Comparative investigation of different silane surface functionalizations of fullerene-like WS₂

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Received: 13 February 2015 / Accepted: 17 April 2015 / Published online: 6 May 2015
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Abstract Inorganic fullerene-like tungsten disulfide (IF-WS₂) nanoparticles are useful additives for polymers and lubricating agents, in particular when their surfaces are functionalized by silane modifiers. However, both the success of such a silanization reaction and its effect on the final dispersion quality are still doubtful. In this work, IF-WS₂ are functionalized using three different silane modifiers and investigated with X-ray photoelectron spectrometry, infrared spectroscopy, titration, thermogravimetric analysis, and mass spectroscopy. Eventually, they are dispersed within ethanol by sonication to compare the dispersing behavior. The combination of the different analytical techniques revealed that the IF-WS₂ surfaces can be functionalized with two of the used silane modifiers, while the third one was repeatedly unsuccessful. The amount of Si on the particles seems to be a fairly clear indication for the success of the functionalization reaction. The IF-WS₂ seems to oxidize during the functionalization process, probably producing acidic SO₂ or SO₃, which can fully acidify a basic surface modifier. The executed treatment without any added silane modifier improved the dispersibility of the IF-WS₂ within ethanol to some extent, but added modifiers deteriorated it significantly. TEM images indicate that IF-WS₂ particles form aggregates, which might be the reason for the limited dispersibility.

Introduction

Inorganic fullerene-like tungsten disulfide (IF-WS₂) nanoparticles are a relatively new class of nanomaterials. They are best known for their outstanding lubricating effect [1, 2], but there are also promising reports on their use as a nanofiller for various polymers [3]. While most research in this field was done on thermoplastics, a few publications dealt with epoxy-IF-WS₂ nanocomposites and showed substantial improvements in adhesion fracture toughness and other mechanical properties [4, 5].

Despite the rather inert nature of IF-WS₂ nanoparticles, it was indicated that it is possible to graft silane surface modifiers onto them in order to improve their dispersibility within lubricating oils [2] and epoxy resins [5], respectively. The lubricating and toughening effects of silane-functionalized IF-WS₂ were superior to those of unfunctionalized IF-WS₂. While the exact course of this silanization reaction is not known, it was assumed that H₂O located at defect sites of the IF-WS₂ plays an important role. Besides the reported improvements, however, a few X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy measurements are the only indications that the silanization reaction did take place [2, 5].

In this work, we investigate the feasibility of a surface functionalization of IF-WS₂ with selected silane modifiers for later use as a nanofiller in epoxy nanocomposites. The aim of the functionalization was to improve the dispersibility of the IF-WS₂ as well as their bonding to an epoxy matrix. Special emphasis was given to detailed characterization of the obtained powders with various analytical methods.

Chlorosilanes are known to be much more reactive than alkoxysilanes, which is not only beneficial for the modification process, but also limits the available functional groups, as many would react with the chlorosilane

Electronic supplementary material The online version of this article (doi:10.1007/s10853-015-9039-4) contains supplementary material, which is available to authorized users.

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themselves. Alkoxysilanes, in contrast, are available with various functional end groups and are usually much more easy to handle which is an important requirement for a possible industrial application.

In this work, treated and untreated IF-WS₂ are dispersed within ethanol by sonication for different time periods. The aim was not to obtain optimum dispersion quality but rather to investigate the effect of the surface functionalization on it. Sonication was chosen as it is a rather well-defined process and as it is a frequently reported technique for dispersing IF-WS₂ in organic liquids [2, 3, 5–8]. A later publication will deal with the dispersion of these particles within epoxy and the resulting properties.

Experimental

Materials

The black IF-WS₂ powder with the trade name *Nanolub R* was received from *NanoMaterials Ltd.* (Israel); this source has been used in earlier research published by other groups [2, 4, 5, 9]. According to the manufacturer, it was produced by high-temperature solid–gas synthesis, the primary particles had diameters of 40–300 nm and they consisted of 10–100 WS₂ layers, with an interlayer spacing of 0.62 nm [10].

The silane surface modifiers are depicted in Fig. 1. The chosen chlorosilane was hexyltrichlorosilane (HTCS, 85 % purity); its rather short carbon chain is expected to interact well with a fairly polar epoxy resin. Moreover, it does not act as a plasticizer as strongly as long carbon chains do. The chosen alkoxysilane modifiers were 3-glycidypropyltrimethoxysilane (GTMS, 98 % purity) and 3-(2-aminoethylamino)propyltrimethoxysilane (AATMS, 80 % purity). Both are expected to improve the miscibility of nanoparticles with epoxy resin and their functional groups should react with either epoxy or the amine hardener, promising good bonding between the nanoparticles and the epoxy resin. All silane modifiers were obtained from *Sigma-Aldrich* (USA).

