Nanoparticles capture on cellulose nanofiber depth filters

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Abstract

A self-standing filter with a porosity of 80% is prepared from naturally abundant cellulose biopolymer in its native state by water-based cationization and freeze-drying processes. The positive surface charge of the filter in a wide pH range favors its interaction with various nanoparticles (NPs), while its tortuous sheet structure builds a contact between cellulose nanofibers (CNF) and the NPs, and hinders them to pass through the filter. Unlike membranes used for the retention of NPs and viruses, the separation in the CNF filter is not only limited to its surface but occurs also in its interior even when the NPs are orders of magnitude smaller than the filter pores. Additional functionalities added to the filter enlarge the spectrum of NPs it can separate. NPs supported onto the filter can thereafter be utilized for the reduction of harmful chemicals into their benign form. The present filter concept may not only address shortcomings of the current membrane systems, but could offer a disruptive technology for the sustainable and universal water purification.

Keywords: nanocellulose; filter; nanoparticles; freeze-drying.

Introduction

Continuous progresses made in nanotechnology over the last decades have enlarged the utilization spectrum of engineered nanoparticles (NPs) in electronic, energy and environment sectors (Ataee-Esfahani et al., 2010; Jiang et al., 2016; Salunkhe et al., 2016; Wang, Jeong et al., 2011; Wang, Yamauchi, 2011). The consequent NPs release into the environment and their exposure for humans and other living organisms have raised concerns over their potential adverse effects. Such effects, not encountered in larger bulk materials, are due to the small dimensions of NPs enabling them to reach the cells of several organs and interact with biological molecules causing, for instance, DNA damage (Oberdorster, Oberdorster, & Oberdorster, 2005). NPs diffusion to target cells becomes many times faster for smaller NPs as it is guided via Brownian motion (Szentkuti, 1997). Hence, new challenges dealing with the effective capture of the smallest NPs from their release point sources, e.g. wastewater streams, have emerged accompanying nanotechnological advances (Gottschalk, Sonderer, Scholz, & Nowack, 2009; Nowack & Bucheli, 2007).

The high stability of NPs in aqueous media combined with their slow settling rate makes their treatment via flocculation and sedimentation processes ineffective (Rottman, Platt, Sierra-Alvarez, & Shadman, 2013). NPs removal from aqueous streams by membranes and filters is an advantageous single-step process which does not require intensive chemical treatment. Conventional filters based on sand and activated carbon fail to retain NPs even after a prolonged contact with them, and this is attributed to the large pores of these filters and to their unfavorable interactions with the NPs (Inyang et al., 2013; Rottman et al., 2013). Membranes can remove NPs when their pores are small enough. Electrospun membranes do not meet this criterion since their fiber constituent and pores are few hundred of nanometers wide. Ultrafiltration membranes exhibit a pore size from ~1 nm to 100 nm, and can thus retain NPs. However, they are mostly prepared from synthetic polymers and organic solvents according to a rather complex phase inversion method requiring a precise control of the process parameters for pore-size tailoring (Guillen, Pan, Li, & Hoek, 2011).

