Scattering spherical voids in nanocrystalline TiO_2 – enhancement of efficiency in dye-sensitized solar cells

Sarmimala Hore,*[a] Peter Nitz,[b] Carmen Vetter,[b] Christof Prahl,[b] Michael Niggemann[b] and Rainer Kern[ab]

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Spherical voids as light scattering centers in nanocrystalline TiO_2 films were realized with polystyrene particles of diameter 400 nm, thus enhancing the photovoltaic performance by 25% on large areas, as well as providing an indication that these films can be used with electrolytes of higher viscosity.

Dye-Sensitized Solar Cell is one of the promising new technologies in the area of thin film solar cells.[1] The device consists of mesoporous nanocrystalline titanium dioxide (TiO_2) film onto which a photoactive dye is adsorbed. The dye adsorbed onto the TiO_2 absorbs the photon energy, thus creating excited state electrons that are then injected into the nanoporous TiO_2, which is in turn responsible for the electron transport in the device. The excited state of the dye after photo-induced electron transfer is regenerated by electron donation from the electrolyte, *e.g.* the iodine/iodide redox couple present in a non-aqueous organic electrolyte.[2]

With particle sizes of about 15–40 nm, the effective surface area of the TiO_2 is large, which is responsible for the optimal dye loading and in turn effective photocurrent generation. Since the light absorption of the dye remains low in the region of 600–800 nm, efficient light scattering in the films becomes important.[3] Light scattering can be achieved by additional scattering layers[4] as well as by scattering centers incorporated in the TiO_2 layer. Due to the small size of the particles (15–40 nm) in the TiO_2 films, the scattering of the primary TiO_2 particles embedded in the electrolyte is very weak (Rayleigh scattering). Instead, the essentially transparent composite of primary particles and the electrolyte can be considered as an effective medium having a refractive index between that of electrolyte ($\eta \approx 1.6$) and that of the TiO_2 ($\eta \approx 2.5$). Due to the high porosity of the TiO_2, this effective refractive index can be approximated as $\eta_{\text{eff}} \approx 2.0$.[3] Thus light scattering can be enhanced by the introduction of domains having refractive index differing from that of the effective medium matrix. Optical modeling described by Ferber *et al.*[3] suggested the use of larger TiO_2 particles of radial dimension 125–150 nm in a TiO_2 matrix of particles of 20 nm diameter.

In this communication we report inclusion of scattering centers as spherical voids. Furthermore, these particular films (Fig. 1) support the diffusion of the electrolyte permeating the porous TiO_2 film, and hence can be used effectively with solvents of higher viscosity, such as molten salt electrolytes[5] where conduction of ions in the electrolyte matrix is low or with the hole conducting polymers.[6] Calculations of scattering effects are compared with measurements on prepared devices. The scattering effect of the spherical voids in TiO_2-films was calculated using Mie theory[7] for single scattering due to the electrolyte-filled spherical voids surrounded by an effective medium. As a measure for the effectiveness of scattering, we first calculated the macroscopic scattering coefficient S as the product of the scattering cross-section (σ_s)[7] and the particle density, which is a ratio between the total volume fraction occupied by the scatters (Φ) and the particle volume (v) itself. Therefore, the quantity $\sigma_s/v = S/\Phi$ is a measure for scattering effectiveness per volume fraction of scatterers. Furthermore, absorption within the device is most enhanced for scattering under large scattering angles. The angular scattering characteristics of a spherical scatterer develop from a forward backward symmetry (weak Rayleigh scattering), to strong forward peaked (strong Mie scattering), with increasing radius. Thus, a backward scattering cross section σ_b defined as

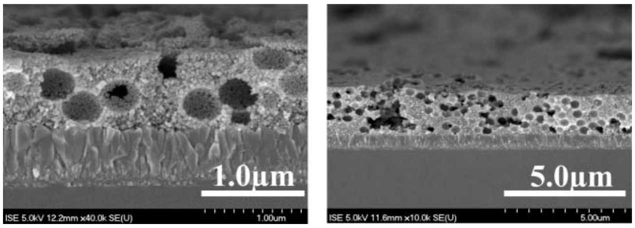

Fig. 1 Spherical voids are left behind in the film of TiO_2 when the polystyrene spheres are burnt out during the heating or the sintering of the films at 450 °C.