Fig. 1 Used silane surface modifiers

Processing

For the surface functionalization with the chlorosilane HTCS, chloroform (CHCl₃) was used as a solvent (stabilized with 1 % ethanol, 99 % purity), while for the functionalization with the alkoxysilanes GTMS and AATMS, ethanol (EtOH) was used (denaturated with 5 % isopropyl alcohol, 99.9 % purity). Approx. 100 ml of these solvents were added to 1.00 g IF-WS₂ and sonicated for 1 min with a 200 W ultrasonic wave generator (*Bandelin Sonoplus HD 2200*) oscillating a Ti₆Al₄V sonotrode (ø3 mm) at maximum intensity. Within a few seconds, the temperature rose to the boiling point of the respective solvent. In the case of the CHCl₃ suspension, all subsequent steps were done under exclusion of air as the highly reactive chlorosilane might otherwise react with air moisture.

The suspensions were further sonicated in an ultrasonic bath at the boiling temperature of the respective solvent while being stirred with a PTFE-mantled overhead stirrer. In separate flasks, 100 mg of the respective surface modifier were dissolved within the respective solvents; these solutions were then added dropwise to the suspensions with a syringe. After 60 min, the sonication was stopped and the suspensions were further stirred with magnetic stirrers. The EtOH suspensions were stirred overnight at 90 °C under reflux while the CHCl₃ suspensions were stirred closed at room temperature.

The day after, the particles were separated from the solvent by centrifuging at 2000g for 3 min per pass. The liquid phase was decanted and kept for further analysis. When all the solvent was removed, fresh solvent was added, the suspensions were mixed thoroughly, and then centrifuged again. This was done three times in order to properly remove the remaining unreacted modifier as well as soluble reaction products. When the liquid phase showed still a gray color tone after centrifuging, the centrifuging step was redone at higher speed and longer times, up to 4000g for 30 min. The remaining slurries were heated to 50 °C in vacuum for 1 h to remove the remaining solvent. The powder was then ground with a mortar and a pestle. Finally, the powders were tempered at 100 °C in vacuum for 1 h to make the residual unreacted silane groups react.

These processes were repeated both with three times the amount of surface modifier and without surface modifier. Table 1 gives an overview over all treated IF-WS₂ powders. All powders were stored in a desiccator over calcium chloride in vacuum (at approx. 5 mbar).

Suspensions of treated and untreated IF-WS₂ within EtOH were sonicated in order to determine which average agglomerate size can be obtained that way. For that purpose, 50 ml of EtOH were added to 18 mg IF-WS₂ in a round-bottom flask (particle volume fraction $\phi_p \approx 5 \times 10^{-5}$). The suspensions were sonicated the same way as mentioned above for up to 60 min.

Table 1 Overview over all treated IF-WS₂ powders

Denomination	Surface modifier		Solvent
	Type	Mass/mg	
Ref-EtOH			EtOH
Ref-CHCl ₃			CHCl ₃
GTMS-1	GTMS	100	EtOH
GTMS-3	GTMS	300	EtOH
AATMS-1	AATMS	100	EtOH
AATMS-3	AATMS	300	EtOH
HTCS-1	HTCS	100	CHCl ₃
HTCS 3	HTCS	300	CHCl ₃

Characterization

Transmission IR spectra were obtained from 4000 to 400 cm⁻¹ with 1.9 cm⁻¹ step size (64 scans, *Bruker Tensor 27*). Approx. 0.5 mg of IF-WS₂ powders were ground in a mortar together with 150 mg KBr (trade name *Spectralanal*, delivered by *Fluka*) and subsequently compressed at 0.75 GPa for 2 min.

All treated IF-WS₂ powders were investigated using an XPS spectrometer (*Physical Electronics Quantum 2000*) to gather additional information on the success of the silanization reaction. The machine uses monochromatic Al K α X-rays ($h\nu = 1486.7$ eV) and operates at a pressure of 3×10^{-7} Pa at room temperature. The electron take-off angle was 45° and the analyzer was operated in the constant pass energy mode at 58.7 eV. The beam diameter chosen was around 150 μ m, and spectra were recorded with a step size of 0.25 eV. The powders were pressed into an In foil and kept in vacuum at least 16 h before the measurement. Electron and Ar⁺ neutralizers were used to compensate for possible surface charging. The samples were measured in randomized order. The spectra were analyzed using the software *MultiPak 8.2B*. A Shirley background subtraction was done on every peak, before its area was calculated by numerical integration. As the W_{4f} peaks overlap with a W_{5p_{3/2}} peak, their areas were instead calculated by fitting those curves with a Gaussian–Lorentzian function, and only the area belonging to the W_{4f} peaks were used. The atomic fractions of the individual elements were calculated from these peak areas using the corrected relative sensitivity factors calculated by the software.