A sustainable water treatment scheme shall consider naturally abundant polymers in their native (undissolved) state processed into membranes/filters from water using industrially relevant processes. While cellulose is undoubtedly one of the most attractive polymers for designing water purification systems, current regenerated cellulose and cellulose derivative membranes make use of organic solvent for cellulose dissolution and regeneration, thus adding an environmental problem associated with solvent management (Klemm, Heublein, Fink, & Bohn, 2005). Novel membranes and filters made from cellulose nanofibrils (CNF), as they exist in their natural plant/algae sources, are likely to provide a more sustainable remediation solution and could radically impact the water purification sector (Carpenter, de Lannoy, & Wiesner, 2015). Nowadays, high-quality CNF can be isolated from plant and algae sources at low cost using high-shear mechanical homogenization or grinding in the presence of water (Henriksson, Henriksson, Berglund, & Lindstrom, 2007; Mihranyan, 2011; Paakko et al., 2007; Saito, Kimura, Nishiyama, & Isogai, 2007; Turbak, Snyder, & Sandberg, 1983; Xiang et al., 2016). The obtained hydrocolloid can thereafter be processed into porous materials via organic solvent-free vacuum-filtration or freeze-drying, two processes that are well-established within paper-making and food industries, respectively (Henriksson, Berglund, Isaksson, Lindstrom, & Nishino, 2008; Sehaqui, Liu, Zhou, & Berglund, 2010; Sehaqui, Michen, Marty, Schaufelberger, & Zimmermann, 2016). CNF “nanopaper” obtained by vacuum-filtering a CNF dispersion has fibrils with random in-plane orientation, and is suitable for membrane application owing to its nanometer sized pores formed by the interspace between the fibrils (Andreas Mautner, Lee, et al., 2015; A. Mautner et al., 2014; Metreveli et al., 2014). In contrast, CNF foam/filter obtained by freeze-drying has a cellular structure, signature of the ice crystals formed during freezing (Sehaqui, Salajkova, Zhou, & Berglund, 2010). The filter pores are ~3 orders of magnitude larger than those of a nanopaper, making it suitable as sorbent material (Pei, Butchosa, Berglund, & Zhou, 2013; Sehaqui, Michen, et al., 2016; Sehaqui, Salajkova, et al., 2010). Process-wise, vacuum filtration is more attractive and straightforward than freeze-drying, although recent advances made in the latter permitted foam preparation at ambient pressure conditions (Josset et al., 2017; Li et al., 2017).

Since the porosity and pore size of fiber networks are proportional to the fiber diameter, CNF from various biological sources result in nanopapers with distinct pore characteristics (Štefelová et al., 2017). Wood fibrils are 3 nm wide and highly flexible, and their corresponding nanopaper is dense (ca. 20% porosity) (Henriksson et al., 2008; Sehaqui, Liu, et al., 2010) and can provide a high flux only as a submicron thick membrane on top of a mechanical support. Such composite membranes were developed by Ma et al. and used both for the size exclusion of oil emulsion, bacteria and a model virus (MS2 bacteriophage), and for the adsorption of radioactive uranyl cation (UO^{2+}) and a positively charged dye (H. Ma, Burger, Hsiao, & Chu, 2011a, 2011b; H. Y. Ma, Burger, Hsiao, & Chu, 2012; H. Y. Ma, Hsiao, & Chu, 2012; Sato, Wang, Ma, Hsiao, & Chu, 2011). However, the small amount of functional nanofibers in the skin layer limits the adsorption capacity of the composite membrane. The first self-standing nanopaper membrane has been made by Metreveli et al. from *Cladophora* (Metreveli et al., 2014). This alga contains fibrils that are highly crystalline and morphologically different from wood CNF as they are thicker, longer, and straighter, and this enables them to form a nanopaper with a porosity of 40-50% and a pore size of ~20 nm (Štefelová et al., 2017). This membrane is able to retain 20 nm polystyrene and gold nanospheres, and is likely one of the cheapest virus removal substrates for biotechnology applications (Gustafsson et al., 2016; Gustafsson & Mihranyan, 2016).

Generally, membrane systems are prone to fouling since the separation process occurs solely in their outer surface layer (Hong & Elimelech, 1997; Le-Clech, Chen, & Fane, 2006). The adsorption of organic and inorganic matter on the membrane surface gradually reduces its permeation flux necessitating regular back-flushing (every ~30 min in large-scale applications) and chemical cleaning, costly operations that reduce the lifetime of the membrane (Peter-Varbanets, Zurbrugg, Swartz, & Pronk, 2009). On the other hand, depth filtration provides a much larger surface for separation available in the core of the filter. Fouling is heavily reduced in the filter whose pores are much larger than the foulant dimensions. Size exclusion and surface interaction may act in exert in a depth filter, and further tuning of the interaction between the filter surface and the adsorbed contaminant can lead to filter cleaning for multiple utilizations (Sehaqui, Michen, et al., 2016; Sehaqui, Schaufelberger, Michen, & Zimmermann, 2017). The

wide array of functionalities added on the CNF surface enables it to adsorb various chemicals and particles making it an excellent filter building-block (Habibi, 2014; Liu et al., 2013; Andreas Mautner, Maples, et al., 2015; Sehaqui et al., 2014; Houssine Sehaqui et al., 2015; Sehaqui, Kulasinski, Pfenninger, Zimmermann, & Tingaut, 2017; Sehaqui, Mautner, et al., 2016; Sehaqui, Perez de Larraya, Tingaut, & Zimmermann, 2015; Zhang, Sèbe, Rentsch, Zimmermann, & Tingaut, 2014). In our previous work, we demonstrated the filter concept wherein cationic CNF prepared by freeze-drying successfully filters humic acid from aqueous solution (Sehaqui, Michen, et al., 2016).

