

Extinction Efficiency of Copper Nano Fibers in the Infrared

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ABSTRACT: This article presents experimental measurements and theoretical calculations of the mass normalized extinction cross section (extinction efficiency) of hydrothermally synthesized copper nanofibers in the infrared spectral region (2–14) μm . The synthesized copper nanofibers have an average diameter of 40 nm, and the length of the fibers has been ultrasonically reduced to achieve the highest possible efficiency in the targeted IR spectral region. A peak extinction efficiency of $\sim 30 \text{ M}^2/\text{g}$ is achieved with an overall efficiency greater than $10 \text{ M}^2/\text{g}$ across the remainder of the infrared window. Such high efficiency fibers make them of high interest for applications that require attenuation of electromagnetic radiation. To the best of our knowledge, this efficiency is the highest that has been reported in literature, and the synthesis procedure is simple and can be scaled-up for mass production of copper nanofibers.

1. INTRODUCTION

Electromagnetic radiation by small particles is of high interest for scientists and engineers for many applications that require efficient electromagnetic shielding or extinction of radiation. For example, highly efficient particles can be used as infrared radiation (IR) attenuators for military applications. Such factors as shape, size, and material content have been studied [1, 2] and determine how efficient these particles attenuate electromagnetic radiation. Mechanisms of attenuation are achieved through scattering and absorption phenomena.

The key parameter for attenuative properties, by the Drude theory, is electrical conductivity. The theory of electromagnetic scattering and absorption by fiber-like particles has been developed for decades, and both analytical and numerical solutions to the problem have been established [3–9]. Experimental measurements in the millimeter wavelength region have been done and verified against the theory [10–18]. In the IR wavelength region, the theory has been verified using (high conductivity) silver nanofibers [19] and carbonaceous (low conductivity) nanofibers. According to the theory, the optimal mass normalized attenuation (extinction) efficiency is also inversely affected by the fiber diameter. With the aid of these theoretical predictions, a search for broad-band high efficiency low-cost fibers (such as copper fibers) in the infrared spectral region has been pursued.

Hydrothermal synthesis of very thin copper fibers has been investigated by numerous investigators [20–26]. In this article, the procedure in [20] was followed to a degree to produce the copper nanofibers. The fibers were then washed, purified, tuned, and measured to determine their extinction efficiency in the IR spectral region (2–14) μm . The measurements were then compared with the theory for a verification of their attenuation potential.

2. SYNTHESIS AND MEASUREMENT

2.1. Hydrothermal Synthesis of Copper Fibers

In our procedure, copper chloride (0.09 g) and glucose (0.19 g) were dissolved in 40 ml deionized water in a flask. Following that, 0.7 g of hexadecylamine was added to the solution and vigorously stirred magnetically for 5 hours. The resulting light blue solution was then transferred to a 100 ml Teflon-lined stainless-steel autoclave. The autoclave was placed in a commercial oven at 120 C° for 13 hours, and then removed from the oven to cool to room temperature. The resulting reddish-brown solution was then centrifuged and washed with water and ethanol sequentially until purified copper fibers and cubic-shaped copper nanoparticles were obtained. The fiber yield was compromised by moderate amounts of cubic-shaped copper nanoparticles with an approximate size of 150 nm. Purification of the fibers is essential for the highest possible efficiency as such nanoparticles would reduce efficiency in the targeted IR spectral region. Using centrifugation, the fibers were largely separated from the nanoparticles. Figs. 1(a), (b), and (c) show a transverse electromagnetic (TEM) sample picture of the washed purified copper nanofibers, an X-ray diffraction (XRD) pattern of the fibers, and a high magnification TEM sample picture that shows the measured diameters, respectively. The diameters of the fibers range from $\sim 20 \text{ nm}$ to $\sim 60 \text{ nm}$ with an average diameter of $\sim 40 \text{ nm}$. The purified copper nanofibers were maintained in ethanol for length reduction, Fourier-transform infrared spectroscopy (FTIR) measurements and to protect them from oxidation, as we see in Fig. 1(b). The XRD pattern shows a tiny trace of CuO which proves that conserving the fibers in ethanol does prevent oxidation. Oxidation of copper nanofibers would significantly degrade the extinction efficiency of the fibers because of the loss of copper conductivity.