As one of the chosen silane surface modifiers, AATMS contains two basic amine groups, its content is measurable by acid–base titration. This was done on AATMS, on the AATMS-treated IF-WS₂ powders and on the EtOH rest

from the two AATMS modifications (called *AATMS-X-rest-EtOH*). For the titration, 100 mg of AATMS were dissolved in 25 ml of EtOH and another 25 ml of H₂O were added; 100 mg of the AATMS-treated IF-WS₂ powders were dispersed in 25 ml of H₂O; and 25 ml of the AATMS-X-rest-EtOH were mixed with 25 ml of H₂O. The titration was done with 10 mmol/l HCl or NaOH in H₂O using a calibrated pH probe. This H₂O had been freshly purified to Grade 1 (*Thermo Scientific Barnstead Nano-Pure*) [11]. The titration curves were evaluated using the *CurTiPot* software [12].

Thermogravimetric analysis (TGA) was performed in order to determine how effective the silanization had worked (*Perkin Elmer TGA 7*). Before the measurement, the powders were heated to 50 °C in vacuum for several hours in order to assure that they were dry. Roughly 6 mg of treated IF-WS₂ powders were heated with 20 °C/min under He flow (purity 4.6). At 600 °C, the gas was switched to O₂ (purity 2.5).

In order to get more information on the origin of the mass loss in the TGA, 100 mg of HTCS-3 and AATMS-3 were further investigated by TGA combined with mass spectrometry (TG/MS, *Netzsch STA 409 CD with QMS 403 C*) at 20 °C/min under He flow (purity 4.6).

Scanning electron microscopy (SEM) images were taken to determine the agglomerate sizes of treated and untreated powders after various sonication times. For this purpose, EtOH suspensions were applied dropwise to a Si wafer and dried at room temperature as it had been done earlier [2]. Images were gathered with a *FEI NovaNanoSEM 230* with a Schottky field emission electron source operating at 5 kV, imaging secondary electrons with a through-the-lens detector at 3×10^{-7} Pa pressure.

Dynamic light scattering (DLS) measurements were performed at 25.0 °C (*Malvern Zetasizer Nano Z*, laser wavelength 534 nm). While this technique is best suited for the measurement of the diameters of well-dispersed spherical primary particles with sizes of 1 to 1000 nm [13], it has also been successfully used for quantifying agglomerate sizes [14–18]. EtOH suspensions were diluted with additional EtOH 1:10 (resulting particle volume fraction $\phi_p \approx 5 \times 10^{-6}$). The viscosity of neat EtOH was used for the calculation of particle diameters. Presented values are the means of 15 individual measurements of 30 s each. As recommended by the respective ISO standard [19], the intensity-weighted average particle diameter $\bar{x}_{DLS}$ was used for evaluation.

For transmission electron microscopy (TEM), a drop of EtOH–IF-WS₂ suspension (sonicated for 60 min) was placed on a TEM grid and allowed to dry. The images were gathered in a Schottky field emission TEM (*JEOL 2200FS TEM/STEM*) operating at 200 kV.

Results and discussion

As mentioned above, there are two reports indicating that IF-WS₂ can be functionalized with chlorosilane or alkoxy silane surface modifiers [2, 5]. As the underlying chemical reaction is, however, not fully understood so far, particular emphasis was given to a critical characterization with different methods.

IR spectroscopy

According to literature reports, the presence of surface modifier on IF-WS₂ can be detected by transmission IR spectroscopy, where IR bands at 2962, 2922 and 2852 cm⁻¹ were attributed to –CH₃ and –CH₂– groups [2]. Indeed, all treated IF-WS₂ showed IR bands at exactly these positions, even Ref-EtOH, which has no surface modifier on it; moreover, these bands were also observed in fresh KBr (data given in the Online Resource). Thus, these IR signals originate most likely from small impurities in the KBr powder rather than from an organic modifier. There was no significant increase observed from the fresh KBr to any of the samples of treated IF-WS₂. This might be due to the high absorptivity of IF-WS₂: Possible IR signals from the functionalization might have been reduced to below the noise level.

XPS

XPS survey scans showed that the elements present on the surfaces of the treated IF-WS₂ powders were mostly those expected: W, S, C, O, Si, and N. Besides these, there was a small signal of In, which stems from the used foil, and a small signal of Se, which is in traces often present in transition metal dichalcogenides. No signal of residual Cl was detected around 200 eV, indicating that no unreacted HTCS was left.

The highly resolved XPS scans are given in Fig. 2. The W_{4f} peaks did not change for any sample, indicating that the surface functionalization did not alter the chemical state of the W. A WO_x signal might be seen as a shoulder around 36.0 eV as was stated earlier [2, 5], but it is too small to draw a clear conclusion from.

