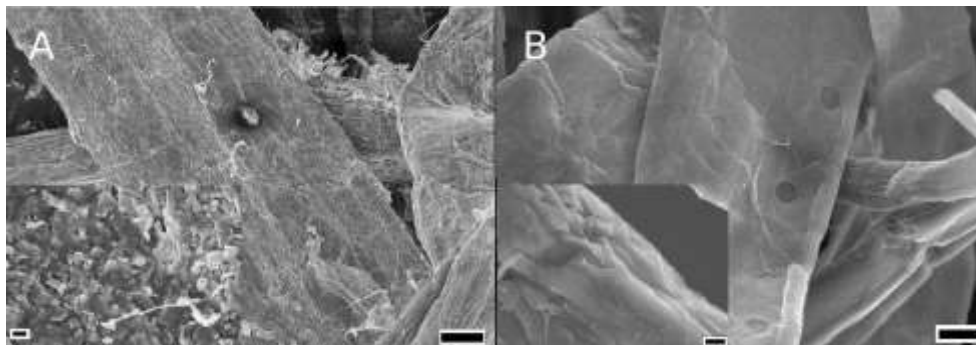

Fig. 3. A SEM image (mag. 1000, scale bar 10 μm) of the LDH adsorbed on pulp fibre surface (A) and a native (B).The inset shows a magnification of the fibre surface. LDH particles are clearly visible in size range of 100 - 300 nm. The inset scale bar = 200 nm in A and 1 μm in B. Fibre surface morphology has changed considerably.

CONCLUSIONS

Bleaching trials were carried out to investigate the potential of using LDH in hydrogen peroxide bleaching of thermo mechanical softwood pulp and oxygen bleaching of hardwood kraft pulp. LDH with terephthalate was observed to increase opacity and brightness while reducing peroxide consumption in TMP process. In oxygen bleaching bare LDH increased the efficiency of lignin removal, as indicated by reduction in kappa number and remarkable increase in ISO brightness. XPS results in combination with methylene blue absorption showed that carboxylic acid content on fibre surface increased in all tested samples. The values were more pronounced with TMP. Fractional basis analysis indicated to re-absorption of lignin and extractives on kraft fiber surface by LDH. Selectivity for lignin removal was accompanied with reduction in anionic groups in bulk as observed in methylene blue adsorption. Contact angle measurements were in line with the XPS results, showing higher hydrophilicity as the relative carbohydrate content increased on TMP fiber surfaces.

The dosage of OBA can be extended with LDH particles due to high retention without accumulating to the waste stream and offering potential savings in water treatment. Our results suggest beneficial bleaching methods for both pulp productions in terms of engineered LDH particles and are especially interesting as opacity was not affected by higher brightness and efficient lignin removal. However, additional investigation is required to address the exact mechanism in detail to conclude on whether it is the active peroxide (HOO^-) or peracid (R-COOOH), or perhaps a synergy of these factors that affects beneficially the peroxide bleaching process.

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REFERENCES CITED

Buchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L., and Vuorinen, T. (1995). "Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp," *TAPPI J.* 78(11), 125-130.

Cavani, F., Trifirò, F., and Vaccari, A. (1991). "Hydrotalcite-type anionic clays: Preparation, properties and applications," *Catal. Today* 11(2), 173-301.

Chin, S. M., Youn, H. J., Ryu, J., and Sim, K. (2012). "Polyelectrolyte multilayering of fibers with different polymer combinations and a comparison of its effect on paper strength with a conventional dry strength agent treatment," *Nord. Pulp Paper Res. J.* 27(5), 922-915.

Choy, J. H., Kwak, S. Y., Jeong, Y. J., and Park, J. S. (2000). "Inorganic layered double hydroxides as nonviral vectors," *Angew. Chem. Int. Ed.* 39(22), 4041-4045.

de Melo, J., Cosnier, S., Mousty, C., Martelet, C., and Jaffrezic-Renault, N. (2002). "Urea biosensors based on immobilization of urease into two oppositely charged clays (laponite and Zn-Al layered double hydroxides)," *Anal. Chem.* 74(16), 4037-4043.

de Oliveira, M. H., Tejado, A., and van de Ven, T. G. M. (2009). "Effects of fillers on the wet web strength of paper," *Nord. Pulp Paper Res. J.* 24(2), 141-147.