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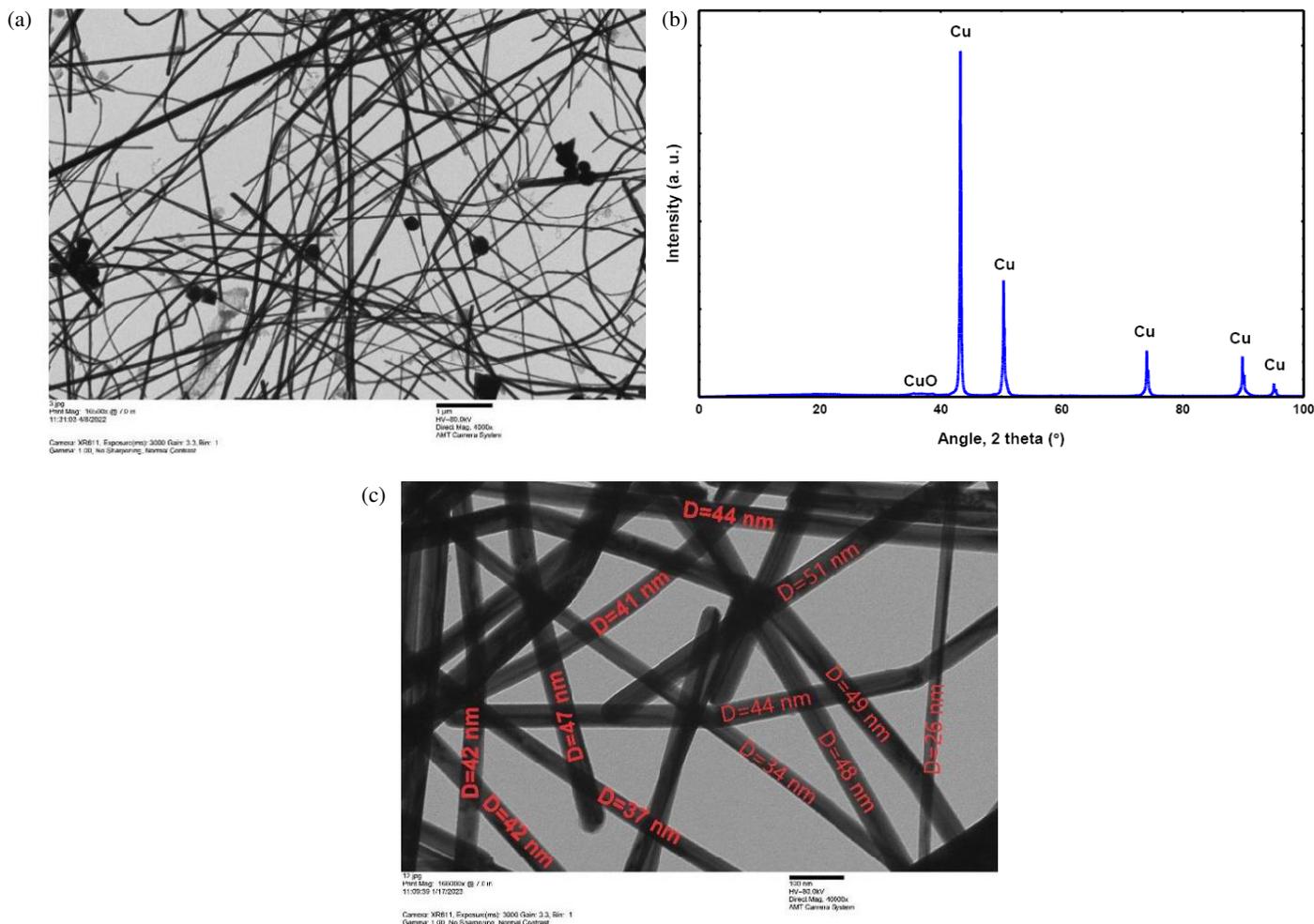


FIGURE 1. (a) TEM image of a cleaned and purified copper nanofiber sample, (b) XRD pattern of the fibers, (c) high magnification image with fiber-diameter measurements.

