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Mechanically flexible and optically transparent three-dimensional nanofibrous amorphous aerocellulose

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ABSTRACT

Aerocelluloses are considered as "third generation" aerogels after the silica and synthetic polymer-based ones. However, their brittleness and low optical translucency keep quite narrow their fields of applications. Here, both issues are addressed successfully through the fabrication of flexible and mechanically robust amorphous aerocellulose with high optical transparency, using trifluoroacetic acid as a solvent and ethanol as a non-solvent. The developed aerocellulose displays a meso-macroporous interconnected nanofibrous cellulose skeleton with low density and high specific surface area. We demonstrate its high efficiency as supporting matrix for nanoscale systems by incorporating a variety of colloidal quatum dots, that provide bright and stable photoluminescence to the flexible aerocellulose host.

1. Introduction

In the past few years, aerogels have drawn increasing attention for different scientific and industrial applications because of their extremely low bulk density and high specific surface area (Du, Zhou, Zhang, & Shen, 2013; Fricke & Emmerling, 1998; Pierre & Pajonk, 2002). In particular, cellulose aerogels (aerocelluloses) have somewhat similar structural properties to silica and synthetic polymer counterparts, but also have the major advantage of being bio-based (Demilecamps, Beauger, Hildenbrand, Rigacci, & Budtova, 2015; Sescousse, Gavillon, & Budtova, 2011b). Several attempts to prepare cellulose-based aerogels have been reported (Granstrom et al., 2011). Commonly, the preparation process of the aerocellulose involves the following three key steps: (i) Solution-sol transition, (ii) Sol-gel transition (gelation), and (iii) Gel-aerogel transition (drying) (Sescousse, Gavillon, & Budtova, 2011a). All three steps determine the microstructure of the aerogel and affect its properties. The first step requires the dissolution of the cellulose in derivatizing (Liebert, 2010) or non-derivatizing solvent (Sen, Martin, & Argyropoulos, 2013). After that, coagulation of the cellulose solution using a non-solvent (regeneration) is followed by solvent exchange and drying under supercritical CO_2 ($scCO_2$). However, the aerocelluloses developed with this strategy do not combine high surface area, strong mechanical properties, superinsulating properties and high transparency in one material (Gavillon & Budtova, 2008; Sescousse et al., 2011a). Yet, such aerocelluloses could find potential applications as photocatalysts (Shao, Lu, Zhang, & Pan, 2013) optical sensors, and detectors (Birks et al., 2010; Katagiri, Ishikawa, Adachi, Fuji, & Ota, 2015). In addition, several groups (Mohanan, Arachchige, & Brock, 2005; Sorensen, Strouse, & Stiegman, 2006; Wang, Shao, Bacher, Liebner, & Rosenau, 2013; Zhang, Yang, Bao, Wu, & Wang, 2013) have also proposed to include quantum dots (QDs) to enhance the functionality of aerogels for solid-state optical applications such as sensors or 3D displays, by exploiting the size- and composition-tunable QDs optical properties (Kovalenko et al., 2015). However, wide-spread applications of silica aerogels have been hindered by their high production cost and brittle/fragile mechanical properties. Only a few papers have reported the fabrication of aerocellulose combining high optical transparency and strong mechanical properties. Recently, cellulose aerogels with a highly porous network were reported to combine toughness and transparency (Mi, Ma, Yu, He, & Zhang, 2016). This was achieved by dissolving cotton pulp in 1-allyl-3-methylimidazolium chloride (AMIMCl) solution followed by coagulation in aqueous solution of AMIMCl (60 wt%). In another work also, aerocelluloses with high transparency, mechan-

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ical toughness, and good heat insulation were prepared from liquid nanocrystalline cellulose (LC-NCell) dispersions (Kobayashi, Saito, & Isogai, 2014). Here, we demonstrate an alternative method for the fabrication of mechanically robust amorphous aerocelluloses that show flexibility and high optical transparency. The method is based on the transformation of microcrystalline cellulose (MCC) into a highly porous three-dimensionally nanofibrous structure with large specific surface area by using for the first time trifluoroacetic acid (TFA) as a solvent. We present the optimized conditions to obtain aerocellulose with high optical transparency, by means of ethanol addition (as a non-solvent) to cellulose-TFA mixture. Under these optimized conditions, we show the effect of cellulose concentration on the physicochemical properties of the transparent aerocellulose. Finally, we demonstrate its potential use in optical applications through the incorporation of colloidal QDs.

2. Experimental

2.1. Aerogel preparation

2.1.1. Materials

Microcrystalline cellulose (MCC), ethanol and trifluoroacetic acid (TFA, 99%) were purchased from Sigma-Aldrich and used as received. All reagents and solvents used were of analytical grade.

2.1.2. Preparation of amorphous cellulosic aerogels

Cellulose solutions with different concentrations (2.0, 4.0 and 5.6% (w/v)) were prepared by dispersing MCC in TFA. The solutions were maintained at 0 °C for 24 h and then were kept at room temperature for 10 days until the cellulose completely dissolved. 11.2 mL of ethanol (28% of the TFA volume) was added to 40 mL of each cellulose solution under constant stirring for 30 min at room temperature (about 25 °C). The mixture was then poured into a circular mold (10 cm^2). The mold was sealed and allowed to stand for 24 h. This resulted in the formation of a free-standing and transparent organogel. The volume of the organogel was reduced by less than 5% compared to its volume in the liquid state (just after the addition of the ethanol).