The shape of the S_{2p} peaks did not change, but a side peak formed at higher binding energy in some cases. Späth et al. have already reported such a side peak in untreated, but aged IF-WS₂ and attributed it to SO_x [9], and this interpretation is shared in the present work. As it was assumed that this side peak came from S_{2p} as well, its area was composed in the measurement of the S content.

Both O_{1s} and C_{1s} are compounded of at least two different peaks each, the ratio of which varies among the

samples. The binding energy of Si_{2p} of approx. 102.4 eV is in good agreement with that reported for siloxanes [20]. A broad, low-intensity peak appeared to be present for all samples overlapping with the Si_{2p} peak (see Fig. 2); as this peak was assumed to be a signal from the W, it was removed by background subtraction before calculation of the Si_{2p} peak area.

The measured atomic fractions of the individual elements are given in Table 2. Note that the absolute measurement uncertainty of atomic fractions determined by XPS is usually in the range of ±10 %, while the relative differences between the individual samples might be measured more accurately. The detection limit depends on the investigated signal and on the background and lies usually at atomic fractions below 1.0 %.

The S/W ratio was generally slightly lower than 2. This might be explained with the substitution of some S atoms by Se, or by the fact that some IF-WS₂ nanoparticles might be broken up and WO₃ from their core might have been measured. Given the limited accuracy of XPS with respect to quantification of composition, however, no further conclusions can be drawn from that. Even though the measurement order was random, the high correlation between similarly treated powders suggests that the S/W ratio is indeed affected by the used modifier and/or the used solvent.

The increase in C_{1s} content might be used as an indication for a successful functionalization as it has been done earlier [2, 5]. However, while the C content is very low in Ref-EtOH, it is much higher in Ref-CHCl₃; this shows that an increase in the C_{1s} peak alone does not necessarily provide proof of successful functionalization. Due to the high surface sensitivity of XPS, already small amounts of contaminants affect the measurement considerably, and C is known to be a ubiquitous contaminant. The shift in the C_{1s} peak of Ref-CHCl₃ is not significantly different from that of the functionalized powders neither.

The same is true for the O_{1s} peak: while it increases strongly and shifts after functionalization, an increase or shift alone is not sufficient to tell whether the functionalization was successful. The strong N_{1s} peak of the AATMS-functionalized powders agrees well with the assumed presence of amines and thus indicates that those powders have been functionalized successfully. However, Ref-CHCl₃ and some powders functionalized with N-free modifiers showed clear N_{1s} peaks as well, which is again presumably due to contaminants.

In contrast, the Si_{2p} peak is clearly measurable for some samples and not detectable for others. It hence seems that this peak provides clear evidence on whether the functionalization process was successful. It can therefore be concluded that both functionalization reactions with GTMS

Fig. 2 XPS spectra of all treated IF-WS₂ powders with the presumed assignment

Table 2 Atomic fractions of the investigated elements as calculated from the curves in Fig. 2 and ratios thereof

	W at. %	S at. %	C at. %	O at. %	Si at. %	N at. %	S/W %	SO _x /S %
Ref-EtOH	31.4	55.2	3.0	10.4	*	*	1.76	*
Ref-CHCl ₃	19.1	37.4	17.4	21.2	*	4.4	1.96	8.9
GTMS-1	30.8	54.5	4.7	9.3	*	*	1.77	*
GTMS-3	25.2	44.1	21.9	8.4	*	*	1.75	*
AATMS-1	15.8	30.8	22.6	23.4	3.4	4.0	1.94	7.1
AATMS-3	11.3	21.5	31.7	26.1	4.2	5.2	1.90	11.1
HTCS-1	12.3	22.9	38.3	20.7	4.3	1.5	1.86	6.2
HTCS 3	13.3	24.7	31.1	23.0	5.6	2.3	1.85	6.5

* Signal below the detection limit

were unsuccessful, while those with AATMS and those with HTCS were all successful. It is unclear why the functionalization with AATMS should be successful when that with GTMS is not as the type of reaction is the same, but the increase in the C_{1s}, O_{1s} and N_{1s} peaks support this interpretation. Moreover, it is not clear whether the silane modifiers attach to the IF-WS₂ by chemical bonds or just by physisorption.

The presence of the SO_x peak correlates strongly with the O content, indicating that it is indeed due to oxidized S. While Späth et al. showed that IF-WS₂ oxidize upon exposure to ambient air for long time periods (3 years) [9], we can see here that the performed treatment can cause

oxidation as well; the SO_x peak of Ref-CHCl₃ shows that the presence of silanes was not necessary for an oxidation reaction. Rather, the reason for this oxidation might lie in the short sonication at the beginning of the treatment. The high local temperatures during the sonication of up to 5000 K [21] might lead to the degradation of the IF-WS₂ or the used solvents and the resulting formation of oxidative degradation products. Späth et al. assumed that the oxidized S might be present in the form of SO₄²⁻. In order to test that, small amounts of treated IF-WS₂ powders and of EtOH rests left from the treatment were mixed with H₂O and BaCl₂. As no precipitate formed in any of these cases, the presence of SO₄²⁻ seems unlikely.

