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Spectral radiative properties of three-dimensionally ordered macroporous ceria particles

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ABSTRACT

Radiative properties of spherical heterogeneous particles consisting of three-dimensionally ordered macroporous (3DOM) cerium dioxide (ceria) are numerically predicted in the spectral range 290–10,000 nm. The particles are 1000 nm in diameter, with interconnected pores of 330-nm diameter and a face-centered cubic lattice arrangement. Predictions are obtained by solving macroscopic Maxwell's equations using the discrete dipole approximation and the finite element method. The scattering and absorption efficiency factors as well as the asymmetry factor are determined as a function of the particle orientation relative to the direction of the incident plane wave. The scattering and absorption efficiency factors show significant dependence on the particle orientation in the spectral range 560–1000 nm. Compared to homogeneous ceria particles, 3DOM particles of the same diameter have a significantly reduced extinction efficiency for wavelengths greater than 560 nm. Approximating the 3DOM particles as a homogeneous sphere with properties calculated from an effective medium theory is also considered. This approach is shown to be valid only for wavelengths much greater than the pore size, which demonstrates that a detailed geometrical representation of the internal particle structure is essential to obtain accurate radiative characteristics of highly ordered nano-structured particles.

1. Introduction

Cerium dioxide (ceria) has been proposed as a novel reactive material to realize solar-driven thermochemical cycles to split water and carbon dioxide for production of hydrogen and carbon monoxide [1–4]. Ceria forms oxygen vacancies in its lattice structure in response to changes in physical conditions, such as temperature and oxygen partial pressure, making the material suitable for non-stoichiometric redox chemical reactions. Three-dimensionally ordered macroporous (3DOM) ceria structures offer high porosity and specific surface area. Faster chemical kinetics were observed for packed beds of 3DOM structures in comparison to the kinetics measured for sintered ceria structures [5]. Synthesis techniques have resulted in improved structural stability, as well as retention of the 3DOM structure when the material undergoes thermochemical cycling, which makes the 3DOM structure more desirable than conventional micro-structured porous ceramics [6]. Radiative properties are needed to determine medium temperature and the reaction rates. For solar-driven reactions, the characteristics of the reactive medium, which can be tailored by modifying medium morphology and composition, should simultaneously allow for (i) efficient absorption of incident concentrated solar radiation, (ii) rapid heat transfer between the absorption and reaction sites, (iii) confinement of the emitted thermal radiation in the close vicinity of the reaction site, (iv) minimum heat losses from

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Nomenclature

a	lattice parameter, m
$\mathbf{A}$	dipole moment coefficient matrix, m F^{-1}
d	dipole lattice parameter, m
D	pore diameter, m
$\vec{\mathbf{E}}$	electric field, N C^{-1}
g	asymmetry factor
$\vec{\mathbf{H}}$	magnetic field, A m^{-1}
k	imaginary component of refractive index
m	complex refractive index
n	real component of refractive index
Q	efficiency factor
p	porosity
$\vec{\mathbf{P}}$	dipole moment vector, J^2 C^{-3}
r_p	particle radius, m
$\vec{\mathbf{r}}$	location in space, m
$\vec{\mathbf{S}}$	time-averaged Poynting vector, W m^{-2}
V	integration volume, m^3
x	particle size parameter

Greek symbols

α	polarizability, m F^{-1}
Γ	integration surface, m^2
ϵ	permittivity, F m^{-1}
η	wavenumber, m^{-1}
θ	particle orientation angle, °
λ	wavelength, m
σ	electrical conductivity, S m^{-1}
ϕ	particle orientation angle, °
ω	angular frequency, rad s^{-1}
Ω	solid angle, sr

Subscripts

abs	absorption
eff	effective
ext	extinction
inc	incident
rel	relative
sca	scattering
tot	total
0	vacuum

the reacting medium by conduction and convection, and (v) rapid chemical reactions. High specific surface area and porosity in addition to varying levels of semi-transparency in the visible and infrared spectral ranges are a desired combination of morphological and optical characteristics to satisfy the above criteria for optimizing reactive media for solar thermochemical applications.

Previous pertinent studies of radiative characteristics of ceria ceramics and packed beds are given in [7–11]. Overall transmittance of ceria with average porosities of 0.08 and 0.72 was experimentally found in [7] for the spectral range 0.3–1.1 μm. Both samples were found to be highly opaque up to 400 nm. Using the same materials for the spectral range 0.9–1.7 μm, it was found in [8] that the mean radiation penetration length is shorter in higher porosity samples suggesting higher scattering. Using the Monte Carlo ray tracing technique along with experimental transmittance data, the transport scattering coefficient of porous ceria was obtained in [11] and found to be in agreement with theoretical estimates based on Mie theory.

Heterogeneous particles and groups of heterogeneous particles were radiatively characterized in the studies [12–17]. Of particular interest to solar thermochemical applications are the effects of internal particle structure on macroscopic radiative characteristics. The effect of porosity on absorption characteristics was previously studied in [12] using the discrete dipole approximation (DDA) for spherical composite particles. It was found that a shift in the inclusion volume fraction corresponded to a shift in the absorption peak of the particle. Results obtained using the DDA for composite particles were in good agreement with observed interstellar extinction efficiency factors [13]. Also using the DDA, Voschinnikov et al. [14] concluded that porosity of particles has only a slight effect on optical properties for porosities less than 0.5. The use of an effective medium theory with exact solutions on approximate geometry, such as the Lorenz–Mie theory, to reproduce scattering characteristics obtained with the DDA as well as the finite element method (FEM) was examined in [15–17]. It was concluded in [15] that effective medium theories agree well with numerical methods directly discretizing the geometry for a wide range of porosities and particle size parameters as long as the effective medium theory assumptions are upheld: statistical uniformity and small inclusions compared to wavelength. Porosities up to 90% were found to be accurately modeled when the inclusions are in the Rayleigh limit [17].

In the present paper, ceria particles of 1000 nm in diameter are studied in the spectral range 290–10,000 nm. The DDA is employed to compute the radiative properties in the entire spectral range for four particle orientations and in the range 380–800 nm for 25 particle orientations. The FEM is applied to solve macroscopic Maxwell's equations to provide a reference numerical solution. The FEM/DDA results are compared to those obtained using the Lorenz–Mie in conjunction with effective medium theories.

2. Problem statement

3DOM ceria structure consists of a face-centered cubic (FCC) lattice of overlapping pores in a continuous matrix of cerium dioxide as shown in Fig. 1a. This geometry can be described by two parameters, the lattice constant a and the pore diameter D, as shown in Fig. 2. In this study, we consider a 3DOM structure with $a = 440$ nm and $D = 330$ nm, for which the width of the interconnecting struts is approximately 90 nm and the porosity is $p = 0.85$.