**TITLE:**

**Enhanced Spectral Emissivity of Single and Coated SiC Micro/Nano-Spheres**

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**SHORT ABSTRACT:**

We describe the fabrication of SiC micro/nano-spheres and coated SiC nano-spheres using the chemical vapor deposition technique. Furthermore, measuring the enhanced spectral emissivity with Fourier Transform Infrared Spectroscopy (FTIR) is characterized.

**LONG ABSTRACT:**

We use fluctuational electrodynamics to determine spectral emissivity for spherical shapes, such as a single sphere and a coated sphere, in a homogeneous and isotropic medium. The dyadic Green’s function formalism of radiative energy for different spherical configurations has been developed. We have shown, that emission spectra of micro- and nano-sized single and coated spheres display several emissivity sharp peaks as the size of object reduces to a nanoscopic length scale1.This theoretical work has to be verified by physical fabrication of SiC micro/nano-spheres and experimental measurement of their spectral emissivity. One uses a vapor-solid approach to create hollow SiC nano-spheres, a reaction between carbon nanoparticles and SiO vapor in an inert atmosphere of Argon. A Chemical Vapor Deposition (CVD) can be used to create the initial amorphous carbon particles as well as be used to coat the SiC small-sized spheres. The FTIR spectroscopy (based on the Michelson interferometer) is one experimental method that will be presented for measuring the spectral emissivity of objects. FTIR offers two ways, the direct and the indirect method, to measure the spectral emissivity of a sample. The direct method is chosen for measuring the spectral emissivity of micro/nano-spheres.

**INTRODUCTION:**

Quantum and thermal fluctuations of electromagnetic fields, which give rise to Planck’s law of blackbody radiation2, are responsible for radiative energy, momentum, and entropy transfer3-13. Classical theory of thermal radiation takes only propagating waves into consideration. Presence of evanescent waves nearby the surfaces leads to near-field effects, such as interference, diffraction, and tunneling of surface waves, which are important when the size of the objects is comparable to the thermal wavelength of objects ( μm at room temperature K).

Thermal radiation due to fluctuations of electromagnetic fields for a single and/or coated object has been investigated well over the past few decades. Near-field radiative energy transfer between flat and curved surfaces has been studied for the past years. Enhancement of radiative energy transfer, wavelength selectivity, and size and scale dependence are typical characteristics of near-field phenomena, which make it more interesting. These characteristics could be exploited in many potential nano-technological applications such as nanoparticles14-17 and wavelength selective absorber and emitters18-22. These phenomena can be described by cross-spectral densities of the electromagnetic field using dyadic Green’s functions of vector Helmholtz equation23-25.

During the past decades, many theoretical works have been published on the topic of the enhanced thermal radiation due to near-field effects. Most of them are focused on the configurations, for example, between planar multilayered structures26-30, coated planar surface31, photonic multilayer crystals32-34, gratings35,36, cylindrical objects37, spheres14,38-42, a sphere and a flat plate17,42-44, and hyperbolic structures45-47. Although considerable amount of work devoted to theoretical and experimental results for near-field radiative energy transfer between objects of the abovementioned typical geometries, these phenomena for a single object requires a further study and a good understanding when the size of the object is reduced to be comparable or less than the thermal wavelength. To the best of our knowledge, most of the works on an individual body rely directly on Rytov’s formalism for fluctuating electromagnetic fields3.

We applied Rytov’s approach and developed a dyadic Green’s function formalism for spectral emissivity for micro- and nano-sized spherical objects, as shown in **Figure 1a and Figure 1b**. It has been demonstrated how fluctuational electrodynamics can be used to determine spectral emissivity for various shapes in a homogenous and isotropic medium. Size dependence and wavelength selectivity of micro- and nano-sized spheres are clearly observed. For small sized objects, the emissivity spectra show sharp peaks at wavelengths corresponding to characteristics of the material’s refractive index. The peaks increase as the size of the object decreases. This is consistent with spectral emissivity calculations done for thin films22.