Due to the contaminations with C, O, and N, only limited conclusions can be drawn from the atomic ratios of these. Analyzing the amount of shifting of the C_{1s} and the O_{1s} peaks did not yield conclusive facts neither.

Titration

The well-reproducible titration curve of AATMS shows two pH steps as it is typical for diprotic bases. However, significantly more than double the amount of HCl had to be added until the second pH step than until the first one, namely 2.4 times that much (see Fig. 3). This indicates that some portion of the AATMS molecules, namely 34 %, had been monoprotonated already before their delivery, making one of their amine groups an ammonium group. This is not

unexpected, given the limited purity of the AATMS and the fact that amines are easily protonated.

The amine group content in AATMS can be quantified by subtracting the amount of HCl necessary until the first pH step (where half of the molecules are protonated once) from that necessary until the second pH step (where half of the molecules are protonated twice). More precise results were obtained with the titration curve fitting software. The measured acid dissociation constants K_a calculated by curve fitting were $10^{-6.57}$ and $10^{-9.77}$ and therefore similar to $10^{-6.86}$ and $10^{-9.92}$ which are stated for ethylenediamine [22]. The amine group content was as high as 9.5 mmol/g and hence higher than the theoretically expected value of 9.0 mmol/g. It seems, therefore, that some diamine was present in the form of the AATMS's precursor, that is to say, without a trimethoxysilane group. Once again, this is not unexpected given AATMS's limited purity. All subsequent calculations were done assuming an amine group content of 9.5 mmol/g.

A comparable titration was done on AATMS-3-rest-EtOH. The titration curve was again well reproducible, and once again showed two pH steps at the same pH values, indicating that there was still AATMS left in the EtOH after centrifugation. This time, the results indicate that 92 % of the AATMS molecules have been protonated already once, which is significantly more than before the treatment. Thus, acidic groups have been added or created during the treatment. Considering the XPS results, this is most likely due to the SO_x surface groups that were sometimes produced during the treatment. It is worth noting that untreated IF- WS_2 leads to acidic pH when dispersed within H_2O which may stem for the H_2S -rich atmosphere usually used for their synthesis [23, 24],

Fig. 3 Measured and calculated titration curves of AATMS and AATMS-3-rest-EtOH

possibly resulting in SO_x surface groups as well. Considering the titration curves, 0.63 mmol acid groups were present before or created during the AATMS-3 functionalization process. The titration indicates that 1.1 mmol AATMS was left in the used EtOH, which corresponds to 74 % of the amount added initially. Assuming that the residual 26 % of the AATMS molecules adhered to the IF- WS_2 particles, one can estimate the maximum organic mass fraction of AATMS-3 to 7.2 %.

In the case of AATMS-1-rest-EtOH, the pH is acidic right from the beginning; the titration was therefore done with 10 mmol/l NaOH instead. The well-reproducible curve shape is similar to those reported above, as there are once again two pH steps at the same pH values (data given in the Online Resource). This indicates that AATMS modifier was present in AATMS-1-rest-EtOH, but more acid groups had been present before or created during the treatment than base groups had been added in the form of AATMS, namely 0.93 mmol. Hence, AATMS-1 is functionalized with diammonium molecules rather than with diamines. The amount of diammonium measured in the sample corresponds to 47 % of the nominally added AATMS. Assuming that the other 53 % adhered on the IF- WS_2 particles, one can estimate the maximum organic mass fraction of AATMS-1 to 5.8 %.

Comparable titrations were done on the modified powders AATMS-1 and AATMS-3 as well (data given in the Online Resource). AATMS-3 results in a basic pH value when dispersed within H_2O while AATMS-1 results in an acidic pH value, which is in good agreement with the results of the respective EtOH rests. However, the obtained titration curves were not as well defined as those and the measured diamine contents far exceeded the expected amounts. This is most likely due to the participation of the IF- WS_2 in the acid–base reaction during the titration, e.g., with their oxidized S groups, thereby wrongly indicating very high modifier contents. Quantitative titration results must therefore be interpreted cautiously.

TGA

In inert atmosphere, IF- WS_2 are stable to above 1000 °C [10], while organic molecules decompose between 200 and 600 °C; it was therefore expected that the organic content of the treated powders could be measured by TGA. Figure 4 shows the mass of all treated IF- WS_2 powders over temperature. The largest mass loss occurs at 600 °C, when the flow gas is switched to O_2 ; here, the W of the outermost WS_2 layers oxidizes to WO_3 and the S oxidizes, e.g., to SO_2 , and vaporizes. The yellow color of the residual powder after the measurement indicates WO_3 as well.

