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Sol-gel nanocomposites as metamaterials: preparation and optical measurements

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Abstract Nanocomposites made of Ag nanowires imbedded in a sol-gel host have been morphologically and optically investigated. Sonication during solidification significantly improved nanowire dispersal. The data from the nanocomposites were compared to the data from pure sol-gels in order to determine the effects of the nanowires. Reflectometry data at 1064 nm show that the presence of ~5% nanowires (by volume) results in a decrease from 1.17 to $\approx$ 1.1 in the real part of the index of refraction accompanied by an increase in the imaginary part. Transmission loss in the pure sol-gel is mainly due to scattering from inhomogeneities, and the inclusion of nanowires (or the process of doing so) appears to result in a significant reduction of the scattering loss.

1 Introduction

Metamaterials comprised of electric and magnetic resonant subunits have been shown by several groups to exhibit simultaneously negative permittivity ε and permeability μ, i.e. negative refractive index [1–3]. Negative-*n* materials exhibit fascinating optical properties such as slab lensing and amplification of the near-field [4]. A significant hurdle in developing negative-*n* materials at near-IR and visible frequencies is that the electric and magnetic subunits must be fabricated on the nanoscale for the medium to be considered optically homogeneous. Podolskiy et al predicted that arrays of aligned nanowires, in which wire pairs form LC resonant loops, could be the basis for negative refraction at near-IR frequencies [5]. This general approach has been successful at producing simultaneously negative ε and μ for a planar array of lithographed gold nano-pillars [6]. However, a planar array cannot function as a slab lens that focuses propagating rays because such a lens must produce an intermediate focus inside itself [4]. There are additional reasons to want economical routes of producing volume metamaterials with negative index at shorter wavelengths.

Random wire arrays supported in a dielectric host may offer such a route. Podolskiy et al speculated in Ref. [5] that a random arrangement of nanowires could have a negative index of refraction. A recent experiment by Chen et al demonstrated the possibility of a non-ordered functional metamaterial using 2.9–3.6 cm microwaves [7]. We chose tetraethyl orthosilicate (TEOS) sol-gel as a dielectric host for randomly distributed nanowires because the nanowires can be added during the solution phase and their positions fixed during gelation. Our goal is an easy method that produces three-dimensional isotropic metamaterials, in which it is hoped that a negative index of refraction may be found for some optical frequencies.

2 Experimental details

We have created a composite medium consisting of Ag nanowires distributed without order throughout a sol-gel host. Silver nanowires were synthesized by reducing $AgNO_3$ in ethylene glycol (EG). Polyvinyl pyrrolidone (PVP) was introduced as a structure directing agent and gold

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nanoparticles were used as seeds. The gold nanoparticles were derived by in situ pre-reducing $HAuCl_4$ in EG [8]. In a typical experimental procedure, 20 mL of EG was put into a three-necked flask equipped with a condenser tube, which was first heated to 160 °C in an oil bath under vigorous magnetic stirring. Then ~2 mL of 0.005 M $HAuCl_4 \cdot 3H_2O$ aqueous solution was added into the above heated EG solution. Four minutes later, ~340 mg of $AgNO_3$ (dissolved in 20 mL of EG) and the given PVP (340 mg PVP dissolved in 20 mL of EG) were added into the flask separately by injection with the same injection rate of 2 mL/min. Silver nanowires began forming at this stage. The reaction went on for another 60 min. During the whole reaction process, the temperature was kept at 160 °C and the vigorous magnetic stirring continued. The reaction mixture was diluted with acetone (5–10 times by volume) and centrifuged at 2,000 rpm for ~20 min. Small amounts of Ag particles were removed by using a pipette after centrifugation. The diameters of Ag nanowires were 60–100 nm and the aspect ratios were ~50. The recipe for sol-gel preparation is from a Berkeley Lab website [9], and is summarized as follows: in a typical procedure for nanocomposite preparation, Ag nanowires were dispersed in TEOS solution containing 10 mL of ethanol and 12.5 mL TEOS under vigorous magnetic stirring. The solution was then sonicated for 45–60 min. After sonication a catalyst solution containing 9 mL of ethanol, 18 mL of water, 0.07 mL of 35% aqueous ammonia, and 0.3 mL of 0.5 M ammonium fluoride was slowly added into the silica solution by injection at a rate of 70 mL/hour. Just after the injection, the mixture was poured into a plastic lab dish and sonicated for 60 min. This kept the nanowires dispersed while gelation began, preventing aggregation. After drying at room temperature for 4 days, the nanocomposite film was taken from the lab dish for optical measurements. Sol-gels without nanowires were prepared in the same way for comparison.