$$\sigma_b := (1 - \zeta)\cdot\sigma_s \qquad (1)$$

may be used as a measure for the desired sideward scattering and absorption enhancement. ζ is the forward scattering ratio giving the ratio of radiation scattered into the forward hemisphere with respect to the incident beam and σ_s is the Mie scattering cross section. Both ζ and σ_s can be calulated directly from Mie coefficients.[7] The quantities σ_s/v for total scattering and σ_b/v for backward scattering at vacuum wavelength $\lambda_0 = 550$ nm are shown in Fig. 2 as a function of particle radius. It can be obtained from the representation in Fig. 2 that the small particles of TiO_2 between 5–20 nm in radius are not efficient scatterers. Effective Mie scatterers are those particles whose dimensions are comparable to the wavelength of light. The backscattering coefficients per volume shown in Fig. 2 suggest that the voids of about 50–100 nm and solid particles of 50–700 nm in radius could be effectively used as back scatterers.

Spherical voids in TiO_2 films were prepared by the following method. Carboxyl groups are known to serve as an efficient

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*sarmimala.hore@fmf.uni-freiburg.de

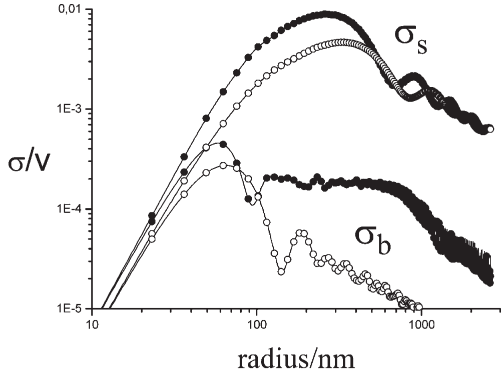

Fig. 2 Total (σ_s/v) and backward (σ_b/v) scattering coefficients per unit particle volume due to the presence of spherical electrolyte-filled voids (○) and due to larger solid TiO_2 particles (●) present in the TiO_2 films as potential scatterers at $\lambda_0 = 550$ nm.

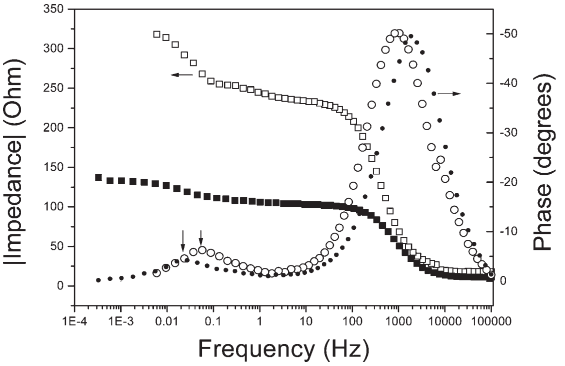

Fig. 4 Impedance spectra of TiO_2 with hollow spheres (□ magnitude and ○ phase; film of thickness 5.8 μm) and solid particles (■ magnitude and ● phase; film of thickness 4.5 μm) in the dark using (20 : 80) acetonitrile and hexyl-methyl-imidazolium iodide containing I^-/I^-_3. The arrows indicate the maxima in the diffusion peak for the respective films.