Even though the powders had been stored in a vacuum exsiccator and dried in a vacuum oven just before the

measurement, all treated powders, whether functionalized or not, lost 0.8–1.5 % of their mass below 220 °C. This is most likely due to firmly bound H₂O molecules that are either hard to remove or that are taken up quickly after drying. The presence of H₂O on IF-WS₂ has been reported earlier and was explained with H₂O molecules in the voids in the center of the IF-WS₂ as well as in defects in the IF-WS₂ structure [25].

Generally, powders that were treated similarly show similar mass loss behavior, showing that the mass loss is affected by the silane treatment. However, Ref-CHCl₃ shows significant mass loss as well, even though it contains no surface modifier. This shows that the TGA mass loss alone is not sufficient as a measure for the organic content of IF-WS₂. In contrast, these results once again indicate that the used solvent affects the powders, as the TGA curve of Ref-CHCl₃ is very similar that of the HTCS-modified powders, which have been treated within CHCl₃ as well.

The AATMS-modified powders are the only ones whose mass loss behavior is significantly different from that of all other powders, including the reference curves. The significant mass loss around 290 °C indicates the decomposition of the supposed ammonium in the AATMS molecule, which might work similar to a Hofmann elimination. Thermal loss of ammonium modifiers has been reported earlier to take place at roughly that temperature [26]. This again indicates that the functionalization with AATMS was successful.

Interestingly, the TGA mass loss correlates strongly with the C, O, N, and SO_x contents measured by XPS (see Table 2). This is in good agreement with the assumption that the TGA mass loss is mainly due to removal of CO₂, H₂O, SO_x and ammonium compounds. Note that the TGA curves of the HTCS-modified powders are entirely different if the tempering step is omitted as unreacted

chlorosilanes might then react during the measurement, releasing HCl (details given in the Online Resource).

TG/MS

The composition of the gas produced during a TGA measurement was analyzed via TG/MS measurements on AATMS-3 and HTCS-3 in order to obtain additional information on the origin of the mass loss; the analyzed ratios of ion mass m to ion charge q were chosen in a way to analyze possible traces of CO₂, H₂O, HCl and ammonium compounds in the gas.

The results support the assumption that the mass loss is mainly due to H₂O and CO₂, and in the case of AATMS-3 possibly also due to succession of ammonium compounds (detailed results and discussion given in the Online Resource). No traces of HCl were detected, indicating that no unreacted chlorosilanes were left after tempering at 100 °C. The detected CO₂ indicates that organic species were present on both samples and hence that these powders had been functionalized successfully. The detection of ammonium compounds further supports this assumption for AATMS-3.

Sonication of untreated IF-WS₂ powders

During sonication, agglomerates are split into two or more differently large parts until a final agglomerate size is reached. As agglomerates can also reform during sonication, it is possible that not all agglomerates will be split even after infinitely long sonication times, hence the final average number of primary particles per agglomerate n_{end} might be more than unity. It is assumed here that the reduction of the average number of particles per agglomerate n over time t is proportional to the difference between n and n_{end} :

$$\tau \cdot \frac{dn}{dt} = -[n(t) - n_{\text{end}}] \quad (1)$$

with the proportionality factor τ being called *time constant*. Integrating gives:

$$n(t) = n_{\text{end}} + (n_0 - n_{\text{end}}) \cdot e^{-\frac{t}{\tau}} \quad (2)$$

with $n_0 = n(t = 0)$. Due to $n_0 \gg n_{\text{end}}$ this can be rewritten to:

$$n(t) = n_{\text{end}} + n_0 \cdot e^{-\frac{t}{\tau}}. \quad (3)$$

The time t_α until a certain ratio α of the final dispersion quality is reached can be calculated:

$$1 - \alpha = \frac{n(t_\alpha) - n_{\text{end}}}{n_0 - n_{\text{end}}} \approx \frac{n(t_\alpha) - n_{\text{end}}}{n_0} = e^{-\frac{t_\alpha}{\tau}} \quad (4)$$