3 Results and discussion

3.1 Nanowire distribution

Scanning electron microscope (SEM) images of representative sol-gel samples can be seen in Fig. 1. Figure 1a shows the aggregation of the nanowires in a sample that was prepared without sonication at the beginning of gelation. Figure 1b shows the improved dispersion of nanowires when the sample is sonicated. The improvement in nanowire distribution comes at a cost of fracture toughness in the sol-gel. The sonicated samples are extremely brittle and are therefore difficult to work with. If the sample is sonicated for too long during gelation (e.g. > 1.5 h for these samples) the sample will never form a rigid gel.

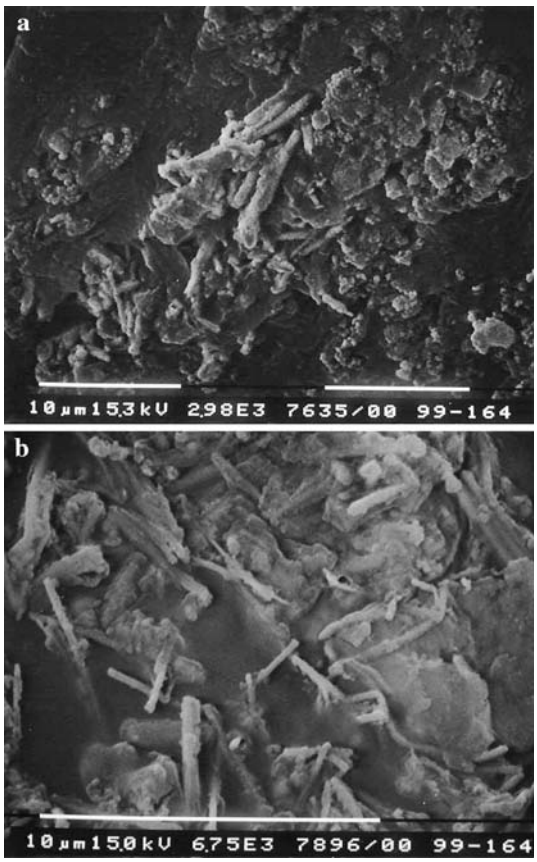

Fig. 1 Distribution of nanowires in a sol-gel (**a**) without and (**b**) with sonication after the addition of the catalyst

3.2 Reflectometry

Angular dependent reflectometry was done at 1064 nm. Linear polarized 1064 nm light was provided by a fiber laser operating at 3 W (Model YLR-20–2064-LP, IPG Photonics, Oxford, MA). A glass beam splitter was used to reduce the power. Polarization of the incident light was selected by using a Fresnel Rhomb quarter wave retarder to create circularly polarized light followed by a Glan laser polarizer to set the linear polarization. Data were taken from 15 to 55° with P-polarized light in order to find the Brewster angle θ_B.

Reflectometry data for P-polarized light are shown in Fig. 2. The Brewster angle for the pure sol-gel is 49.5°, and therefore the real part of the index of refraction n_{Re} is 1.17. Since the pure TEOS sol-gel is a dielectric and the surface roughness of the samples ranged from 10 to 25 nm, we assume that the observation of $R_p \neq 0$ at θ_B is due to scattering from internal inhomogeneities. The samples appear white translucent. Because of this scattering, we could not apply straightforward R vs θ fitting of the Fresnel equations to obtain both real and imaginary parts of the index of refraction, n_{Re} and n_{Im}. Nevertheless, the presence

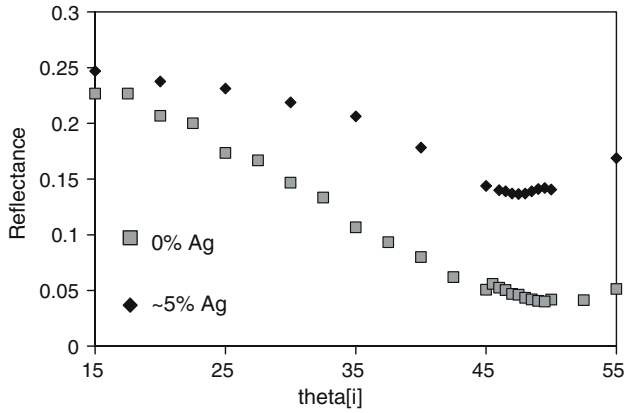

Fig. 2 P-polarized reflectance for pure sol-gel and nanocomposite sol-gel with 5 wt% nanowires. The increase in reflectance at the Brewster angle indicates an increase in the imaginary part of the index of refraction

of a pseudo-Brewster angle at 47.5° for the nanocomposite indicates n_{Re} is ≈ 1.1. The significantly larger P-polarized reflectance at θ_B in the nanocomposite is likely due to increased n_{Im} rather than increased scattering upon introduction of the nanowires, for reasons discussed below.