The present work aims to investigate NPs capture by CNF filters. Aqueous dispersions comprising polymeric, metallic or inorganic NPs having various shapes and at least one dimension from 2 to 100 nm are filtered onto CNF carrying positive charges, although the concept is also demonstrated for negatively charged CNF. We show that gold NPs adsorbed onto the CNF filter can further catalyze the reduction of 4-nitrophenol and methylene blue in aqueous solution.

Experimental

Materials

A pulp residue from pulp and paper industry with a cellulose and hemicellulose content of 95 % and 4.75 %, respectively, was kindly provided by Processum AB, Sweden. 2,3-epoxypropyl trimethyl ammonium chloride (EPTMAC), and aqueous dispersions of ZnO and TiO₂ at 20wt % and ~35wt %, respectively, were purchased from Sigma Aldrich. Aqueous dispersions of gold and silver nanoparticles were purchased from BBI solutions. Suspensions of carboxylate-modified polystyrene nanospheres were purchased from Polysciences Inc (Fluoresbrite YG, nominal diameter of 50 and 100 nm) and from Thermofischer Scientific (FluoSpheres, red fluorescent 580/605, nominal diameter of 20 nm). Multiwall carbon nanotubes (NC7000) were acquired from Nanocyl SA. Graphene nanoplatelets (xGnP) were acquired from XG Sciences. Characteristics of the nanoparticles are given in Table 1.

CNF preparation

The cellulose pulp was dispersed in water, swollen in a 3 wt% sodium hydroxide solution, and thereafter reacted with 1 ml EPTMAC per gram of cellulose at 80 °C for 8 hours under mechanical

stirring. The reaction mixture was then neutralized with hydrochloric acid, filtered and washed thoroughly with deionized water. The chemically modified pulp dispersed in water at a concentration of 0.75 wt% was mixed for 10 min in an ultra-turrax (IKA T25), and disintegrated using a microfluidizer system (M-110EH, Microfluidics Ind., Newton, MA) at a chamber pressure of up to 1200 bars, resulting in cationic CNF. Negatively charged carboxylated CNF with a carboxyl group content of 3.8 mmol g⁻¹ were prepared via the reaction of cellulose with succinic anhydride followed by mechanical disintegration, as reported in our previous work (H. Sehaqui et al., 2017).

CNF characterization

Transmission electron microscopy (TEM) investigations were carried out on a JEOL 2200 FS at 200 kV, using plasma-treated copper grids and stained CNF with methylamine vanadate solution (NanoVan). The ammonium group content of cationic CNF was determined by conductometric titration of chloride ions using AgNO₃ (Hasani, Cranston, Westman, & Gray, 2008). ζ-potential measurements were performed on CNF dispersions at 0.1 wt% using a Zetasizer NanoZS instrument (Malvern, UK) by monitoring the electrophoretic mobility.

CNF filter preparation

The filter was prepared via freeze-drying. 150 ml of the CNF dispersion at 0.75 wt% was placed in a 15×15 cm² copper container, frozen at -50 °, and the ice was thereafter sublimated under vacuum in a Lyovac freeze-dryer (SRK system technik GMBH). This yielded a porous CNF foam which was subsequently hot-pressed for 10 min at 80 ° and 2.2 bars (Carver Inc., USA) giving the CNF filter with a basis weight of 50 g m⁻².