2.2. Fiber Length Reduction and Extinction Measurements

The produced fibers are too long and have a peak resonance outside our targeted IR spectral region. A Branson Digital Sonifier 250 was used to fracture the fibers and shorten the length distribution. A 3/8 in diameter submersible probe was used operating at 50% total output power at 20 kHz. The sonifier was used in pulse mode pulsed “on” for one second and “off” for one second for a total “on” sonication time of 3 minutes to reduce the fibers lengths to approximately that of their prime resonances in the IR. The resulting length distribution was peaked, but further investigation of the options for sonification might provide an even narrower distribution for a potential improvement on the extinction efficiency values. After the length reduction process, a very low-density ethanol fiber-loaded drop was deposited on a TEM substrate, and random TEM photographs were taken for length analysis using the commercial software Image-J. A TEM sample image of the reduced length measured copper nanofibers is shown in Fig. 2, and the normalized length distribution is shown in Fig. 3.

The extinction spectra were obtained using spectral transmission measurements via a Perkin Elmer Spectrum 100 FT-IR. A

short path length liquid cell with ZnSe windows was mounted inside the spectrometer used in transmission mode.

3. RESULTS AND DISCUSSION

The measured extinction spectra represented by the normalized length distribution in Fig. 3 are shown in Fig. 4. For the calculation of the spectra, Alyones et al. code [7–9] was used and applied to the normalized distribution. Calculations were done using the actual data points of the length distribution, not the curve fit. As we see in Fig. 4, a broad-band high extinction efficiency is achieved with a peak value of $\sim 30 \text{ M}^2/\text{g}$ and an efficiency above $10 \text{ M}^2/\text{g}$ across most of the targeted IR spectral region. Also, the calculated extinction spectra agree well with the measurements as shown in the figure. The difference between the measured and calculated spectra may be attributed to two factors. The first is that even after purification of the fibers, there are still a small percentage of cubic nanoparticles in the measured sample. The second is that Alyones code assumes the fibers to be straight, while the measured sample does contain a number of bent fibers to varying degrees. We have shown in a previously published article [27] that this should



FIGURE 2. Sample TEM image of the reduced length measured copper nanofibers.

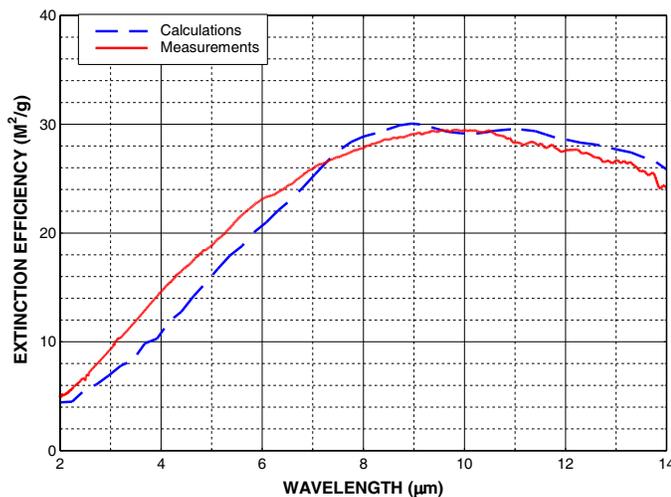


FIGURE 4. Measured and calculated extinction spectra for a sample of copper fibers (with average diameter = 40 nm) represented by the length distribution in Fig. 3.

have a small effect on the measured spectra. It is worth mentioning that to the best of our knowledge, the highest extinction efficiencies were reported in [19] for silver fibers. The reported peak value was around $21 \text{ M}^2/\text{g}$ at $6 \mu\text{m}$, and the extinction values across the atmospheric spectral window ($8\text{--}12 \mu\text{m}$) ranged from $15 \text{ M}^2/\text{g}$ to $4 \text{ M}^2/\text{g}$. The values reported in this study are greater, and given that copper is cheaper than silver, this option presents a big improvement.

