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Surface modification of MoS_2 nanoparticles with ionic liquid–ligands: towards highly dispersed nanoparticles†

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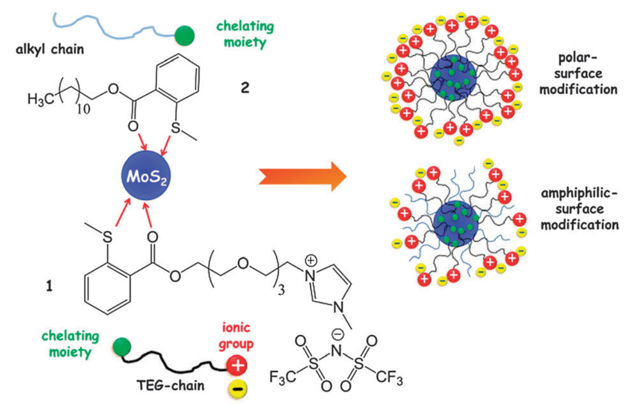
Highly dispersible MoS_2 nanoparticles have been prepared *via* surface-modification using a novel tetraethylene glycol-based ionic liquid containing a chelating moiety attached to the cation. The choice of the respective ligand enables the generation of highly dispersible MoS_2 nanoparticles with either polar, hydrophobic or "amphiphilic" surfaces, forming highly stable dispersions or microemulsions.

A wide range of applications for molybdenum sulfide (MoS_2) arises from the highly anisotropic nature of this layered compound, most of all in its catalytic activity and lubricating properties, either in bulk or as supported material.[1] Thus MoS_2 compounds are of interest for such diverse fields as nanotribology,[2] photocatalysis,[3] hydrogen production,[4] or solar cells.[5] Within one layer the structure of MoS_2 can be viewed as a two-dimensional macromolecule with each Mo ion surrounded by six sulfur anions in a trigonal prismatic arrangement, resulting in a weak interaction with the next layer. Thus the van der Waals gap is an important feature of interest for its intercalation and lubrication properties, whereas the active centers of MoS_2-based catalysts are located on the edges of the layers, where sulfur vacancies are formed. Not surprisingly, the catalytic activity and lubricating properties especially of MoS_2-nanoparticles (NPs) thus strongly depend on their dispersion.[1]

As generally known for metal-nanoparticles and colloids, MoS_2 nanoparticles (NPs) tend to aggregate due to their large surface energy. Thus one of the most attractive approaches towards highly dispersed MoS_2-NPs is so called "surface-capping" with the surfaces protected by compounds that strongly interact and/or react with the inorganic material.[1a,b,2e,6] Due to their unique properties, ionic liquids (ILs)[7] have received a great deal of attention in the past decade, in particular for the stabilization of colloids. By varying the cation–anion combination ILs can be specifically "designed" for the stabilization of metal nanoparticles, due to the classical steric hindrance of the agglomeration, as well as *via* electrostatic repulsion.[8] Additionally, the attachment of coordinative functional groups such as thiol-, ether-, hydroxyl- or carboxy groups can lead to a significant stabilization of the colloidal particles *via* chelation of the ILs to the NP-surface.[8,9]

In this communication, we report on the surface modification of MoS_2 nanoparticles with the polar ionic liquid–ligand (IL) (tetraethyleneoxide 2-(methylthio) benzoate (**1**)), containing 2-methylthio-benzoic acid as a specifically surface chelating moiety (see Scheme 1), which in turn allows the generation of highly dispersed MoS_2-NPs. Depending on the mixing ratio of the used IL–ligand **1** with an additional hydrophobic ligand **2** (dodecyl-2-(methylthio) benzoate) MoS_2 nanoparticles with either polar (ligand-**1**) or "amphiphilic" properties (mixture of **1** and **2**) could be addressed (Scheme 1).

As ionic liquid–ligand (**1**) we have chosen the chelating group (2-methylthio-benzoic acid) fixed on one end of the



Scheme 1 Schematic illustration of the surface modification of MoS_2 nanoparticles.

