Antimony-doped tin oxide nanoparticles for conductive polymer nanocomposites

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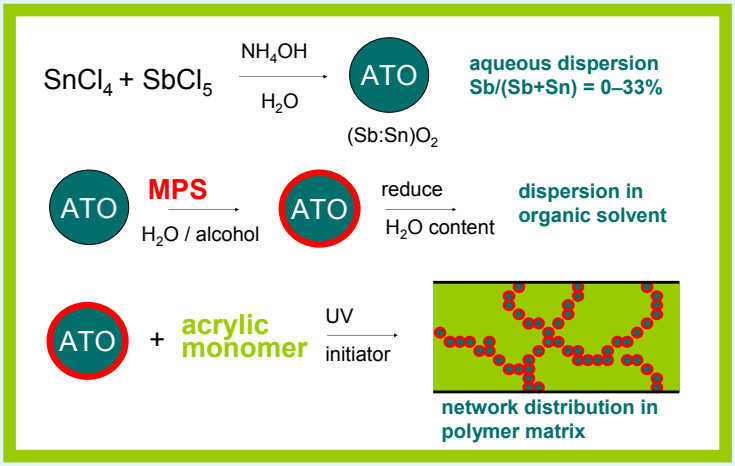
Conductive polymer nanocomposites

We used antimony-doped tin oxide (ATO) nanoparticles to make transparent semiconductive polymer nanocomposites, by dispersing them through an acrylate matrix in a percolating network distribution. The particles are prepared from coprecipitation of metal chlorides from solution, followed by hyddrothermal treatment. This way, aqueous dispersions of particles with 0–33% Sb doping were prepared. Modification of the particle surface is done with the silane coupling agent 3-methacryloxypropyltrimethoxysilane (MPS) to facilitate dispersion of the hydrophilic particles in the acrylate matrix. After mixing the modified particles with an acrylate monomer, the mixture is cast on a substrate with an applicator and then UV cured.



Particle characterization

Before preparing nanocomposite films we characterized the nanoparticles, as knowledge of surface and bulk composition of the nanoparticles will probably be essential in understanding the σ_v-$\phi_{particle}$ relation in ATO/acrylate nanocomposites [1]. XRD showed that antimony ions are incorporated in the tetragonal cassiterite SnO_2 structure up to the highest doping levels. From BET N_2 adsorption (Figure 1) we see that the particle size decreases with Sb doping from 8.2 nm (0% Sb) to 5.0 nm (33% Sb), which may be explained by segregation of Sb to the surface of the ATO nanoparticle, decreasing the rate of crystal growth. Heating at 300 °C results in an increase in particle size, however, the particle stability increases with Sb doping.

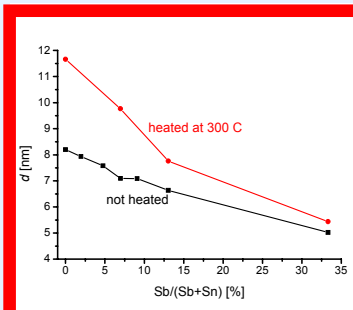


Fig. 1: Effect of Sb doping on particle size, determined from specific surface are (BET N_2 adsorption), assuming spherical particles with ρ = 6.99 g cm^{-3}.

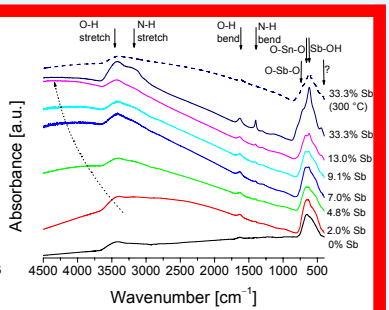


Fig. 2: FT-IR spectra of ATO nanoparticles for different Sb doping. The dashed spectrum shows the effect of heating at 300 °C. The arrow indicates the shift of the plasmon peak.

FT-IR spectra of ATO powders in KBr pellets are shown in Figure 2 for 0–33% Sb. It shows a broad absorbance over almost the complete spectral range. This absorbance is absent for undoped SnO_2 and can be attributed to plasmon vibrations due to Sb doping. The large peak from 400-800 cm^{-1} is characteristic for the ATO particle. It changes from a single peak (SnO_2) into a double peak with increasing Sb doping. Furthermore, we see an increasing peak at 1400 cm^{-1}, which disappears upon heating. This peak can be attributed to adsorbed NH_3, originating from NH_4OH that was used in particle production.