Fig. 4 TGA curves of all treated powders

$$t_\alpha = -\tau \cdot \ln(1 - \alpha). \quad (5)$$

The n in Eq. (3) can be substituted by the average agglomerate volume V or the average agglomerate diameter d due to $n \propto V \propto d^3$:

$$d^3(t) = d_{\text{end}}^3 + d_0^3 \cdot e^{-\frac{t}{\tau}} \quad (6)$$

In order to measure agglomerate sizes after sonication, SEM imaging was used in a first attempt as it was done in an earlier work [2]. Some differences are visible between SEM images of samples sonicated for very short and very long time periods, respectively (e.g., for 10 s and 60 min; see Fig. 5, additional images in the Online Resource): while individual primary particles can be seen in most samples, agglomerates of micrometer dimensions are visible more often in samples that had been sonicated for shorter time periods, which shows that sonication is generally able to break agglomerates. However, nanoparticles tend to reaggregate upon drying due to their van-der-Waals interaction, which is the stronger the smaller the particles are. The IF-WS₂ agglomerates had hence quite likely been significantly smaller within the EtOH suspension before it dried. Moreover, SEM images are very difficult to quantify sensibly. In contrast, DLS is done directly on suspensions and is statistically much more useful, which is why it was considered a superior tool for measuring agglomerate size distributions.

The IF-WS₂ suspension became dark black within a few seconds of sonication, indicating successful dispersion. Nevertheless, large agglomerates were visible as well, even after 60 min of sonication. Hence, it seems that the sonication resulted in a polydisperse, bimodal agglomerate size distribution. DLS is very sensitive to polydispersity; already few large agglomerates will result in a measurement outlier. Such outliers appeared very frequently, even though most large agglomerates sedimented quickly and thus did not affect the DLS measurement. Unfortunately, the automatic outlier detection by the DLS software did not work reliably enough, which is why some outliers had to be excluded manually. Figure 6 shows the measured $\bar{x}_{\text{DLS}}$ after two different sonication set-ups (different probe diameter, with and without stirring). The empty points indicate excluded data. The remaining data were fitted to Eq. (6) and the fit is given in Fig. 6 with its 95 % confidence interval.

Each sample was measured twice with the DLS, and the results normally agreed well. This shows that the repeatability of the DLS was reasonable, but that some of the samples contained large agglomerates that caused problems. Interestingly, the results appeared to be better when a probe of smaller diameter was used and when the liquid was not stirred. However, this is probably just because the large agglomerates were mostly sedimented on the bottom

Fig. 5 SEM images of dried Ref-EtOH after sonication for 10 s (top) and 60 min (bottom), respectively, showing IF-WS₂ agglomerates

of the beaker and hence fewer of them were collected for measurement. These results are thus probably not representative for the real agglomerate size distribution.

Figure 6 shows that Eq. (6) fits the *selected* data points quite well and seems to be more appropriate than models suggested elsewhere [14]. The fit parameters are listed in

Fig. 6 $\bar{x}_{\text{DLS}}$ over sonication time of IF-WS₂ within EtOH as measured by DLS with two different sonication set-ups. The data were fitted using Eq. (6); the bands represent the 95 % confidence interval

Table 3 Fit parameters of the curves in Fig. 6, giving the final average diameter of particles after sonication d_{end} , their initial diameter d_0 and the time constant τ as modeled with Eq. (6)

Probe ϕ	d_{end}/nm	d_0/nm	τ/min
13 mm	239 ± 21	1020 ± 67	1.29 ± 0.22
2 mm	247 ± 11	626 ± 16	1.75 ± 0.18

Fig. 7 TEM image of IF-WS₂ nanoparticles after 60 min of sonication in EtOH. The framed area is magnified in the *bottom left corner* with enhanced contrast

Table 3: Independently of the set-up, τ was below 2 min. Inserting these values into Eq. (5) gives $t_{0.99} < 10$ min, meaning that 99 % of the final dispersion quality will be obtained within 10 min for both investigated sonication set-ups. The d_{end} agrees very well for both sonication set-ups, but in both cases it is still much larger than the diameter of the primary particles. Thus, it seems that agglomerates remain even after long sonication times.

The agglomerate sizes visible in TEM images agree reasonably well with the SEM and DLS results: while individual primary particles do exist, there are also agglomerates of different sizes even after 60 min of sonication. It seems as if some of the particles were broken up; however, it cannot be stated if these particles had broken up during sonication or if they were broken up already before. Likewise, it is unclear to what extent the nanoparticles had reagglomerated upon drying on the TEM grid, analogous to the possible reagglomeration on the Si wafers as observed via SEM.

Two of the primary IF-WS₂ particles in Fig. 7 share some WS₂ layers with each other. Hence, the adhesion

between them is not just due to van-der-Waals forces but they are conjoined by covalent bonds. Such conjoined nanoparticles could be observed several times. Thus, it seems as if some agglomerates are rather aggregates, or agglomerates of aggregates. The fact that the final agglomerate diameter is significantly larger than that of the primary particles supports the assumption that a significant fraction of the IF-WS₂ is present in the form of aggregates.

Sonication of treated IF-WS₂ powders

The treated powders were sonicated within EtOH the same way as the untreated ones (examples given in Fig. 8). Once again, some measurement results had to be excluded arbitrarily, but the data generally obey Eq. (6). The fitting parameters are given in Table 4.

