3 Characterization methods for small particles

From the great number of analyzing techniques that may be applied for characterizing physical properties of nanostructured materials here only those are introduced which were extensively used in the present work. These are electron microscopy, electron magnetic resonance and optical spectroscopy. By **electron microscopy** at its highest level structural characteristics of specimens under investigation may be retrieved down to the atomic scale of resolution. While electron microscopy is used for directly imaging a certain specimen area, the other methods use the response of a sample upon perturbations by a magnetic field or by visible light. The general name electron magnetic resonance is used for **electron paramagnetic resonance** (EPR) applied to the study of paramagnetic species like ions from a physical and chemical point of view, and for **ferromagnetic resonance** (FMR) applied to the study of the magnetic properties of superparamagnetic nanoparticles. The optical absorption and elastic scattering of light by particulate matter is extensively studied and corresponding **optical spectroscopy** measurements allow to draw conclusions on a number of structural features. Therefore, the optical properties of the materials prepared sensitively reflect how close a certain approach meets the intended structures.

3.1 Transmission electron microscopy

Electron microscopy is a powerful method to investigate nanoparticle composite materials from the morphological and structural point of view. Morphological properties of the samples are studied using transmission electron microscopy (TEM) and the structural characterization of nanoparticles is performed with high resolution electron microscopy (HREM). Because in the following only a short description can be given, for complete understanding of the electron microscopy technique numerous textbooks are available [Bet87, Wil96].

3.1.1 Image formation

Fig. 3.1 shows a schematic drawing of the main components of a transmission electron microscope. They cooperate in the following functional units: *(i)* illumination system composed of electron source and condenser lenses, *(ii)* specimen stage for shift, titling and rotation, *(iii)* image formation
system that consists of objective lens and aperture, intermediate and projective lenses and \((iv)\) image recording system formed by the screen and photo recorder (camera or video).

The interaction of the electron beam with the object results in scattering of the electrons in the all directions. In the particular case of crystalline materials this results in electron diffraction. The variation of the image intensity due to variation of the object characteristics like thickness or composition defines the image contrast. For crystalline materials the image contrast depends on the orientation and lattice type. Additional contrast features may be due to lattice defects and to superposition of crystal slabs. Two types of imaging modes depending on the scattering processes can be applied. Bright-field imaging provides a distinct image contrast, available when excluding scattered or diffracted beams by means of an objective lens aperture. Dark-field imaging, i.e. selection of certain diffracted beams of the scattered electron wave by beam tilting or objective aperture displacement, is used for imaging specimen regions of specific orientation, structure or composition [Yac80, Hof82b, Hof82a].

TEM images provide only projections of three-dimensional objects. Information on the object topography (e.g. thickness changes) of crystalline objects is available by the weak-beam dark-field imaging mode [Yac80, Hof82b].
A crystal may be described in terms of a periodic arrangement of scattering elements (atoms, ions or molecules). The crystal lattice expresses this periodicity in three dimensions. Elastic scattering of an incident plane wave (electrons) by a crystal, i.e., a periodical distribution of identical scattering elements, causes diffraction effects. A geometric formulation of the diffraction condition is given by the Bragg equation

\[ 2d(hkl) \sin \theta = n\lambda \]  

(3.1)

which describes the diffraction of electrons of wavelength \( \lambda \) by a set of lattice planes \((hkl)\) of spacing \(d\), \(n\) being the reflection order. Interaction of the electron beam with the object, situated in the front focal plane of the objective lens, produces an intensity distribution in the back-focal plane where, e.g., beams diffracted by object regions of equal lattice characteristics (orientation, spacing) meet at the same position. This produces distinct spot patterns for one or few single crystals, or ring patterns for polycrystalline objects (or particulate objects with random orientation).

In this work the TEM investigations are performed with a conventional JEM 1010 transmission electron microscope operating at 100 kV accelerating voltage. The high resolution measurements are done with JEM 4000EX and JEM 4010 electron microscopes operating at 400 kV.

### 3.1.2 Sample preparation and image analysis

All used samples are in the form of powders which require another preparation method as for bulk or thin film samples [Wil96]. Agglomerated powders are first subject to milling in a mortar. Then the powder is dispersed in isopropanol (2-propanol) under vigorous shaking or using a ultrasound bath and a small quantity of the liquid is applied on a copper grid using a dropper. The copper grid (PLANO) is covered by a very thin perforated carbon film. This preparation method allows imaging of the specimen area above such holes without influencing the image contrast by the carbon layer.