There are a few different methods used to create hollow SiC nano-spheres. One uses a vapor-solid approach to create the hollow SiC nano-spheres, a reaction between carbon nanoparticles and SiO vapor in an inert atmosphere of argon. This method creates an outer diameter of 100-200nm and a shell thickness of 30-50nm48. The carbon nanoparticles are generated from a pyrolysis of toluene (CH3) introduced in to a horizontal tubular quartz reactor by bubbling an argon (Ar) flow through with the toluene vapor. This type of reactor is a type of CVD process however; this uses a quartz tube inside the furnace. Argon at 40ml/min is first used purge the reactor of air and creates an inert atmosphere initially, then an increased amount of bubbled Ar at 240ml/min is introduced with the toluene vapor at 300ml/minto form the amorphous carbon particles49. **Figure 2a** shows a diagram of a horizontal tubular quartz reactor setup for creating carbon nano spheres. The result of the amorphous carbon nanoparticles are added separately to an alumina crucible with silicon (Si) and silica (SiO2). The crucible is placed into a resistance heating furnace using coils of a heating element like alloy and a programmable temperature controller to adjust the heat. This time of furnace is used because the temperature of Bunsen burners only reaches 1200°C. While the crucible is at 1300°C, a combination reaction with the new SiO vapor and carbon creates the resulting SiC. The reaction Si + SiO2 <-> 2SiO occurs, then 3C + 2SiO <-> 2SiC + CO2 48. The SiO vapor compositing on the carbon by an Ar carrier is the siliconization stage, see **Figure 3**. A SiC shell forms over a carbon core (SiC-C) see **Figure 2b**. The carbon core can be removed by oxidation to create SiC-C hollow nano-sphere shell. Oxidation in carbon can occur between 600-1000°C in air while SiC oxidation occurs over 1200°C creating SiO2.

A scanning electron microscope (SEM) can be used to measure the diameter of carbon and SiC hollow spheres as shown in **Figure 4** (Fig. 1a and 1c in Ref. 48). After the creation of the hollow SiC micro/nano-spheres the Plasma-Enhanced Chemical Vapor Deposition (PECVD) can put them through a coating process50. In traditional CVD coating processes, usually for thin films, substrates are heated to high temperatures and exposed to precursor materials in the gaseous state. In PECVD reactors, the plasma is created by radio frequencies or DC discharge between electrodes. The precursors react or decompose on the substrate surface to create a coating of the required material as shown in **Figure 5** (Fig. 1 in Ref. 51). In PECVD, is used to enhance the deposition used to deposit dielectric films at lower temperature, which is important to construct insulation layers, because Boron Nitride (BN) is a very good electrical insulator. Boron Nitride in this system is created using nitrogen (N2) and diborane (B2H6) at pressures lower than 1 Torr (.0013 atm) and temperatures lower than 500°C. The gas flows are controlled by mass flow controllers, and the gases exhaust and pumping speeds are controlled by an automatic throttle value. Rates of B2H6, radio-frequency (RF), temperature, and deposition time can be varied to obtain a different thickness. To obtain thicknesses around 30-120nm, rates and time can vary: B2H6 7-30sccm, 200-400°C heater temperature, and deposition from 90-110mins, N2 is constant at 60 sccm51.

FTIR is a method for measuring infrared spectra of samples. FTIR uses the fact that the peak positions in an infrared spectrum depend on the molecular structure. Furthermore, FTIR has the following characteristics. Because of the low energy of electromagnetic waves, they rarely damage the sample. Additionally, the sample can be in various states, like solid, crystal, fiber, film, liquid or gas. Moreover, infrared spectroscopy can use infrared absorption, reflection, emission, as well as photo acoustic spectroscopy52. These interferometers can be designed in different ways, but the basics of interferometer operation are similar for all interferometer types. Most common today is the Michelson interferometer, which mainly consists of a fixed and a moving mirror, and a beam splitter. The beam splitter partly transmits the light towards the fixed mirror, and partly reflects the light towards the moving mirror. After that, the mirrors reflect the light back to the beam splitter and depending on the optical path difference; the reflected waves interfere constructively or destructively. Thus, cosine waves of the intensity are generated and this interferogram will be Fourier transformed into an infrared spectrum53.