4. CONCLUSION

Copper nanofibers have been hydrothermally synthesized, purified, and tuned to efficiently attenuate electromagnetic radiation in the IR spectral region. An extinction efficiency greater than $10 \text{ M}^2/\text{g}$ is achieved across most of the targeted IR region ($2\text{--}14 \mu\text{m}$), with a peak value of approximately $30 \text{ M}^2/\text{g}$ across

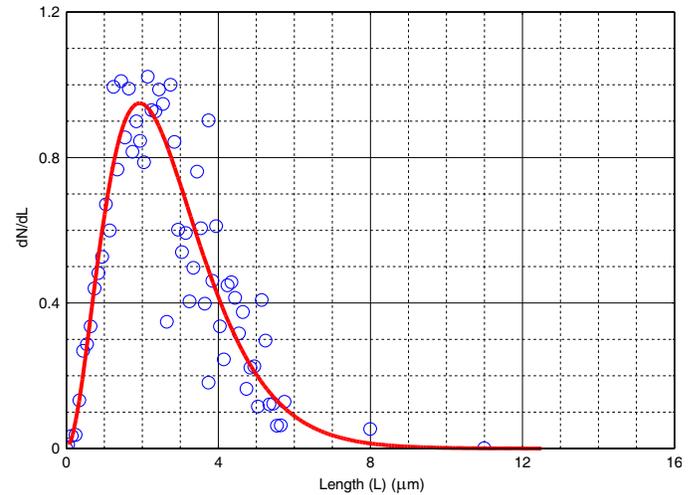


FIGURE 3. Length distribution of a cleaned and purified copper nanofiber sample after 3-minute-high power sonication.

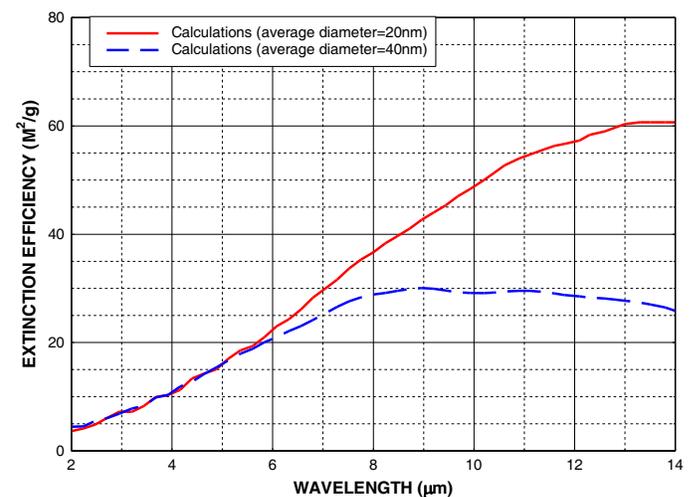


FIGURE 5. Extinction spectra for an average diameter of 20 nm vs an average diameter of 40 nm for the sample represented by the length distribution in Fig. 3.

the $8\text{--}12 \mu\text{m}$ atmospheric spectral window. The synthesis procedure is fairly simple and has the potential of mass production with low cost. To the best of our knowledge, the values of extinction efficiency reported here are considerably higher than other values reported in literature. Also, it is worth noting that a further increase in efficiency can be achieved if smaller diameter fibers can be made through improvement and modification of the synthesis procedure conditions. To illustrate, Fig. 5 shows the calculated extinction spectra for the same distribution in Fig. 3, but assuming that the average fiber diameter is reduced from 40 nm to 20 nm. As we see in Fig. 5, the resulting efficiency would approach $\sim 60 \text{ M}^2/\text{g}$ at the peak but shifted to a longer wavelength as expected [7]. Further investigations are under way to increase the extinction efficiency, including increasing the yield of fibers and reducing the diameters of the synthesized fibers.

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