Dorris, G., and Gray, D. (1978). "The surface analysis of paper and wood fibers by ESCA (electron spectroscopy for chemical analysis). I: Application to cellulose and lignin," *Cellulose Chem. Technol.* 12(1), 9-23.

Fardim, P., and Holmbom, B. (2003). "Fast determination of anionic groups in different pulp fibers by methylene blue sorption," *TAPPI J.* 2(10), 28-31.

Fardim, P., and Holmbom, B. (2005). "Origin and surface distribution of anionic groups in different papermaking fibers," *Colloids Surf. A* 252(2-3), 237-242.

Fardim, P., Hejnesson Hultén, A., Boisvert, J. P., Johansson, L. S., Ernstsson, M., Campbell, J. M., Lejeune, A., Holmbom, B., Laine, J., and Gray, D. (2006). "Critical comparison of methods for surface coverage by extractives and lignin in pulps by X-ray photoelectron spectroscopy (XPS)," *Holzforschung* 60(2), 149-155.

Frey, S., Guilmet, S., Egan III, R., Bennett, A., Soltau, S., and Holz, R. (2001). "Immobilization of the aminopeptidase from *Aeromonas proteolytica* on Mg^{2+}/Al^{3+} layered double hydroxide particles," *Appl. Mater. Inter.* 2(10), 2828-2832.

Freudenberg, K., and Neish, A. (1968). *Constitution and Biosynthesis of Lignin*, Springer, Berlin.

Gärdlund, L., Wågberg, L., and Gernandt, R. (2002). "Polyelectrolyte complexes for surface modification of wood fibers: II. Influence of complexes on wet and dry strength of paper," *Colloids Surf. A* 218(1-3), 137-149.

Giannelis, E., Nocera, D., and Pinnavaia, J. (1987). "Anionic photocatalysts supported in layered double hydroxides: Intercalation and photophysical properties of a ruthenium complex anion in synthetic hydrotalcite," *Inorg. Chem.* 26(1), 203-205.

Haakana, S., Sinisalo, L., Solismaa, P. and Sipilä, M. (2013). "Process for improving wet strength and paper product with improved wet strength," WO 2008003827 A1 20080110.

He, J., Wei, M., Li, B., Kang. Y., Evans, D. G., and Duan, X. (2006). "Preparation of layered double hydroxides," in: *Layered Double Hydroxides*, X. Duan and D. G. Evans (eds.), Springer, Berlin, pp. 89-119.

Heiskanen, I., Axrup, L., Norborg, M.-A., and Knoeoes, I. (2013) "Process for producing dispersion comprising nanoparticles and a dispersion produced according to the process." SE 1150997 A1 20130427

Ikeda, T., Amoh, H., and Yasunaga, T. (1984). "Stereoselective exchange kinetics of L- and D-histidines for Cl$^-$ in the interlayer of a hydrotalcite-like compound by the chemical relaxation method," *J. Am. Chem. Soc.* 106(20), 5112-5115.

Khan, A. I., Lei, L., Norquist, A. J., and O'Hare, D. (2001). "Intercalation and controlled release of pharmaceutically active compounds from a layered double hydroxide," *Chem. Commun*. 22, 2342-2343.

Koljonen, K., Österberg, M., Johansson, L. S., and Stenius, P. (2003). "Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM," *Colloids Surf. A.* 228(1-3), 143-158.

Korpinen, R., and Fardim, P. (2009). "Lignin extraction from wood biomass by a hydrotropic solution," *O Papel* 70(5), 69-82.

Kozhevnikov, I. V. (1998). "Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions," *Chem. Rev.* 98(1), 171-198.

Laine, J., Stenius, P., Carlsson, G., and Ström, G. (1994). "Surface characterization of unbleached kraft pulps by means of ESCA," *Cellulose* 1(2), 145-160.

Lange, C., Farid, T., and Fardim, P. (2013). "Hybrid clay functionalized biofibers for composite applications," *Compos. Part B Eng.* 47, 260-266.

Lange, C., Lundin, T., and Fardim, P. (2012). "Hydrophobisation of mechanical pulp fibers with sodium dodecyl sulphate functionalised layered double hydroxide particles," *Holzforschung* 66(4), 433-441.