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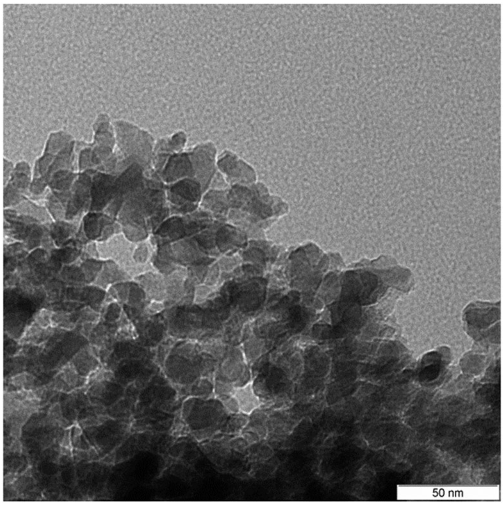

Fig. 1 TEM images of the bare MoS_2 nanoparticles (scale-bar: 50 nm).

tetraethylene glycol (TEG) chain and the 3-methyl-imidazolium cation anchored to the other end of the chain, containing bis(trifluoromethylsulfonyl)imide as the anion (see Scheme S1, ESI†).

Bare MoS_2 nanoparticles were synthesized *via* a hydrothermal route at 180 °C for 24 hours as previously described in the literature,[10] using sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and thiourea ($CS(NH_2)_2$) as precursors and a binary mixture of an ionic liquid (1-butyl-3-methyl-imidazolium chloride, [BMIM]Cl) and water as solvent. The size of the obtained MoS_2 NPs was approx. 24.4 nm as determined *via* dynamic light scattering (DLS, methanol) and was confirmed *via* TEM imaging (Fig. 1).

Subsequent surface modification of the MoS_2 nanospheres was achieved by suspending bare MoS_2-NPs and the corresponding either pure or mixed IL–ligands **1** and **2** in methanol and refluxing for 48 h. Different ratios of MoS_2 and the corresponding ligands have been evaluated in order to achieve optimal synthetic conditions (ESI†). As expected, the increase of the particle size compared to bare MoS_2 NPs was observed, with a value of 31.7 nm for **1**-modified NPs and 30.0 nm for **2**-modified NPs. Assuming the capping of the Mo-atoms on the nanoparticle surface with IL–ligand **1**, we deduct a nearly fully stretched conformation of the ligand, which explains the observed dimensional increase in size.

The presence of the corresponding ligand on the surface of the MoS_2 NPs was confirmed *via* IR (see ESI†) and thermogravimetric analysis (TGA), whereby the native ligands **1** and **2** could be clearly distinguished showing degradation temperatures ($T_{\mathrm{d,onset}}$) of 322 °C and 246 °C, respectively. The grafting density of the ligands on the surface of MoS_2 NPs was calculated from the observed weight loss,[11] resulting in optimized values of up to 0.14 chain per nm^2 for **1**-modified NPs and 0.16 chain per nm^2 for **2**-modified NPs, depending on the reaction conditions (see ESI†). In the case of the "amphiphilic" modification (both ligands **1** and **2** in a 50 : 50 molar ratio) two separate decomposition steps could be observed in the TGA-curve (see Fig. 2), one at 256 °C (assigned to the decomposition of ligand **2**), and the second step at 325 °C indicative of the decomposition of ligand **1**, enabling the determination of grafting densities of 0.1 chains per nm^2 and 0.12 chains per nm^2, respectively.

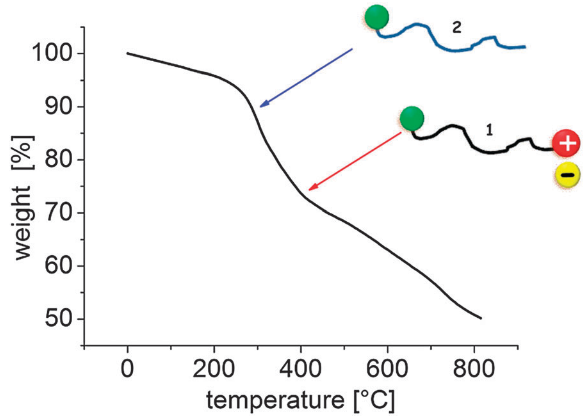

Fig. 2 TGA curve of the "amphiphilic" MoS_2 nanoparticles modified with a 50/50-molar mixture of the ligands **1**/**2**.