The direct method takes the ratio of the sample radiation and the blackbody radiation to generate the emissivity spectrum, while it is generated from the measured transmission and reflectivity of the sample using the indirect method. The conduction of the experimental measurement will be described using the direct measuring method54.

**PROTOCOL:**

**1. Fabrication of hollow SiC micro/nano-spheres**

1.1) To create carbon nanoparticles use a horizontal tubular quartz reactor with Ar and CH3 containers attached into the inlet direction as described in 48.(see **Figure 2a**)

1.1.1) Heat the reactor to 1000°C at 10°C/min, at the same time flow argon through between 20-40 ml/min. The rates are controlled by the mass flow controllers.

1.1.2) When the reactor reaches 1000°C, add the bubbled argon at a rate of 240-300ml/min and bubbled toluene at a rate of 90-300ml/min. Allow this run for 60mins.

1.1.3) Collect the resulting carbon nanoparticles from the wall of the quartz reactor after the furnace has cooled to room temperature using metal tweezers.

1.2) Next, place the carbon nanoparticles as well as a 1:1 molar ratio of silicon and silica into a 5mm diameter alumina crucible. (See **Figure 2b**). Let the carbon nanoparticles be close to the gas outlet direction.

1.2.1) Place the crucible in the resistance heating furnace. Heat the crucible in the temperature range on 1300⁰C as well as inlet Ar at 40ml/min. NOTE: The silicon and silica create SiO vapor and this reacts with the carbon micro/nano-spheres. This should take 1-3h. SiC-C should be left in the crucible after the crucible has been cooled down.

1.3) Finally, oxidized the powder at in air for 2h to eliminate the carbon core using a temperature plate to get the accurate temperature reading. NOTE: The result is a SiC hollow nano sphere. (see **Figure 3**)

1.4) Measure the diameter of the SiC spheres using a SEM as described in 48. NOTE: The diameter of the spheres should be around 100-200nm. (see **Figure 4**)

1.5) Then put SiC micro/nano-spheres through a PECVD coating process using the PECVD machine. (see **Figure 5**). Wait for the machine to heat up to about 300°C after initiating start up. Vent the chamber of the air; this may take a few mins. Then load the SiC nano particles on the substrate inside the chamber.

NOTE: Create any recipe needed depending on the parameters. An example of a recipe to obtain a very thick shell around 120nm would include N2 at a constant rate of 60sccm,B2H6 at 15sccm, an RF of 300mW/cm2, a temperature of 400°C, and a run time of 400mins. After this is done, vent the chamber and unload the SiC nanoparticles coated in BN using metal tweezers.

**2. Measurement of the spectral emissivity with FTIR**

**2.1) Preparation of sample42.**

2.1.1) After fabrication, attach the single/coated micro/nano-sphere to the free end of the micro-cantilever (thickness: 20 μm, length: 200 μm, material: Si3N4), as described below and shown in **Figure 6**.55

2.1.1.1) Draw silica fibers from micropipettes using butane fuel laboratory burner. NOTE: The thickness of the fiber is ca. 50 μm, so that the micro/nano-sphere can be easily attached to it by van der Waals force. Two fibers are needed to attach the sphere, each of approximately 5 cm. Coat the fiber-tip with a thin layer of thermal epoxy by dipping it into the glue.

2.1.1.2) Position the micro-cantilever under the optical microscope with the non-reflective side facing upward and clamp the glass chip (micro-cantilever protrudes from glass chip) to fixate the cantilever. Then, focus the microscope on the tip (free end) of the micro-cantilever. (See **Figure 6a**)

2.1.1.3) Touch the tip of the micro-cantilever carefully with the fiber with thermal epoxy coating to deposit glue onto the cantilever. NOTE: The size of the drop size of the glue is dependent on the size of the sphere (ca. 1/3 of the sphere diameter). (See **Figure 6b**)

2.1.1.4) Pick a micro/nano-sphere with another clean fiber. NOTE: Spheres are put on glass microscope slide with Teflon tape coated. The purpose of the tape is to decrease the van der Waals force between the sphere and the glass slides. (See **Figure 6c**)

2.1.1.5) Transfer the sphere, which is attached to the clean fiber, onto the tip of the micro-cantilever where the thermal epoxy is applied. (See **Figure 6d**)

2.1.1.6) Once the micro/nano-sphere is attached to the micro-cantilever, transfer the micro-cantilever to a hot plate with a temperature to cure for 10 minutes, so that the sphere is bound rigidly to the tip of the micro-cantilever.