The reference powders and the nominally GTMS-functionalized powders show strongly reduced d_{end} , d_0 , and with one exception, τ . Thus, the treatment improved the initial dispersion quality as well as the dispersibility of the powders, even though there was no modifier added to the reference powders and the GTMS functionalization was probably unsuccessful. The improvements are most likely due to the short sonication and the grinding with mortar and pestle during the treatment.

In contrast, the successfully functionalized powders had an increased d_0 and with one exception an increased d_{end} when compared to the untreated powders; moreover, the scatter was strongly increased. Hence, the silane functionalization deteriorated the dispersibility of IF-WS₂ rather than to improve it, even though the treatment itself was shown to improve the dispersion quality significantly. It seems, therefore, that the silane modifiers caused the IF-WS₂ agglomerates to stick together.

Fig. 8 $\bar{x}_{\text{DLS}}$ over sonication time of two treated IF-WS₂ within EtOH as measured by DLS. The data were fitted using Eq. (6); the bands represent the 95 % confidence interval

Table 4 Fit parameters of the DLS measurement results of all treated IF-WS₂ dispersed within EtOH, fitted by Eq. (6)

	d_{end}/nm	d_0/nm	τ/min
Ref-EtOH	210 ± 4	306 ± 12	0.73 ± 13
Ref-CHCl ₃	228 ± 11	384 ± 27	0.70 ± 24
GTMS-1	211 ± 4	282 ± 8	0.99 ± 15
GTMS-3	222 ± 3	345 ± 7	1.85 ± 22
AATMS-1	422 ± 34	1226 ± 145	1.76 ± 23
AATMS-3	620 ± 52	1714 ± 204	1.41 ± 14
HTCS-1	223 ± 64	1350 ± 75	2.43 ± 45
HTCS-3	309 ± 36	1844 ± 440	0.11 ± 04

These results indicate that surface functionalization of IF-WS₂ with organic molecules is possible, but does not necessarily improve its dispersibility in fairly polar solvents like EtOH. The forces holding the individual IF-WS₂ particles together are very small to begin with and are hence not reduced by silane surface modifiers. Possible positive effects of the surface functionalization on the long-term dispersion stability [2] might not be related to improved dispersion quality. Likewise, the enhanced properties of IF-WS₂-epoxy nanocomposites [5] might be caused by other factors.

Conclusion and outlook

This work deals with three types of silane surface functionalization of IF-WS₂ their characterization and their dispersion within EtOH. Various measurements indicate that the modifications with HTCS and AATMS were successful while that with GTMS was not. The most direct evidence for successful modification was the presence of the Si_{2p} peak in the XPS curves, while the increase in the C, O, or N contents were considered inconclusive.

The performed treatment, both with and without silane modifiers added, resulted in the formation of SO_x groups, most likely SO₂ or SO₃. These decrease the pH of the suspension and can hence partially or fully protonate the surface modifier. As long as this effect is taken into account, acid–base titration of the residual solvent left from the treatment can be used to determine indirectly the presence and to some extent the quantity of basic or acidic surface modifier on the nanoparticles.

Strongly bound H₂O was still present on the IF-WS₂ powders after drying them at 50 °C in vacuum for several hours. Together with the evaporation of SO_x, this complicates the determination of organic contents with TGA. Only the amine-functionalized IF-WS₂ could be clearly discriminated from the references.

The powders were dispersed within EtOH by sonication down to agglomerate diameters of approx. 200 nm, which is still larger than the nominal average primary particle size (around 100 nm). The development of agglomerate sizes over sonication time could be measured by DLS reasonably well, although several outliers had to be excluded, likely caused by bimodal polydispersity. Equation (6) approximated the evolution of the measured agglomerate size over sonication time reasonably well. After 10 min, further sonication does not seem to reduce the agglomerate sizes any further. TEM images show that some of the primary particles were conjoined with each other, forming aggregates; this might explain why the agglomerate size could not be reduced any further.

The performed treatment *can* hence help to limit the initial agglomerate size and to accelerate the size reduction upon sonication, but barely reduces the final agglomerate size. Moreover, the successfully functionalized powders showed significantly inferior dispersibility in EtOH to the unfunctionalized references. This shows that the chemical interaction between the IF-WS₂ and the dispersion solvent is not the factor limiting the dispersion quality.

In an upcoming work, these IF-WS₂ powders will be used to manufacture epoxy nanocomposites with special focus on the resulting fracture toughness. Special emphasis will be given to the obtained dispersion quality and the bonding between the IF-WS₂ particles and the epoxy matrix.

Acknowledgements The authors would like to thank Anja Huch, Beatrice Fischer, Jörg Patscheider, Lassi Karvonen and Matthias Nagel for their experimental and theoretical support.

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