Rheology and Stability of Functionalized Particle Loaded Inkjet Inks

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Abstract

In this study, we investigate the rheological properties as well as the stability and the electrical properties of inkjet inks based on silane-functionalized TiO_2-particles. At first, we describe the preparation of the surface modified TiO_2-particles, the formulation of the inks and the measurement procedures. The results of the measurements are presented and mechanisms, which could explain the observed characteristics, are discussed. Based on these findings, we discuss the limits of application of the surface modified nanoparticle inks for functional inkjet printing. Furthermore, we show the successful application of a surface modified nanoparticle ink for inkjet printing of photo electrodes for photo assisted water splitting.

Introduction

In the course of the last 15 years, inkjet printing has proven to be an efficient production process for a variety of functional structures. Examples are electronic components, PLED/OLED devices, RFID transponders, sensors, semiconductor solar cells and applications in biotechnology [1-3]. The surface of the particle can be modified by connecting functional groups to the surface. Thus, the properties of functional structures can be tuned. Today, surface modification of nanoparticles via chemical processes is commonly used for a variety of applications [4-6]. Also, reports about the successful application of inks based on surface modified nanoparticles for inkjet printing can be found in literature [7, 8].

In a former publication, we have shown that a surface modification of TiO_2-nanoparticles with functional Si-groups is beneficial for the performance of photo electrodes due to an enhanced transport of the generated charge carriers to the conductive substrate [9]. Moreover, we have shown that the successful manufacturing of photo electrodes in inkjet printing is possible on the basis of pristine particles as well as on the basis of surface modified particles [10, 11].

In doing so, we have noticed that the flow characteristics of an ink based on surface modified particles differ considerably from the characteristics of an ink based on pristine particles. Furthermore, we suspected that the inks will exhibit different characteristics concerning the inter-particulate attraction due to the surface modification. Both factors can strongly impact on the print-ability and the stability of the ink against sedimentation and aggregation. [12, 13].

Therefore, in this study, we investigate the rheology and the stability of inkjet inks based on surface modified nanoparticles. The viscoelastic properties of the inks are examined directly via rheological viscosity measurements. Conclusions about inter-particulate interactions are drawn by stability measurements and rheological oscillation measurements. By these means, we can show the influence of the surface modification of the nanoparticles on the behavior of the ink and thus on its applicability.

Besides, we show the successful application of an ink based on surface modified nanoparticles. To this end, photo electrodes for the photo assisted water splitting are inkjet printed and the photo catalytical performance of the electrodes is determined.

Experimental

Ink Preparation

TiO_2-nanoparticles P25 (25% Rutile, 75% Anatase) having a mean diameter of 21 nm are purchased from Sigma Aldrich Co. LLC., US. The particles are functionalized chemically with (3-Chloropropyl)triethoxysilane at a reaction temperature of 60 °C. The presence of functional groups on the surface of the particle is confirmed by infrared spectroscopy and thermogravimetric analysis. Further details concerning the preparation and characterization of the functionalized particles can be found elsewhere [11]. **Figure 1** shows a scheme of the chemical structure of a surface modified TiO_2-nanoparticle.

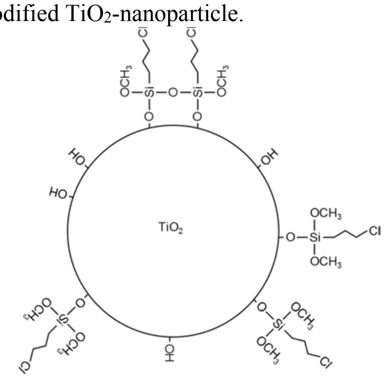

__Figure 1__. