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Ultra-low permittivity porous silica-cellulose nanocomposite substrates for 6G telecommunication

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Abstract
The continuously increasing demand for faster data traffic of our telecommunication devices requires new and better materials and devices that operate at higher frequencies than today. In this work, a porous composite of silica nanoshells and cellulose nanofibers is demonstrated as a suitable candidate of dielectric substrates to be used in future 6G frequency bands. The hollow nanospheres of amorphous SiO$_2$ with outstanding electromagnetic properties were obtained by a template-assisted Stöber process, in which a thin shell of silica is grown on polystyrene nanospheres first, and then the polymer core is burned off in a subsequent step. To be able to produce substrates with sufficient mechanical integrity, the nanoshells of SiO2 were reinforced with cellulose nanofibers resulting in a porous composite of very low mass density (0.19 ± 0.02 g cm$^{-3}$), which is easy to press and mold to form films or slabs. The low relative dielectric permittivity ($\varepsilon_r = 1.19 \pm 0.01$ at 300 GHz and $\varepsilon_r = 1.17 \pm 0.01$ at 2.0 THz) and corresponding loss tangent ($\tan \delta = 0.011 \pm 0.001$ at 300 GHz and $\tan \delta = 0.011 \pm 0.001$ at 2.0 THz) of the composite films are exploited in substrates for radio frequency filter structures designed for 300 GHz operation.

Keywords: silica nanoshells, cellulose nanofibers, porous dielectric composites, ultra-low dielectric permittivity, 6G applications

1. Introduction
Because of the growing number of wireless communication devices and the increasing demand for faster data traffic, the currently used frequency bands are already or soon becoming congested. Although, some applications can be supported by the present mobile networks, it is clear that we need to increase the operating frequency from the currently used 4G and experimental 5G bands to the terahertz bands (0.1–10 THz) of 6G to satisfy mobile broadband communication in the future [1–6]. High-speed radio hardware of wireless communications needs several technical aspects to be considered. Among them are the linearity of transmitters, broad bandwidth and high output power. For the receiver, broad bandwidth, low noise and high linearity are required. High spectral efficiency together with...
high data rates can be available if the used frequency range is high enough to support wide bandwidth for the information signal. In 4G wireless systems, the typical information bandwidth is 1 GHz; whereas in 5G, the bandwidth is 10 GHz, which could be increased to 100 GHz (e.g. at 300 GHz of center frequency) in 6G networks [7–10].

Dielectric materials are used as substrates for radio frequency devices including filters, resonators and antennas [11, 12]. Usually, planar devices offer the best options, when the size, weight, ease of installation, performance and cost are constraints. For instance, in the case of microstrip antennas, the structure consists of a very thin metallic strip above the metallic ground plane, which are separated by a dielectric sheet [13–15]. In the design of such antennas, the properties of the substrate play key roles. Ultra-low-permittivity dielectrics provide very low signal propagation delay, and their ultra-low-loss characteristics grant low signal attenuation, which both increase the output power of the transmitter and increase the signal-to-noise ratio of the receiver. In the typical radio-frequency structures, low permittivity materials perform wider bandwidths and higher quality beam in the antenna since the wave propagation medium behaves almost like air causing only small reflections and interferences in the signal. The need to integrate RF components smaller by using high permittivity materials is becoming invalid due to the combination of wavelength in 6G frequencies, and the line widths used in fabrication technologies. Low permittivity materials are also likely to be more tolerant for assembly variations in electronics packaging because of previous reasons [11, 16, 17].

For microstrip antennas and filters operating above 100 GHz, dielectric materials include polymers (e.g. polytetrafluoroethylene [18] and polyimide [14, 19, 20]), silica [21, 22] and glass reinforced polymers [23] with relative permittivity from 2.1 to 4.0 and loss tangent from $4 \times 10^{-4}$ to $2.5 \times 10^{-3}$. In addition, device integration on Si may be an option too [15]. Considering that both permittivity and loss tangent are affected by the density and microstructure of the dielectric material, introduction of pores into the structure is a feasible approach to lower those values even further [17, 24, 25], and has been applied for several dielectrics meant for high frequency applications as listed in table 1.

Since silica is intrinsically a low permittivity and loss material ($\varepsilon_r = 3.8$ and $\tan \delta = 0.005$ at 300 GHz), and a number of different procedures can be applied to develop porous materials (e.g. soft template-assisted on polymers [33–35], biopolymers [36], emulsions [37, 38] and colloids [39]; hard templating on polymers [40], oxides [41, 42] and metals [43]; selective leaching of metal alloys [44, 45], inorganic [46] and polymer-inorganic composites [47]; foaming [48–50]; anodization [51, 52]; freeze-drying [53–55], freeze-casting [56] and phase separation [57], it seems to be a plausible strategy to synthesize porous silica based materials, whose properties are expected to be outstanding at high frequencies.

Accordingly, in this work, we synthesize hollow silica nanospheres (i.e. nanoshells) with ultra-low dielectric permittivity and loss, using polymer template-assisted Stöber synthesis. The nanoshells are further reinforced with cellulose nanofibers to demonstrate advanced environmentally friendly substrate materials for high frequency applications. We show that the new composite is suitable for planar filters operating at 300 GHz, and probably even beyond as suggested by the properties measured up to 2 THz.

### 2. Experimental

#### 2.1. Materials and methods

**2.1.1. Materials.** Styrene, polyvinylpyrrolidone ($M = 10,000$ g mol$^{-1}$), potassium-persulfate, hexadecyltrimethylammonium bromide ($\geq 99\%$), tetraethyl orthosilicate ($\geq 99\%$), ammonium hydroxide solution ($25$ wt.$\%$) and absolute ethanol ($99.5$ wt.%.) were purchased from Sigma-Aldrich and Altia, respectively.

Cellulose nanofibers were synthetized from bleached birchwood pulp pre-treated in a deep eutectic solvent similar to that described earlier [58]. In brief, 107.5 g choline chloride and 92.5 g urea were heated in oil bath at $100$ °C until a colorless liquid is obtained, then 2 g dry cellulose fibers were added and kept in the liquid for 2 h. Two hundred milliliters of deionized water was added to the mixture, then the cellulose fibers were filtered and washed with deionized water. A diluted aqueous dispersion ($0.5$ wt.$\%$) of the pre-treated cellulose was further treated in a microfluidizer (Microfluidics M-110EH-30) passing through 400 and $200 \mu$m chambers five times at 1000 bar, and then the obtained cellulose nanofiber gel was stored at $4$ °C until use.

Substrate preparation. The synthesis of hollow silica nanospheres followed a template-assisted route similar to that reported earlier [59]. First, the polymer beads were synthesized by emulsion polymerization. In a two neck round bottom flask, 0.1 g polyvinylpyrrolidone stabilizer was dissolved in 180 ml water then 20 g styrene monomer was added and...
N\textsubscript{2} gas was bubbled through the solution, and simultaneously, stirring at 250 rpm was applied. After 20 min, 0.2 g potassium persulfate initiator was dissolved in 20 ml water and added to the reaction mixture. The temperature was raised to 70 °C and maintained for 24 h, after which it was allowed to cool down to room temperature and the polystyrene nanospheres product was dried at 40 °C for 24 h.

To obtain silica coated structures, 2 g of the polystyrene nanospheres and 0.625 g hexadecyltrimethylammonium bromide were dispersed in the mixture of 30 ml absolute ethanol and 25 ml water using ultrasonic agitation. Next, 3 ml ammonia solution was added to the dispersion and stirred for 3 min, and then 2 ml tetraethyl orthosilicate was added while continuing stirring at room temperature for 2 h to facilitate polycondensation. The polystyrene-silica core–shell particles were centrifuged (10 min at 3500 rpm), decanted and washed with water. The purification process was repeated five times, and then dried overnight at 40 °C. Hollow silica nanospheres were made by burning off the polystyrene core in a tube furnace at 550 °C in air for 5 h.