Particle surface modification

To investigate the grafting of MPS to the particle surface [2] we removed the ungrafted part of MPS by centrifugation. Figure 3 shows FT-IR spectra for different MPS/ATO ratios. For MPS/ATO = 0.045 g/g centrifugation has no effect, but for MPS/ATO = 0.20 g/g part of the MPS is removed, indicating that not all MPS is grafted to the particle surface. From the detected C-content (elemental analysis) we determined the total grafted amount (Figure 4) and a plateau value is reached (3.2 μmol m^{-2}) that is close to the value for parallel monolayer coverage as determined for MPS grafting on SiO_2 [3].

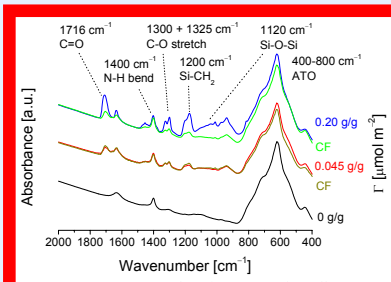


Fig. 3: FT-IR spectra of ATO particles for different initial MPS/ATO ratios.

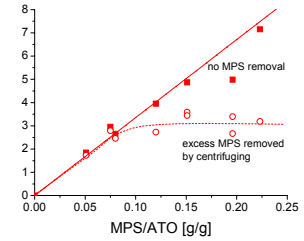


Fig. 4: Grafted amount of MPS, determined from C-content with elemental analysis.

ATO/acrylate nanocomposites

The volume conductivity σ_v of prepared films was determined by a four-point probe technique, as a function of particle filler content. Figure 5 shows that a very low percolation threshold, $\phi_c \approx 0.3$ vol% is reached and that with increasing MPS σ_v decreases considerably. Figure 6 shows an increase in σ_v with increasing Sb doping. TEM imaging (Figure 7) shows separated clusters below ϕ_c. Just above ϕ_c somewhat larger clusters can be seen, which may be part of a connected particle network on a larger scale than the sample thickness (≈ 100 nm). At higher ϕ the connected particle network is visible and TEM tomography (Figure 8) reveals the 3D character of this connected particle network.

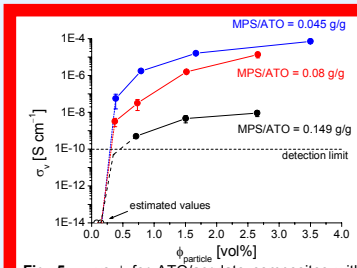


Fig. 5: σ_v vs ϕ for ATO/acrylate composites with different MPS/ATO ratios. 13% Sb.

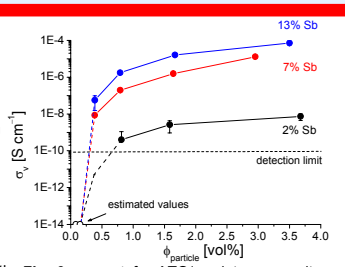
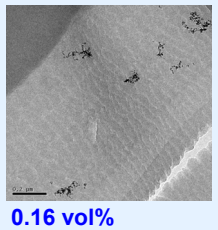
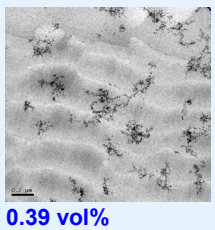


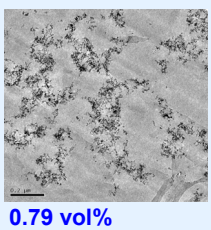
Fig. 6: σ_v vs ϕ for ATO/acrylate composites with different Sb doping. MPS/ATO = 0.045 g/g.



0.16 vol%



0.39 vol%



0.79 vol%

Fig. 7: TEM images of ATO/acrylate nanocomposites for different particle filler amounts. 13% Sb; MPS/ATO =0.045 g/g.

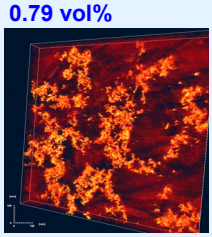


Fig. 8: Reconstructed 3-D TEM tomography image from a series of images at different tilting angles. 13% Sb; MPS/ATO = 0.045 g/g; ϕ = 0.79 vol%.

References

1. W.E. Kleinjan, J.C.M. Brokken-Zijp, et al., *J. Mater. Res.* **23**, 869-880 (2008)
2. W. Posthumus, P.C.M.M. Magusin, et al., *J. Colloid Interf. Sci.* **269**, 109-116 (2004)
3. J.D. Miller, H. Ishida, *Surf. Sci.* **148**, 601-622 (1984).

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