3.3 Transmission

Wavelength dependent transmission data were taken at normal incidence by passing a collimated white light beam from a tungsten halogen lamp (Model LS-1-Cal, Ocean Optics, Dunedin, FL) through the sample and detecting the beam with a fiber optic spectrometer (Model USB 2000, Ocean Optics, Dunedin, FL).

The normal incidence transmittance of pure sol-gel and nanocomposite samples are shown in Fig. 3. Data are shown for two sets of samples prepared independently under the same conditions. The nanocomposite shows an increase in transmitted light relative to the pure sol-gel at wavelengths below 790 nm and a decrease above it. The pure sol-gel sample shows a strong slope toward lower transmission in the blue. This is consistent with the scattering loss due to internal inhomogeneities hypothesized above on the basis of physical appearance and R_p vs θ data. The slope of the transmission is much flatter in the nanocomposite, suggesting a reduction of scattering. It could be that the introduction of nanowires or the associated processing improves the physical homogeneity of the sol-gel host, or that the nanowires themselves improve the optical homogeneity of the composite.

One should consider the possibility of a chemical change in the sol-gel during preparation caused by the addition of nanowires that may alter the optical properties. However, such an interpretation requires an alternate

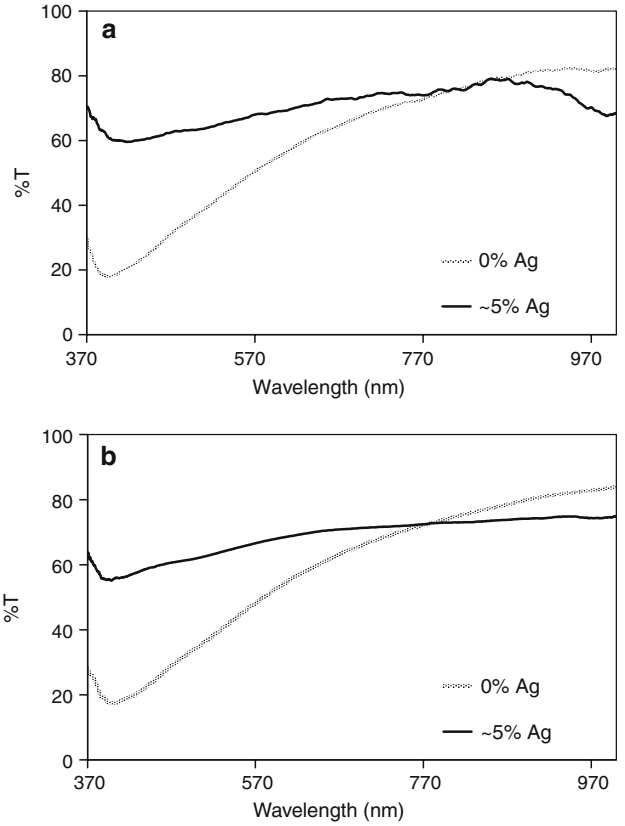

Fig. 3 Transmission data for two sample sets (a,b) cast from different batches of ~5% nanowire loading. The nanocomposite transmits more light than the pure sol-gel below 790 nm

hypothesis for the strong blue attenuation in the pure sol-gel sample, attributing it to electronic absorption in the blue and supposing that processing of the nanocomposite chemically altered those transitions. But such a hypothesis is inconsistent with the white translucent appearance of the samples, so the interpretation based on scattering by inhomogeneities is preferable.

4 Conclusions

Nanocomposites made by imbedding Ag nanowires in a sol-gel were prepared by sonicating the sample while it was still a solution. Sonication is critical for approaching random nanowire distribution. Nanowires in the composite appear to increase n_{Im} and reduce n_{Re} at 1,064 nm and they produce a flatter spectrum of transmission loss from 370 to 1,000 nm, with net increase of transmission from 370 to 790 nm. More work must be done to explain these results.

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