Filter characterization

The density of the filter (ρ_{filter}) was calculated by dividing its basis weight by its thickness determined by a digital caliper. The filter porosity (P) is given by $P = 1 - \rho_{\text{filter}}/\rho_{\text{cellulose}}$ where $\rho_{\text{cellulose}} = 1500 \text{ kg m}^{-3}$. The specific surface area of the filter was determined according to the multipoint Brunauer–Emmett–Teller (BET) method by N₂ physisorption at relative vapor pressure of 0.05–0.2 on a surface area and pore size analyser (Coulter SA3100, Beckman coulter Inc). Prior to each measurement, samples were degassed at 105°C for one hour. Similarly, moisture sorption measurements were performed in a VTI-SA+ dynamic vapor sorption analyzer (DVS, TA-

Instruments, New Castle, USA) at a temperature of 25 °C and at a relative humidity range of 0–30%. The specific surface area of the filter with water as adsorbate was then estimated according to the BET equation. Total porosity and average pore size of the dry filters were evaluated by mercury intrusion porosimetry (MIP) at a pressure range of 0.01–200 MPa (Pascal 140/440; Thermo Fisher; Germany). Scanning electron microscopy (SEM) was carried out using a FEI Nova NanoSEM 230 instrument (FEI, Hillsboro, Oregon, USA) at an accelerating voltage of 5 kV and a working distance of 5 mm. Before SEM observation, tensile fractured cross-section of the filter was placed on a specimen holder, and sputter-coated with a platinum layer of about 7.5 nm (BAL-TEC MED 020 Modular High Vacuum Coating Systems, BAL-TEC AG, Liechtenstein) in Ar as a carrier gas at 5×10^{-2} mbar. Permeance of water through the CNF filter was determined in a dead-end Sterlitech device (HP4750, Kent, USA). 100 ml of deionized water was forced through the CNF filter deposited on a porous stainless steel plate at room temperature using nitrogen at a head pressure of 1 bar. The permeance for the active filtration area (1460 mm²) was obtained by measuring the volume permeated per unit area and time.

NPs preparation and characterization

For the filtration test, gold and silver suspensions were used as received. Polystyrene, ZnO and TiO₂ dispersions were diluted by the addition of deionized water and then mixed in an ultrasonic bath (15 min, Telsonic TUC-150). The final concentration of the NPs is given in Table 1. Similarly, carbon nanotubes and graphene dispersions were prepared from dried powder by the addition of deionized water to reach concentrations of 300 and 700 mg L⁻¹, respectively. These were thereafter sonicated at an amplitude of 55% for 30 min (Branson digital sonifier, model 102C), and supernatants were used.

Table 1. NPs characteristics. Au refers to gold NPs, Ag refers to silver NPs, PS refers to polystyrene nanospheres, ZnO refers to Zinc oxide NPs, TiO₂ refers to titanium dioxide NPs. The number following the NPs refers to the average particles size of the NPs.

	Graphene	CNT	Au-2	Au-5	Ag-20	PS-20	PS-50	PS-100	ZnO	TiO ₂
Particle size range (nm)	-	-	1–5	4–15	15–45	15–45	25–100	40–200	50–200	25–150
Concentration (mg L ⁻¹)	700 ^a	300 ^a	12	63	3.1	250	250	250	70	70

Volume	10	10	10	10	10	50	50	50	10	10
filtered (mL)										
Absorbance	0.64	0.26	0.19	0.78	0.94	$4.7 \cdot 10^5$	$2.5 \cdot 10^5$	$4.7 \cdot 10^4$	0.75	1.2^b
A_0 or Intensity										
I_0										
Wavelength at	240	265	525	515	404	610	513	565	367	255
A_0 or I_0 (nm)										

^ainitial concentration. ^b3 times diluted solution.

Transmission electron microscopy (TEM) investigations were carried out on a JEOL 2200 FS at 200 kV. Before depositing the dispersions onto the copper grid, metal and metal oxide NPs were treated with Bovine Serum Albumin (BSA), as reported elsewhere (Benjamin Michen et al., 2015), in order to prevent drying artifacts. ζ -potential and particle size distribution analyses of the NPs were performed on the dispersions using a Zetasizer NanoZS instrument (Malvern, UK), by monitoring the electrophoretic mobility and dynamic light scattering, respectively. Due to the small diameter of 2 nm gold NPs, their particle size distribution was determined by image analysis of TEM micrographs using ImageJ. Aqueous dispersions of carbon, metal and metal oxide NPs were analysed by UV-vis spectrophotometry (Cary 1E spectrophotometer, Varian). Aqueous dispersions comprising fluorescent polystyrene nanospheres were analysed by fluorescence spectroscopy (Fluorolog-3, Horiba JobinYvon). The excitation wavelength was set at 441 and 554 nm for Fluoresbrite YG and red FluoSpheres, respectively, and the fluorescence intensity was registered in the emission ranges of 470–550 and 590–630 nm, respectively. The $\log_{10}$ reduction value (LRV) was calculated as the logarithm of the ratio of the area under the curve of the reference and filtrate solutions.