Silica-cellulose nanocomposite slabs were prepared by mixing the nanoshells (5.0 wt.%) in the cellulose nanofiber (0.5 wt.%) gel using a spatula. Aliquots of the mixture were dispensed on a smooth plate and pressed (~5 kPa at room temperature) with a counter plate to form films of ~2 mm in thickness and ~15 mm in diameter. Finally, the films were dried at 105 °C for 2 h (figure 1) while applying an uniaxial pressure of ~2 kPa.

2.2. Characterization

2.2.1. Materials and structures. The morphology and microstructure of the synthesized materials were assessed using field emission scanning electron microscopy (FESEM, Zeiss Ultra Plus) and transmission electron microscopy (TEM Jeol Jem-2200FS). Particle size distributions of the synthesized polymer spheres, silica coated polymer core–shell structures and silica nanoshells were determined by analyzing 100 particles of each in FESEM and TEM micrographs using Fiji ImageJ software. The crystal structure of the nanoshells was analyzed by Raman spectroscopy (Horiba Jobin-Yvon LabRAM HR800) and x-ray diffraction (XRD, D8 Discover, Bruker). The surface chemistry of the silica nanospheres was analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, Bruker Vertex V80 vacuum FTIR spectrometer). The density and porosity of composites were calculated from the dimensions and weight of dried films.

2.2.2. Electromagnetic measurements. THz spectroscopy (Terapulse 4000, 60 GHz–2.5 THz spectral range and 90 dB dynamic range at the peak, high-resolution mode with 10 ps pre-scan extent, 100 ps optical delay extent, 200 ps s\textsuperscript{-1} sweep speed and 50-fold averaging) was applied to determine the dielectric properties of the materials. First, air (reference) and then the composite films were measured through a metallic aperture of 5.0 mm in diameter. The measured transmitted amplitude-time data were Fourier transformed to obtain the corresponding transmission spectra, from which the real and imaginary parts of dielectric permittivity were calculated.

3. Results and discussion

The polystyrene templates synthesized by emulsion polymerization are spherical with an average diameter of 667 ± 28 nm. After the polycondensation reaction, a thin ~30 nm silica shell covers the polystyrene spheres with a total diameter of 696 ± 33 nm for the core–shell structure. The morphology of the shell resembles the surface of raspberries. After firing the core–shell structure at 550 °C in air for 5 h, we obtain nanoshells of silica with average diameter and wall thickness of 601 ± 27 nm and 43 ± 13 nm, respectively. The shells are not entirely continuous; their structure seems like composed of smaller particles occasionally separated with pores and voids. It is interesting to note that the particle diameter distributions of the template, core–shell structures and the product are quite narrow, indicating the synthesis process is robust and feasible for good size control (figure 2).
The broad bands appearing in the Raman spectrum (figure S2) at around 495 cm$^{-1}$ (4-membered siloxane rings), 605 cm$^{-1}$ (three-membered siloxane rings) and at 820 cm$^{-1}$ (random network of Si–O–Si) are signatures of amorphous silica. It is important to note here that the vibration of three-membered siloxane rings 605 cm$^{-1}$ is not typical for Stöber silica; however, it appears in our silica nanoshells because of the heat treatment (550 $\degree$C in air for 5 h) used for burning off the polystyrene core [60]. XRD analysis of the silica shells (figure S3) shows a very broad reflection of the (101) planes at $\approx$21.6$\degree$ indicating a long range disorder in the solid in agreement with Raman measurements.