Liukkonen, A. (1997). "Contact angle of water on paper components: Sessile drops versus environmental scanning electron microscope measurements," *Scanning* 19(6), 411-415.

Luna, M. N., Severiano, P. O., Gutierrez, A. J., Pamanes, B. R., De Haene, R. G. J., and Gomez, C .J. (2013). "Hydrophobic paper or cardboard with self-assembled nanoparticles and a method for the production thereof," WO 2013154414 A1 20131017.

Mjöberg, P. (1981). "Chemical surface analysis of wood fibers by means of ESCA," *Cellul. Chem. Technol.* 15, 481-486.

Nunan, J. G., Himelfarb, P. B., Herman, R. G., Klier, K., Bogdan, C. E., and Simmons, G. W. (1989). "Methanol synthesis catalysts based on Cs/Cu/ZnO/M_2O_3 (M = Al, Cr, Ga): Genesis from coprecipitated hydrotalcite-like precursors, solid-state chemistry, morphology, and stability," *Inorg. Chem.* 28, 3868-3874.

Orblin, E., Eta, V., and Fardim, P. (2011). "Surface chemistry of vessel elements by FE-SEM, μ-XPS and ToF-SIMS," *Holzforschung* 65(5), 681-688.

Orblin, E., Lindström, N., and Fardim, P. (2012). "Probing the chemical and surface chemical modification of vessel cell walls during bleaching of eucalyptus pulp," *Holzforschung* 66(8), 945-950.

Plesnicar, B. (1978). "Oxidation with peroxy acids and other peroxides." in: *Oxidation in Organic Chemistry Part C*, W. S. Trahanovsky (ed.), Academic Press, New York, p. 211.

Pranovich, A., Sundberg, K., and Holmbom, B. (2003). "Chemical changes in thermo-mechanical pulp at alkaline conditions," *J. Wood Chem. Technol.* 23(1), 89-112.

Rutanen, A., and Toivakka, M. (2012). "Effect of coating solids content and thickener type on the depletion of fine particle size coating color components in the blade coating process," *Nord. Pulp Paper Res. J.* 27(3), 590-595.

Stepien, M., Chinga-Carrasco, G., Saarinen, J. J., Teisala, H., Tuominen, M., Aromaa, M., Haapanen, J., Kuusipalo, J., Makela, J. M., and Toivakka, M. (2013). *Wear* 307(1-2), 112-118.

Ström, G., and Carlsson, G. (1992). "Wettability of kraft pulps: Effect of surface composition and oxygen plasma treatment," *J. Adhesion Sci. Technol.* 6(6), 745-761.

Talma, A. G., De Jong, A. J., Brujin, S., Baltussen, J. J. M., Van Lare, C. E. J., and Reedjk, M. F. (2009). "A process to make a clay comprising charge-balancing organic ions, clays thus obtained, and nanocomposite materials comprising the same," MX 2010006865 A 20101005.

Tarasov, K. A., O'Hare, D., and Isupov, V. P. (2003). "Solid-state chelation of metal ions by ethylenediaminetetraacetate intercalated in a layered double hydroxide," *Inorg. Chem.* 42(6), 1919-1927.

Tyurin, E. T., Zuykov, A. A., Osminin, E. N., Tovstoshkurova, D. U., Ermakova, T. I., Bychkov, V. A., and Azanova, G. N. (2013). "Method of production of paper pulp," RU 2499094 C1.

Wang, L., Su, S., Chen, D., and Wilkie, C. A. (2009). "Fire retardancy of bis[2-(methacryloyloxy)ethyl] phosphate modified poly(methyl methacrylate) nanocomposites containing layered double hydroxide and montmorillonite," *Polym. Degrad. Stab.* 94(7), 1110-1118.

Wang, S., Huang, J., and Chen, F. (2012). "Study on Mg-Al hydrotalcite in flame-retardant paper preparation," *BioResources* 7(1), 997-1007.

Wang, Q., and O'Hare, D. (2012). "Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets," *Chem. Rev.* 112(7), 4124-4155.

Yan, D., Lu, J., Wei, M., Han, J., Ma, J., Li, F., Evans, G. D., and Duan, X. (2009). "Ordered poly(p-phenylene)/layered double hydroxide ultrathin films with blue luminescence by layer-by-layer assembly," *Ang. Chem. Int. Ed.* 48(17), 3073-3076.