Retention test

NPs dispersed in water were vacuum-filtered at 100 mbar on top of the CNF filter deposited on a glass filter disc (Duran, NW 19, Por 2). The active filtration area is 254 mm². The flux was obtained by measuring the volume permeated per unit area and time. Reference samples were prepared by filtering the NPs on top of the glass filter disc alone, and were found to be similar to the original NPs dispersions. The concentration of the NPs and the volume filtered are given

in the Table 1. Subsequent to the vacuum filtration, aqueous solutions of the NPs were analysed by spectrophotometry or fluorescence spectroscopy. UV-vis absorbance and fluorescence intensity data of the reference NPs dispersions are given in Table 1.

Catalysis experiments

Gold NPs were loaded onto the CNF by vacuum-filtering the gold dispersion onto the filter as described for the retention test. The dispersion volumes were arbitrarily selected to have 0.5 wt% or 2.5 wt% of gold NPs related to the CNF. A first solution was prepared by adding 2 ml of NaBH_4 at 30 mM to 4 ml of 4-nitrophenol at 0.2 mM. A second solution was prepared by adding 0.5 ml of NaBH_4 at 30 mM to 4 ml of methylene blue at 0.4 mM. The first and second solutions were filtered onto the CNF filter containing 2.5 wt% and 0.5 wt% of gold NPs, respectively. To exclude any effect coming from the adsorption of 4-nitrophenol and methylene blue onto the cationic CNF, a reference experiment was conducted wherein the first and second solutions were filtered onto the bare CNF filter. Finally, the reduction of 4-nitrophenol and methylene blue was examined by measuring the UV-Vis absorbance of the feed and filtrate solutions.

Results and discussion:

Quaternary ammonium functionalized cellulose nanofibers with a diameter of ~ 4 nm (Fig.1a) were obtained from NaOH swollen wood pulp via the water-based reaction between hydroxyl groups of cellulose and a functional epoxy reagent (2,3-epoxypropyl trimethyl ammonium chloride), followed by mechanical disintegration (Pei et al., 2013). The scheme of the reaction is given in Fig. S1 (see ESI). The presence of 0.37 mmol of the ammonium functions per gram of CNF is equivalent to a degree of substitution is 0.08, and this provide CNF with a positive surface charge in acidic and basic pHs (Fig.1b), making them suitable for the adsorption of negatively charged species (Andreas Mautner, Maples, et al., 2015; Pei et al., 2013; Sehaqui, Mautner, et al., 2016; Sehaqui, Michen, et al., 2016; H. Sehaqui et al., 2015). After freeze-drying and compressing the CNF, a filter having a density, porosity and specific surface area of 0.275 g cm^{-3} , 80%, and $5 \text{ m}^2 \text{ g}^{-1}$, respectively, is obtained. The filter exhibits the typical sheet structure of freeze-dried CNF resulting from the growth of ice crystals during freezing which pushes CNF in their interstices (Fig.1c) (Paakko et al., 2008; Sehaqui, Salajkova, et al., 2010).

The sheets are many microns large and are randomly distributed in the filter providing pores and a tortuous path necessary to enhance the contact time between the filter and the incoming NPs. SEM micrographs and mercury intrusion into the filter reveal that the pore size ranges from ca. 0.25 to 10 microns (Fig.1d), and is therefore larger than the NPs.

Fig.1 (a) TEM micrograph of CNF. (b) ζ -potential of CNF at various pHs. (c) Photograph (upper left) and fractured cross-section SEM image of the CNF filter. (d) Pore-size distribution of the CNF filter.