2.1.2) Depending on the required sample temperature, either mount the cantilever with attached sphere in an emission adapter () or a high temperature cell ().

2.1.3) For self-made black body reference samples, heat the surface of a roughened metal sheet evenly with the butane fuel laboratory burner for 1 minute, so that a sufficiently thick soot layer appears on the surface. Alternatively, purchase adaption of a black body cavity source, which approaches the radiation of an ideal black body.

**2.2) Setup of blackbody and sample radiation source** (**Figure 7**).

2.2.1) Connect the external platform with the blackbody cavity source to the FTIR spectrometer. NOTE: Besides the beam path of the cavity source, the emission platform includes a beam path for a 2nd source which is software selectable via an automated mirror.

2.2.2) Connect either the emission adapter or the high temperature cell to the second source position.

**2.3) Setup of the FTIR spectrometer 56.**

2.3.1) Switch FTIR spectrometer on and wait at least 10 minutes for the electronics and the source to stabilize thermally. Check the HUMIDITY, LASER, and STATUS LED lights on FTIR spectrometer (see **Figure 8**).

2.3.2) If needed, purge the spectrometer with dry air or nitrogen gas (indicated by a red HUMIDITY LED). NOTE: Take great care when changing the detector and sampling accessory. Do not touch any part of the mirrors and windows. These components are very fragile and sensitive to dirt.

**2.4) Conduction of measurements** (see **Animation 1**).

NOTE: Because the spectral emissivity of the sample and the blackbody are measured under the same ambient conditions no background measurement is required54. However, the micro/nano-sphere is attached to a micro-cantilever, so that a noise-correction for the cantilever has to be applied.

2.4.1) Connect the computer with the LAN cable to the FTIR server. Open the Internet Browser and type in the IP address of FTIR: 192.169.1.1. Observe that the *“Home Server Menu”* of FTIR opens. Click on “*Measuring Menu”*, so that main menu for the conduction of measurements opens (see **Figure 9**).

2.4.2) Set the automated mirror in position for measuring the reference blackbody radiation, to run reference blackbody radiation measurement with the blackbody cavity source (see **Figure 10**).

2.4.3) Click on “*Start Measurement”*. Observe the “*Measuring Status Menu*” opens. If the measurement is conducted, click on the “*file name”* to download the file (see **Figure 11**).

2.4.4) Set the automated mirror in position for the 2nd source with just the cantilever and without any micro/nano-sphere attached to measure the noise radiation. Run the noise radiation measurement of the thermal chamber with just a micro-cantilever in 2nd source position.

2.4.5) Click on “*Start Measurement*”. Observe the “*Measuring Status Menu*” opens. If the measurement is conducted, click on the “*file name”* to download the file.

2.4.6) Replace the micro-cantilever by a micro-cantilever with an attached micro/nano-sphere to measure the sample radiation. Run the sample radiation measurement with the micro/nano-sphere in 2nd source position (see **Figure 12**).

2.4.7) Click on “*Start Measurement*”. Observe the “*Measuring Status Menu*” opens. If the measurement is conducted, click on the “*file name”* to download the file.

2.4.8) After the measurements are conducted, click on the software icon on the desktop to open the FTIR software on the computer and log in.

2.4.9) Click on “File” and then on “Load File”. Load the downloaded files (see **Figure 13**). Observe the measured spectra. Subtract the spectral emissivity data of the cantilever from the total spectral emissivity measurement of the cantilever with attached micro/nano-sphere (noise-correction). An arbitrary spectrum is shown in **Figure 14**.

**REPRESENTATIVE RESULTS:**

We have theoretically shown the size dependence and wavelength selectivity of emission spectrum of the micro/nano-scale single and coated spheres for small radii. The spectral emissivity of sharp peaks can be observed at wavelengths corresponding to the characteristics of the material’s refractive index and improved as the size of object decreases.