The obtained gel was immersed in an ethanol bath (200 mL). The ethanol was exchanged twice every day for at least four consecutive days in order to eliminate all trifluoroacetyl ester groups (Fig. S1). After solvent exchange by ethanol the volume of alcogel was reduced by 5–10%. The obtained alcogel was then dried using supercritical CO_2 ($scCO_2$) chambers (Malvern, USA). First the system was pressurized at 50 bar, and 10 °C under CO_2 liquid for 5 h and then the system was pressurized at 80 bar and 37 °C for 1 h. The chamber was then gradually depressurized at 37 °C for 30 min.

The resulting aerogels were conditioned at room temperature and 58% RH for one week before analyses.

2.2. Preparation of colloidal quantum dots (QDs)

2.2.1. Materials

Cadmium oxide (CdO, ≥99.99%), selenium (Se, 99.99%), trioctylphosphine oxide (TOPO, ≥90%) and trioctylphosphine (TOP, ≥97%) were obtained from Strem Chemicals; zinc diethyldithiocarbamate (97%), octadecylphosphonic acid (ODPA, 97%), oleic acid (OA) (90%), toluene (≥99.7%), methanol (≥99.9%), ethanol (≥99.8%, without additive), chloroform (99.0–99.4%) and tetrachloroethylene (TCE, anhydrous, ≥99%) from Sigma-Aldrich; $PbCl_2$ (99.999%) and sulfur (S, 99.999%) were purchased from Alfa-Aesar; oleylamine (OlAm, 80%) from Acros Organics.

2.2.2. Synthesis of CdSe QDs

To synthesize *CdSe QDs*, we use a published protocol by Carbone et al. (2007) with slight modifications. TOPO (3.0 g), ODPA (0.28 g) and CdO (0.06 g) were mixed in a 50 mL flask and heated to about 150 °C under vacuum for 1 h. Then the system was purged with nitrogen and heated to above 300 °C to dissolve the CdO until a clear and colorless mixture was obtained. At this point, 1.5 g of TOP was inserted into the flask, the temperature was adjusted to the required injection temperature, and a Se:TOP solution (0.058 g of Se with 0.360 g of TOP) was injected. The injection temperature and the reaction time were modified in order to synthesize CdSe QDs of different sizes.

2.2.3. Coating of CdSe QDs with ZnS

To coat CdSe QDs with ZnS (shell thickness 1–1.5 monolayers), we adapted a procedure from Dethlefsen & Døssing, (2011) decomposing zinc diethyldithiocarbamate in an amine solution. Typically, a QD toluene suspension containing 4 μM of core CdSe QDs was injected in 5 mL of OlAm in a three-necked flask. Then the zinc precursor was added in a range from 0.2–0.9 g, depending on the core diameter (2.1–5.1 nm), at room temperature under stirring. The mixture was heated to 200 °C under argon atmosphere and kept for 30 min to complete the zinc salt decomposition. Afterward, the mixture was cooled to room temperature. The QDs were purified 3 times by repeated addition of methanol followed by centrifugation to precipitate the QDs. The QDs were finally suspended in chloroform.

2.2.4. Synthesis of Oleic acid-capped PbS QDs

Oleic acid-capped PbS QDs were prepared using a slight modification of the method described in Moreels et al. (2011) Briefly, for the synthesis 1 g of $PbCl_2$ and 7.5 mL of OlAm were degassed for 30 min at 125 °C in a three-neck flack under Argon. Then, the temperature was adjusted to 120 °C, and 2.25 mL of a 0.3 M OlAm-S stock solution was added. The reaction proceeded for 1 min to achieve the desired size. After synthesis, the OlAm ligands were replaced by adding OA to the QD suspension in toluene, followed by precipitation with ethanol and resuspension in toluene. The diameter was determined from the spectral position of the first absorption peak.

2.3. Preparation of cellulose QD composite aerogels

The aerogels were cut into pieces of 1 cm × 1 cm × 0.1 cm using a sharp blade and were dipped into QD dispersions in chloroform, at various QD concentrations (5 and 15 μM) for 24 h. The obtained composites were then immersed in ethanol for further solvent exchange and subsequently dried with $scCO_2$.

2.4. Characterization

The density of the obtained aerogels was determined by measuring their weights and dividing them by their volumes.

High-Resolution Scanning Electron Microscopy (HRSEM) images were acquired on a JEOL JSM 7500FA (Jeol, Tokyo, Japan) equipped with a cold field emission gun (cold-FEG), operating at 10 kV acceleration voltage. The samples have been carbon coated with a 10 nm thick film using an Emitech K950X high vacuum turbo system (Quorum Technologies Ltd, East Sussex—UK).

The specific surface area and pore size distribution were evaluated by nitrogen physisorption measurements carried out at 77 K in a Quantachrome gas sorption analyzer, model autosorb iQ. The specific surface areas were calculated using the multi-point BET (Brunauer–Emmett–Teller) model, considering 6 equally spaced points in the P/P^0 range of 0.05–0.30. The pore size distribution was evaluated from the desorption branches of isotherms according to the Barrett–Joyner–Halenda (BJH) method. Prior to measurements, samples were degassed for 22 h at 50 °C under vacuum.

The aerogels were immersed in water for four days and subsequently analyzed by thermogravimetric analysis (TGA) to quantify