The hydrophilic character of the filter is shown by its null contact angle and by the quasi-immediate absorption of a water drop laid on its surface. The water absorption by the filter opens its surface making it as high as $200 \text{ m}^2 \text{ g}^{-1}$, as determined by dynamic vapor sorption experiment. Hence, the specific surface areas of the CNF filter in the dry and wet states are 2-4 orders of magnitude larger than the $0.02 \text{ m}^2 \text{ g}^{-1}$ external surface of a membrane having the same basis weight, i.e. 50 g m^{-2} . This, together with the CNF hydrophilicity, and the reported antimicrobial properties of quaternary ammoniums compounds (Gilbert & Moore, 2005), would make the present filter less prone to fouling than CNF-based membrane systems and operational for much longer times.

The CNF filter has a thickness of $180 \text{ }\mu\text{m}$ resulting in a water permeance of $65 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$. The flux registered under vacuum-filtration is $50 \text{ L h}^{-1} \text{ m}^{-2}$. For comparison, wood CNF

nanopaper provides 1-2 orders of magnitude lower permeance (Andreas Mautner, Lee, et al., 2015; Andreas Mautner, Maples, et al., 2015; Sehaqui, Michen, et al., 2016). The best self-standing CNF membrane reported so far is made of *Cladophora* CNF and provides a permeance and flux of $45 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}$ and $33 \text{ L h}^{-1} \text{ m}^{-2}$, respectively, for a three times thinner membrane having the same basis weight (chapter S2, ESI). The reported water permeance for 6-67 μm thick *Cladophora* membranes is $10\text{-}150 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$ (Gustafsson et al., 2016; Gustafsson & Mihranyan, 2016). Thinner membranes exhibit a higher permeance, to the detriment of their separation performance (Gustafsson & Mihranyan, 2016).

NPs investigated here are displayed in TEM micrographs in Fig. 2a. Their surface charge and particle size data are shown in Fig. 2b&c. These include emerging carbon nanomaterials (graphene nanoplatelets and multiwall carbon nanotubes) widely used in electronic, energy, and composite applications. The theoretical thickness of a single graphene layer is 0.335 nm (Jussila, Yang, Granqvist, & Sun, 2016). This is smaller than any other NP investigated herein although the two other dimensions of graphene being in the micrometer scale. Multiwall carbon nanotubes (CNT) have a diameter of 5-10 nm and a length above one micron. With a diameter of 2 and 5 nm, gold nanospheres are the smallest 3D NPs investigated here. Gold and silver NPs are being used/researched for their sensing, therapeutic and catalytic effects, and the latter is suitable for its antimicrobial properties (Daniel & Astruc, 2004; Kim et al., 2007; Nyström, Fernández-Ronco, Bolisetty, Mazzotti, & Mezzenga, 2016). Fluorescent carboxylate-modified polystyrene nanospheres are suitable model particles representing well dispersed non-coagulated viruses owing to their nanodimension (20, 50 or 100 nm) and negative surface charge (Armanious, Münch, Kohn, & Sander, 2016; Gustafsson & Mihranyan, 2016). TiO_2 and ZnO nanofillers, widely used in coatings, cosmetics and as photocatalysts, have herein an irregular shape and an average particle size of 50 and 90 nm, respectively. TiO_2 was investigated at two solution pHs where it has opposite surface charges and the same particle size distribution, the isoelectric point of TiO_2 being ~ 6 (Fig. S3, ESI). With the exception of TiO_2 at pH 4 and graphene, all NPs display a negative surface charge (Fig. 2c).

Fig. 2 (a) TEM micrographs, (b) Particle size distribution, and (c) ζ -potential of investigated NPs. Au, Ag and PS denote gold, silver and polystyrene, respectively, and the accompanying number is the average particle size.

The filter performance has been investigated by vacuum-filtering aqueous dispersions containing various nanomaterials on top of CNF, and thereafter comparing the signal of the filtrate with that of the feed solution registered by UV-vis spectrophotometry or fluorescence spectroscopy. Results are shown in Fig.3. The initially black yet translucent color of the graphene and CNT dispersions combined with their TEM images suggest that these carbon nanomaterials were well dispersed in water prior to filtration, which is a result of the ultrasonication treatment. Filtering these dispersions onto CNF results in clear filtrate solutions and black filters containing the carbon nanomaterials. The absorbance of graphene and CNT in the filtrate is below the detection limit of the UV-vis spectrophotometer, we therefore expect that at least 99% of the carbon nanomaterials were removed by the CNF filter. Since graphene and CNT nanomaterials present at least one dimension larger than the smallest pores of the filter, it is probable that size exclusion and surface adsorption act jointly for the removal of the carbon nanomaterials by the filter. The positive surface charge of graphene indicates that specific interactions beyond electrostatics may lead to its adsorption onto CNF.