Additionally, the conducted IR-transmission measurements revealed the appearance of characteristic bands (for ligand (**1**)) at 1689–1692 cm^{-1} (C=O), 1249–1274 cm^{-1} (C–O) and 1083–1101 cm^{-1} (SO_2) confirming the successful modification of the surface of MoS_2 NPs. Subsequently, surface modification of the MoS_2 NPs was investigated *via* SAXS and WAXS measurements. According to the synthetic procedure described by Luo *et al.*, the prepared MoS_2 NPs have a form of hollow nanospheres.[10] As can be seen in Fig. 3 the SAXS/WAXS profile of bare MoS_2 NPs shows a broad scattering peak at 4.0 nm^{-1}, which can be explained by the scattering of the inner surfaces of the MoS_2 hollow nanospheres. Surface modification of MoS_2-NPs thus led to a shift of the scattering peak maxima towards lower *q* values (2.8 nm^{-1} for IL-modified NPs and 3.1 nm^{-1} for "amphiphilic" NPs, respectively) which can be explained by the formation of a soft-layer around the NPs (approx. 2 nm), indicative of the surface modification of the MoS_2 NPs. Additionally, a sharp scattering peak at 5.1 nm^{-1} was observed, which indicates the stacked layer structure of MoS_2 NP_2 with the distance between the layers of approx. 1.2 nm. This is in accordance with the diffraction peak (002) already reported for the stacked-layer MoS_2 structures and indicates that no intercalation has taken place.[10]

As expected, modified NPs exhibited different dispersibility behavior depending on the attached ligand: whereas **1**-modified NPs could be finely dispersed in water, methanol or toluene,

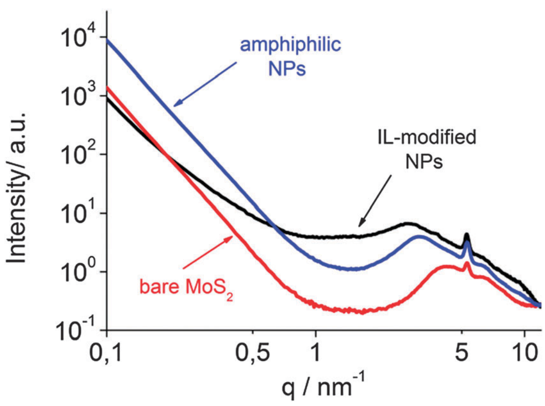

Fig. 3 SAXS/WAXS profiles of the MoS_2 nanoparticles.

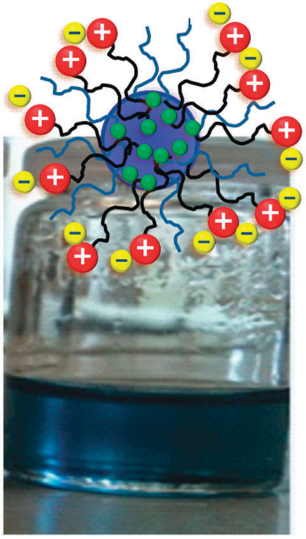

Fig. 4 Microemulsion with amphiphilic MoS_2 nanoparticles: stable decaline in IL microemulsion containing. 8 : 92 : 0.2 wt% of D : ([EMIM][$BuSO_4$]) : MoS_2 NPs (blue color due to the dispersed MoS_2 NPs).

2-modified NPs could be finely dispersed only in toluene. We decided to evaluate the obtained "amphiphilic" MoS_2 NPs as solid phase surfactants for stabilization of oil–ionic liquid microemulsions, similar to Bink-emulsions.[11] For this purpose we used decaline (D) as the apolar organic phase and the ionic liquid, 1-ethyl-3-methylimidazolium *n*-butylsulfate ([EMIM][$BuSO_4$]) as the polar phase. As can be seen in Fig. 4 0.2 wt% of the "amphiphilic" MoS_2-NPs led to stable decaline-in-ionic liquid microemulsions (ratio 7.8 : 92 : 0.2 wt% of D : ([EMIM][$BuSO_4$]) : MoS_2 NPs) with a stability of approx. 2–2.5 h (ESI†).

In summary, we have developed a novel ionic liquid bearing the 2-methylthio-benzoic acid chelating moiety which is capable of surface modification of MoS_2 nanoparticles. Using the IL–ligand (**1**) as a polar ligand and dodecyl 2-(methylthio) benzoate as an apolar ligand (**2**), a series of surface-modified (polar, hydrophobic and "amphiphilic") MoS_2 have been prepared. As an example, "amphiphilic" MoS_2 NPs were successfully evaluated as solid phase surfactants forming stable oil in ionic liquid microemulsions. We believe that the use of chelating ionic liquids for the surface modification of MoS_2 NPs can significantly influence their dispersivity, hence broadening their application in catalysis or as lubricating additives in the near future.

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