The electron micrographs are digitized using a CCD-camera of TiETZ which gives an additional magnification of about 8×. From these digitized images usually more than 250 particles of a specific sample were measured to determine particle size and distribution. Two approaches were used to calculate the size distribution. The first one is taking the automatic measuring routines of the software being very useful in regions where the contrast of the substrate is not too high or where a background can be subtracted. The second way is by measuring each particle manually. From these data the mean sizes of the particles \( \bar{d} \) and geometrical standard deviations \( \sigma_d \) are calculated using the statistical formula

\[ \bar{d} = \frac{1}{n} \sum_{i=1}^{n} n_i d_i \]  

and  

\[ \sigma_d = \left\{ \frac{1}{n-1} \sum_{i=1}^{n} (d_i - \bar{d})^2 \right\}^{1/2} \]  

(3.2)
3.2 Optical spectroscopy

Alternatively, the particle statistics may be estimated from a fitting function of the histogram, e.g., a LogNormal function as described first by Granqvist [Gra76]. Metal particles with mean sizes below 20 nm can be fitted preferentially by LogNormal functions of the type

$$f_{LN} = \frac{1}{(2\pi)^{1/2}\ln\sigma} \exp\left\{-\frac{(\ln d - \ln \bar{d})^2}{2\ln^2\sigma}\right\} \quad (3.3)$$

where $d$ is the particle diameter and $\ln\sigma$ is the logarithm of the standard deviation which is also a measurement of the width of the histogram [Gra76]. The coverage of the oxide surface by metal nanoparticles was estimated by considering the particle size distribution and the mean area density of metal nanoparticles.

For measuring the spacing of lattice plane fringes in HREM images either intensity plots across the fringe direction are used (real space evaluation) or the distance of reflexes in diffractograms obtained by Fourier Transformation (reciprocal space image evaluation). Prerequisite of both methods is the correct scaling of magnification applied to the digitized image.

3.2 Optical spectroscopy

The optical properties of the nanoparticulate composite materials were investigated by using optical spectroscopy in the visible region. To this aim a measuring system for thin film optical analysis of THEISS as schematically represented in fig. 3.2 was used. The system consists of a 50W stabilized halogen light source (S), two ETA-CSB50 grating spectrometers with 512 pixel diode array for simultaneous measurement of transmittance (T) and reflectance (R) in the spectral range 380 to 1050 nm. The connection from the source to the sample stage is guided by quartz optical fibers. The spectrometer is connected and controlled via two serial ports to a computer where the spectra

![Fig. 3.2: Schematic representation of the optical spectrometer.](image-url)
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are recorded using appropriate software. To reduce background signals and noise all measurements were done in the dark and averaged over multiple measurements (about 150).

Since the materials investigated were always obtained in powder form and the spectrometer is mainly suited for thin film measurements, appropriate sample preparation methods are needed. The first one used employs the dispersion of metal coated oxide nanospheres as powder in alcohol (e.g., isopropanol) or deionized water followed by dropwise or spinning deposition on microscope glass slides. The second preparation method uses a single component liquid adhesive of NORLAND for embedding the powder in a transparent thin film. The sample is homogenized and then dropped on microscope slides. For solidification the samples are exposed to UV-light (365 nm) for less than 5 minutes. The adhesive has a transmission higher than 95% in the spectral range 400 to 2000 nm, that was measured separately and has therefore no influence on the recorded spectra.

The optical properties of metal particles are deduced from the measurement of the transmittance defined as the ratio between the transmitted and incident light intensity \( T = I / I_0 \). The extinction coefficient is given by the Lambert-Beer law

\[
\sigma_{ext} = -\ln T
\]  


To illustrate the connection of color and spectrum two examples are given of metal particles interspersed in between silica nanospheres. These samples have been prepared from a colloid-disperse solution of silica nanospheres of high weight percentage (40%). They have more or less regular arrangement of cavities in between the spheres which may be utilized as template for metal nanoparticle formation by controlled reduction of metal complexes added to the solution and subsequent evaporation of the solvent. Fig. 3.3 shows a sample with silver prepared at room temperature (top) and gold (bottom) nanoparticles prepared at 60°C on LUDOX SiO\(_2\). The silica nanospheres used in these experiments have a mean size of 29 ± 4 nm being much smaller than as those used for nanoparticle coating experiments. By electron microscopy it could be shown that the metal particles have the tendency to precipitate in the cavities between the silica spheres. This finding is similar to that obtained for nanolithography with latex spheres, that produces two dimensional arrays of metal particles [Bur98, Bur99, Bur00].