In contrast to carbon nanomaterials, all other NPs investigated in this work have their 3 dimensions smaller than the filter pores, and hence the separation process should arise from the interaction of CNF with the nanomaterials. The negative zeta-potential value for gold and silver NPs versus the positive surface charge of the filter suggests that the interaction between the two components is mainly electrostatic. The interesting feature of the present CNF filter lies in its ability to remove nanoparticles as small as 2 nm, and even dissolved molecules as we have shown in our previous work (Sehaqui, Michen, et al., 2016). Such separation would be very challenging via size-exclusion, as it would require high filtration pressure and a membrane with a pore size well below 10 nm. 2 nm and 5 nm gold NPs were successfully filtered onto CNF resulting in a clear filtrate and a filter loaded with gold NPs. The peak at ~520 nm due to the surface plasmon resonance of gold NPs completely disappears in the filtrate and this is equivalent to a $\log_{10}$ reduction value (LRV) above 2, a similar performance like that recorded for the removal of 20 nm silver NPs. Note that a control sample made of unmodified CNF does not retain Au-5 NPs (Fig S5, ESI). The colorless solutions obtained after filtration of 20, 50 and 100 nm surrogate polystyrene nanospheres have a fluorescence intensity reduced by 1.75, 3.4 and 4.8 orders of magnitude compared to the feed solutions. In the pioneer work on virus clearance using *Cladophora* CNF nanopaper, Metreveli and Gustafsson successfully retained 20 to 500 nm polystyrene and gold nanospheres after filtration onto the algal membrane whose pores are ~20 nm large (Gustafsson et al., 2016; Gustafsson & Mihranyan, 2016). We show in S2 that *Cladophora* CNF membrane does not provide retention of 5 nm gold NPs (details in ESI). The present CNF filter is thus the first reported substrate made exclusively of cationized native cellulose nanofibers and capable of removing extremely small NPs from water.

Filtration of metal oxide nanoparticles onto CNF reveals a limitation of the present filter. This latter exhibits an excellent filtration performance for ZnO comparable to that for other nanomaterials (LRV>2), attributed to the negative zeta-potential value for ZnO. On the other hand, TiO₂ removal by the CNF filter shows a distinct pH-dependent performance. At a pH of 4, the retention of TiO₂ by the CNF filter is moderate as indicated by the UV absorption of the filtrate solution containing TiO₂. This is attributed to the repulsion between positively charged

TiO₂ and CNF. In contrast, TiO₂ has a negative surface charge at pH 10 and displays a much better retention onto the CNF filter without any UV detectable traces in the filtrate. The performance of the CNF filter towards the removal of positively charged TiO₂ NPs can be enhanced by placing underneath it a negatively charged filter prepared from highly carboxylated cellulose nanofibers reported in our previous work (H. Sehaqui et al., 2017). The log₁₀ reduction value (LRV) is then above 2 at pH 4, and the flux is 10 L h⁻¹ m⁻² (Fig. S4b, ESI). We anticipate that alternating CNF filters with various functionalities provides a universal water treatment technology addressing various pollutants entering water.

Fig.3 Signal of the feed and filtrate solutions registered by UV-vis or fluorescence spectroscopy. A and I refer to the absorbance and intensity of the sample, respectively. A₀ and I₀ refer to the maximum absorbance and intensity of the feed solution in the investigated wavelength, respectively. A₀ and I₀ values are given in Table 1 together with the feed concentrations. The signal of Au-2 was intensified by concentrating the feed and filtrate solutions five times. The photographs show the feed (colored) and filtrate (clear) solutions as well as the CNF filter at the end of the filtration.