Theoretical calculations give representative results of the spectral emissivity of a SiC half-space, single SiC spheres and a SiC sphere coated with a BN, as shown in **Figure 15b**. The black dotted line shows the spectral emissivity of a half-space, which has a low emissivity at the wavelength between eV and eV. It can be observed that, as the radius of the sphere reduces, the sharp peaks occur in the emission spectrum. The emission spectrum (blue curve) starts fluctuating when the sphere size ( μm) is comparable to the thermal wavelength; when the sphere size is reduced to μm, the emission spectrum (green curve) occurs an obviously high peak of emissivity at wavelength of eV and meanwhile a small peak can also be observed at wavelength eV which corresponds to the Reststrahlen band ( and ) in the dielectric function (**Figure 15a**); and when radius ( μm) is close to the absorption depth of SiC, the emission spectrum (red curve) displays two sharp peaks at wavelengths eV and eV, respectively. These two emission peaks are exactly corresponding to the frequencies at which the dielectric function reaches its minimum value. Other explanation to understand the existence of these sharp peaks in emission spectrum is the absorption depth of electromagnetic waves in comparison to the size of the object. When the radii of spheres become comparable to the absorption depth at mode wavelengths, at which the dielectric functions become negative or very close to zero, the reflection and transmission of a micro/nano-sized sphere are weakened, and the emission is enhanced at those characteristic wavelengths due to multiple reflections and Mie scattering within the object. The emission spectrum of a coated SiC sphere (magenta curve) of radius μm and a BN layer of thickness μm displays four sharp peaks. Among them, there are two extra sharp peaks at wavelengths of eV and eV, respectively, which are attributed to a BN thin coating. In comparison with emission spectrum (blue curve) of a single SiC sphere of radius μm, it can be seen that the two peaks to the right (magenta curve) occur exactly at the same wavelengths because of sphere core of the same material as well as size. The spectral emissivity can be weakened or strengthened due to a coated thin film or multiple coatings.1

**FIGURE LEGENDS:**

**Animation 1: Setup and radiation path of FTIR measurement.** The red line represents radiation of the blackbody source. The blue line represents radiation of the micro/nano-sphere.

**Figure 1: Schematic of various spherical geometries.** (a) A sphere of radius (material 1, green), and (b) a sphere of radius (material 1, green) coated with a thin film of thickness (material 2, orange) in material 3 (blue). The short arrows on either side of the interface between two materials denote the spherical electromagnetic waves ( and waves). is vector spherical wave functions of order , and superscript refers to the radial behavior of the waves. is wavenumber in medium , and are the Mie reflection and transmissioncoefficients due to spherical electromagneticwaves from medium tomedium , respectively. Re-print with permission from Ref. [1].

**Figure 2a: Turbular quarts reactor setup.** Showing a possible diagram of a horizontal tubular quartz reactor setup for creating carbon micro/nano-spheres**.** The rate of argon from 20-40ml/min is the initial purging gas. After furnace is heated to 1000°C a bubbled Ar and toluene are introduced at 240ml/min and 300ml/min respectively. The initial rate purges the reactor of air and creates an inert atmosphere as the furnace is heating.

**Figure 2b: Setup of alumina crucible.** Argon inlet from the top of a 5mm diameter crucible and gas outlet on the bottom. Reacting (Si + SO2) + 3C <-> 2SiC +CO2, Ar is the now reaction carrying gas from 2SiO to carbon.

**Figure 3: Micro/nano-sphere synthesizing process.** An illustration showing the procedure for synthesizing SiC hollow nano-spheres.49

**Figure 4:** **Created spheres.** (a) Carbon micro/nano-spheres, and (b) SiC hollow spheres. Re-print with permission from Ref. [48].

**Figure 5:** **Plasma-Enhanced CVD process.** N2 and B2H6 gases, deposited as a solid on the SiC hollow spheres (inset). The plasma is generally created by a discharge between two electrodes. Re-print with permission from Ref. [51].

**Figure 6: Attachment process.** (a-d) Illustration of the steps to attach the micro/nano-sphere to the cantilever with thermal epoxy. Re-print with permission from Ref. [55].