The calculation of extinction spectra using the Mie theory for nanoparticles embedded in a dielectric matrix and the extension of this theory for core-shell structures is based on a program described by Kreibig [Kre95] for dipolar approximation and one by Bohren [Boh98] for multipolar approximation. The program for multipolar approximation solves the Bessel-Ricatti functions using backward recurrence. To achieve a better performance the limitations for the order of the calculated Bessel-Ricatti functions are changed using the size parameters proposed by Wiscombe [Wis79]. All calculations are performed by applying the size dependence of the dielectric function as given in equation (2.25).
3.3 Electron paramagnetic resonance

The physico-chemical interpretation of paramagnetic resonance spectra requires to take into account the quantum mechanical description of atoms with several electrons. Since the quantum theory of electron magnetic resonance is well known from the literature (e.g. [Pak62, Mor80]) here only the techniques used for measuring and interpretation of magnetic absorption spectra are described.

The most important parameters which can be determined from electron magnetic resonance are the splitting factor (g-factor) characterizing the localization of unpaired electrons responsible for the absorption phenomena, as well as shape and width of the absorption line depending on type and strength of the interaction in the sample, and finally the line intensity depending on the number of unpaired electrons in the sample. In order to evaluate these parameters the measured spectra must be compared with calculated ones according to models which are already described in Chapters 2.2 and 2.3. The g-factor defines the Zeeman energy $h\nu_0 = g\mu_B H_0$ with $\mu_B$ being the Bohr magneton and $\nu_0$ the resonance frequency. The electron paramagnetic resonance method is
used to investigate the interaction between particles, between particles and oxide support, and also oxide surface modifications due to metal precursor decomposition.

**Fig. 3.4: Schematic representation of the magnetic spectrometer.**

The electron magnetic resonance measurements are performed using a X-band spectrometer (ESR 220, ZWG Berlin-Adlershof), working at 9.3 GHz equipped with a frequency divider (K) and frequency counter 5215A (HEWLETT PACKARD) (F) and a nuclear magnetometer type MJ 110-R (RADIOPAN) (B) for measuring frequency and magnetic field. The schematic representation of the magnetic spectrometer given in fig. 3.4 present also the sample (S) and the microwave cavity (C). The measurements are made at various temperatures in the range of -150 to +150°C using controlled flow of liquid nitrogen for the low temperature range (T).

In order to measure the evolution of signals with time the as-prepared samples are sealed in quartz-tubes under vacuum during the first measurements. The quartz-tubes are exposed to the ambience only for subsequent electron microscopy and optical spectroscopy measurements, or for repeated measurements to keep track of sample stability under normal conditions.

The simulated magnetic resonance spectra are generated by means of appropriate programs translated to Borland Delphi 5. For ferromagnetic resonance the program considers the model proposed by Schlömann [Sch58] for both weak and large anisotropy and also the model proposed by Suran [Sur73] without taking into consideration the demagnetization energy. The program used to simulated the paramagnetic spectra is based on the theory proposed by Withe [Whi76] which takes into account only the spin Hamiltonian in the second order perturbation. There is a good agreement between the experimental and simulated spectra. Both Lorenzian and Gaussian line shapes are considered for all simulations in order to achieve better results.
From the temperature dependence of the relative intensity of the absorption signal the mean size of the particles can be calculated as described by Mörke [Mör90] using the relation

\[
\frac{I(T_1)}{I(T_2)} = \frac{\coth \left( \frac{H\nu M_s T_1}{k_B T_1} \right) - \frac{T_1 k_B}{H\nu M_s T_1} M_s T_1}{\coth \left( \frac{H\nu M_s T_2}{k_B T_2} \right) - \frac{T_2 k_B}{H\nu M_s T_2} M_s T_2}
\]  
(3.5)

or using the more general Griscom formalism [Gri81]

\[
\frac{I_{T_1}}{I_{T_2}} = \frac{M_{s,T_1}}{M_{s,T_2}} \left[ \frac{1 - e^{-x}}{1 - e^{-(2x+y)}} + \frac{e^{-y}}{1 - e^{-y}} \left[ \frac{1}{x} (x-y)(1 - e^{-2x}) - (1 - e^{-2(x-y)})e^{-y} \right] \right]
\]  
(3.6)

where \(x = M_{s,T_1} vH/(k_B T_1)\) and \(y = g\mu_B H/(k_B T_1)\), \(M_{s,T_1}\) represent the saturation magnetization at temperature \(T_1\), \(v\) is the volume of the particles, \(H\) the intensity of the magnetic field, and \(k_B\) is Boltzmann’s constant. \(I(T_1)\) and \(I(T_2)\) represent the derivative of the signal intensity taken at temperatures \(T_1\) and \(T_2\), respectively.