The central part (through the thickness) of the CNF filter with polystyrene nanospheres was investigated by scanning electron microscopy (Fig.4). The micrographs show abundant NPs deposited on the CNF sheets and this proves that the separation occurs in the core of the filter, expected from its large pores. NPs stacking in the sheet indicates that the separation process is governed by the interaction of polystyrene NPs with the CNF and also by interactions (e.g. van der Waals interactions) between deposited polystyrene NPs, and this explains the good performance of the filter.

Fig.4 Fractured cross-section SEM image of the central part of CNF after filtration of fluorescent polystyrene nanospheres having a diameter of (a) 20 nm, (b) 50 nm, and (c) 100 nm. Upper left in Fig. 4c is a lower magnification of the CNF sheet containing PS-100 (scale bar is 3 μm).

Apart from the direct use of CNF as a sorbent material for water purification, the possibility to utilize the CNF filter loaded with NPs in other applications is interesting as it could reduce the carbon footprint of the water purification technology. In the work on the collection of carbon nanotube aerosols on CNF membranes, Toivonen et al. showed that the membrane can thereafter be compacted and used as a transparent, conductive, and flexible conducting film for electronic devices (Toivonen, Kaskela, Rojas, Kauppinen, & Ikkala, 2015). Nyström et al. demonstrated the sensing and catalytic properties of amyloid templated gold aerogels (Nyström et al., 2016). Similarly, we aim in this work to exploit the catalytic properties of gold NPs on the CNF filter for the reduction of chemicals in aqueous media. Model nitro-aromatic and dye compounds were filtered through CNF containing or not gold NPs in the presence of NaBH_4 . The bare CNF filter results in a poor reduction/adsorption of 4-nitrophenol and methylene blue indicated by the strong absorbance peaks of these compounds in filtrate solutions registered at 400 nm and 670 nm, respectively (Fig.5). In contrast, the filter loaded with gold NPs is catalytically active, resulting in a complete reduction of 4-nitrophenol to 4-aminophenol indicated by the disappearance of the absorption peak at 400 nm and the appearance of a new peak at 300 nm. The discoloration of methylene blue solution after filtration onto CNF containing gold NPs (inset) and the strong reduction of its absorbance peak at 670 nm indicate the formation of the reduction product leuco methylene blue (Fig. 5). The reduction of 4-nitrophenol and methylene blue compounds is due to an electron transfer mechanism from BH_4^- ions to the functional nitro and sulfur groups, respectively, catalyzed by gold NPs (Ciganda et al., 2014; Guo et al., 2016; Vidhu

& Philip, 2014). These two experiments show that the CNF / gold NPs hybrid filter can be successfully used for environmental catalysis in aqueous media.

Fig.5. UV-vis spectra of filtered solutions through the bare CNF filter (0% Au-5), and through the CNF filter loaded with 2.5 wt% and 0.5 wt% gold NPs, used respectively for the reduction of 4-nitrophenol and methylene blue.

Conclusion

A filter for NPs capture is made exclusively of cationized native cellulose nanofibers without their dissolution via cationization of wood pulp in water, mechanical disintegration, freeze-drying and pressing. The CNF filter offers an alternative to separative membranes and permits the retention of NPs in its interior area, governed by attractive forces between the NPs and the CNF. Consequently, retention of NPs and molecules in the CNF filter is not limited by a “size/molecular-weight cut-off” and is demonstrated for 2 nm gold NPs that are more than two orders of magnitude smaller than the filter pores. The filter is made of randomly oriented sheets which form a cascade permitting a good contact between the NPs and the positively charged CNF. The water permeance through the filter is $65 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$, higher than the permeance of state-of-the-art CNF membranes. While the present filter exhibits an excellent performance for the removal of negatively charged NPs, its moderate performance towards positively charged NPs can be enhanced by placing a negatively charged filter underneath it. Data obtained with surrogate gold and polystyrene nanospheres suggest that the present filter would be suitable for the removal of water-borne viruses, which generally possess negatively charged surfaces and remain one of the main drinking-water risks in developing countries (B. Michen & Graule, 2010; Peter-Varbanets et al., 2009). We stipulate that the filter performance in terms of flux and pollutants retention can be enhanced by diversifying the CNF functionalities and by controlling

the sheets orientation in the filter, leading to an efficient, universal and sustainable water purification technology.

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