**Figure 7:** **External platform for direct emission measurements.** The blackbody cavity source serves as reference. Depending on the application either the emission adapter A540 or the high temperature cell can be adapted as 2nd source. Re-print with permission from Ref. [56].

**Figure 8: Spectrometer display.** The spectrometer display shows three LEDs: HUMIDITY, LASER and STATUS. Their LED light can either be green (i.e. OK) or red (i.e. not OK).

**Figure 9:** **Measurement menu of FTIR server.** Screenshot of measurement menu.

**Figure 10: Blackbody radiation measurement.** The rotating mirror is in position for the blackbody cavity source.

**Figure 11:** **Measurement status and file download.** Screenshot of measurement status and how to download the file with the measurement data from FTIR server.

**Figure 12: Micro/nano-sphere radiation measurement.** The rotating mirror is in position for the sample source.

**Figure 13:** **FTIR software main screen and load file.** Screenshot of FTIR software main screen and how to load the downloaded file with the measurement data.

**Figure 14: Example spectrum.** Screenshot of arbitrary example spectrum loaded in the FTIR software.

**Figure 15:** **Refractive index and spectral emissivity of single/coated SiC spheres of different sizes.** (a) Real and imaginary parts of the refractiveindex, , of SiC and (b) spectral emissivity of a SiC half-space, singleSiC spheres of radii μm, μm, and μm and a SiC sphere ( μm)coated with a Boron Nitride (BN) layer of thickness ( μm) atroom temperature K. Re-print with permission from Ref. [1].

**DISCUSSION:**

Fluctuations of electromagnetic fields lead to radiative energy transfer between objects. The radiative energy transfer between planar objects have been studied during the past decades while that between other geometries, such as spherical or cylindrical shapes, have not been investigated well. Therefore, the experimental investigation of those is of great importance to verify the theoretical work.

There are several methods to synthesizing hollow SiC micro/nano-spheres. This method uses the vapor of SiO and amorphous carbon particles along with oxidization to obtain the hollow SiC micro/nano-spheres. The creation of the spheres has a wide range of reaction parameters such as temperatures, gas flow and heating rates which can alter the amount of nano particles obtained, diameters, and shell thicknesses however, high temperatures are needed. The shell thicknesses can be controlled by the siliconization degree and carbon nano particle multilayer structures. Troubleshooting of this technique takes experimentation of the different parameters needed to create the perfect hollow SiC micro/nano-spheres.

The process of attaching the sphere to the micro-cantilever depends on the size of the sphere. Very small spheres (< 5 μm) can limit the process because the size of the glue drop might not be controllable to be as small as needed.

FTIR spectroscopy has been used for different studies of high-temperature spectral emissivity measurements57,58. Moreover, FTIR has several practical advantages. The biggest advantage is that the whole spectrum is detected simultaneously. In addition, FTIR has a very high increase in source throughput, which ranges from 10 to 250 over the infrared frequency range52. The described experimental setup for the measurement of the spectral emissivity is simple and an economic solution. However, using black reference samples can just approximate an ideal black body as described by Planck’s radiation law. Furthermore, there are also so-called emissiometers available to determine the spectral emissivity. However, the information content of such measurements is limited compared to FTIR based emissivity analysis. FTIR spectroscopy gives a more detailed characterization and deeper understanding of material properties54.

As no one conducted the experimental measurement of the emissivity spectrum of micro/nano-spheres before, one limitation could be the sensitivity of the detector, in comparison to the strength of the emissivity of the micro/nano-sphere. Therefore, the practical feasibility of this structure has to be validated. Furthermore, critical steps within the protocol are the use of the software for the FTIR spectrometer. The structure and operation of the software varies with different spectrometer manufacturers, so that the exact steps could vary.

The study of fluctuation-induced radiative energy for spherical shapes has great applications in the nanoscale engineering, e.g. nano-beads, nanoparticle-nanofiber composites, and multilayer-coated spherical shells. It deserves further theoretical and experimental investigation on the study of enhanced wavelength selectivity of radiative thermal properties of nano-sized particles1.

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**DISCLOSURES:**

The authors have nothing to disclose.

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