While it is possible to press films made of the silica nanoshells, their mechanical structure is poor, and it is difficult to process those further. To have a better cohesion, the silica nanoshells are mixed to an aqueous gel of cellulose nanofibers to obtain a composition of 5.0 wt.% silica and 0.5 wt.% cellulose. After pressing slabs and drying those to form films, the composites show sufficient mechanical integrity that are easy to handle and post-process. The $\text{–OH}$ groups of cellulose and the Si–OH surface groups of silica identified by DRIFTS (figure S4) suggest the constituents of the composite are held together by intermolecular hydrogen bonds. The density of the composite material is $\rho = 0.19 \pm 0.02$ g cm$^{-3}$ as determined by measuring their dimensions and mass. Such a low density (being only 9% of bulk fused silica) indicates that the structure is highly porous, which is caused by two effects. One is the presence of cavities in the hollow silica shells, and the other being the disordered microstructure of the composite. The cavities account for $\approx$37% considering the average shell diameter and wall thickness values, whereas the rest $\approx$24% is due to the disorder of the nanoshells in the composite caused by the presence of cellulose nanofibers, that do not allow for a close-packed microstructure (which would actually account for a much higher space filling factor of $\approx$74%). FESEM analysis (figure 3) confirms that the microstructure is indeed disordered as we find clumps of nanoshells in the films that are connected and bound together by the cellulose nanofibers leaving considerable amounts of voids in the composite structure and serves porosity of 92%.

To be able to design the planar filter structures, first the dielectric properties of the composite films are analyzed using THz spectroscopy. Due to the high porosity of the nanocomposite, both relative dielectric permittivity and loss tangent are very low at the measured frequencies. The value of $\varepsilon_r$ is lightly decreasing with frequency from 1.21 $\pm$ 0.01 at 100 GHz to 1.17 $\pm$ 0.01 at 2.0 THz, whereas $\tan \delta$ scatters around 0.011 $\pm$ 0.004 in the measured spectral window (figure 4). The very low measured permittivity is in good agreement with the Maxwell–Garnett effective medium model giving 1.13 for $\varepsilon_r$ (figure S5), and lower than those of other porous dielectrics and composites listed in table 1.

Planar filter (double split-ring resonator) arrays were sputtered on the composites through a shadow mask that we
Porous nanocomposites of silica nanoshells and cellulose nanofibers with extremely low relative dielectric permittivity and loss factor from 100 GHz up to 2.0 THz were prepared and used as substrate materials. Planar radio frequency filters operating at 300 GHz center frequency were demonstrated by sputtering matrices of microscopic double split-ring resonators on the composite films. Although the out-of-band attenuation of the filter structures still needs to be improved by further optimization of the surface roughness and metal micropattern definition, the accurate center frequency and the very large bandwidth of 70 GHz (at 80% transmission) make the silica-based porous composites very promising for future high frequency applications even in the 6G bands.

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4. Conclusions

Figure 4. (a) Dielectric permittivity and (b) loss factor of composite films.

Figure 5. Experimental and simulated high frequency transmission of planar filter structures. Schematic drawing of the measurements setup is displayed in the inset of the plot. Panels on the right show a camera image and an optical micrograph of the filter device and double split-ring resonators, respectively.

laser-cut from a thin brass foil. The thickness of the deposited silver micropatterns was ~500 nm. Measured and simulated transmittance vs. frequency spectra of the filters (figure 5) show good spectral match, i.e. excellent transmittance at the designed 300 GHz with an insertion loss of only 5% for our filters. However, the out-of-band attenuation is only 50% (low-pass) and ~30% (high-pass) in contrast to the anticipated attenuation of 36.8% (i.e. 1−e−1), which is probably due to the limitations of micropattern edge definition that could be improved e.g. by optimizing the metal evaporation and surface roughness of the composite. The bandwidth of the filters (at transmittance of 80%) is about 70 GHz, which is quite good considering that current research has been focusing only on 20 to 50 GHz bandwidths at the 300 GHz band [61, 62, 63].

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