Table 1 Comparison of the IV characteristics of the devices derived from TiO_2 films with and without scattering centers

	I_{sc}/ mA cm^{-2}	V_{oc}/ mV	FF (%)	η (%)
TiO_2 without scattering centers	12.0	740	60.8	5.4
Hollow scattering spheres	13.0	740	69.5	6.7
Solid scattering centers	12.3	731	61.0	5.5

functional group for anchoring onto TiO_2.[2] Hence, carboxyl stabilized polystyrene spheres of radius 200 nm were used in order to generate spherical voids. Polystyrene spheres[8,9] (Aldrich) were dispersed into the TiO_2 colloidal paste[10] in a ratio of 1 : 5 by volume and the mixture was then placed in an ultrasonic bath at room temperature for intimate mixing. Upon sintering these films at 450 °C, the polystyrene particles burn out thus leaving a reverse structure in the films. Solid particles of TiO_2 ranging from 75–150 nm in radius (from Fluka) were added to particles of 25 nm in a ratio of 1 : 5 by volume.

Reflectance measurements of the TiO_2 films without dye and electrolyte (Fig. 3) with hollow spheres embedded in a matrix of TiO_2 of 20–25 nm particle size illustrate that these films scatter efficiently with respect to the films comprised of 20–25 nm particles of TiO_2. Both films indicated in Fig. 3 were of thickness ~ 4 microns.

Diffusional properties of the ions in the electrolyte films with spherical voids and solid spheres embedded in TiO_2 were measured using electrical impedance spectroscopy (EIS). It has previously been shown[11] that the minimum frequency peak at low frequency range corresponds to a diffusion limited process in the electrolyte. Using electrolyte of higher viscosity such as (20 : 80) acetonitrile and hexyl-methyl-imidazolium iodide containing I^-/I^-_3, it was demonstrated in the dark that for those films containing spherical voids, the lower frequency peak is shifted to a higher frequency in comparison with the films containing solid particles of comparable dimensions (Fig. 4). This effect shows that films with voids facilitate diffusion.

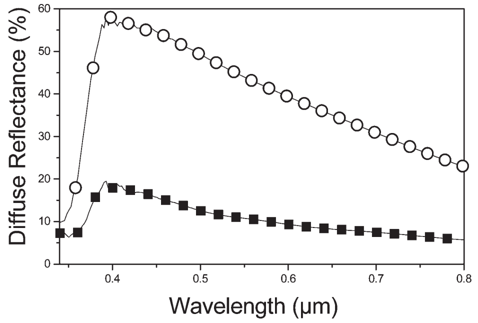

Fig. 3 Measured diffuse reflectance of films without dye or electrolyte. (■) Semi-transparent TiO_2 film, and (○) TiO_2 films with spherical voids. Since the system under investigation is without dye or electrolyte, the effective refractive index of the medium *i.e.* air is significantly lower than in the device.

Dye-sensitized solar cells were fabricated[12] with the screen printing technique in a semi-automated baseline.The electrolyte is composed of 0.6 M tetrabutylammonium iodide, 0.1 M LiI, 0.1 M I_2, and 0.5 M 4-*tert*-butylpyridine in acetonitrile. Layer thicknesses for the TiO_2 with and without the spherical voids, and layer with solid scattering particles[3] are about 10 microns. For the impedance measurements nanoporous TiO_2 layers with hollow spheres and solid particles were printed on a platinized TCO glass. As counter electrode a platinized TCO glass was used. Photovoltaic performance of large area devices (2.5 cm^2) under A.M 1.5 simulated sunlight given in Table 1 indicates improved performance of the devices with TiO_2 containing hollow spheres.

In conclusion, we have successfully incorporated voids of radius 200 nm in films of TiO_2 which enhances the scattering properties of the films and hence the light capture inside the device. EIS measurements demonstrate that the films can be used in devices for electrolytes with higher viscosity where the diffusion constant of the ions in the electrolyte is low. Using hollow scattering voids an increase in fill factor as well as the current density was observed, thus increasing the overall efficiency of the devices by 25%.

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Sarmimala Hore,*[a] Peter Nitz,[b] Carmen Vetter,[b] Christof Prahl,[b] Michael Niggemann[b] and Rainer Kern[ab]
[a]*Freiburg Materials Research Center, Stefan Meier Strasse 21, 79104, Freiburg, Germany. E-mail: sarmimala.hore@fmf.uni-freiburg.de*
[b]*Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstrasse 2, 79110, Freiburg, Germany*

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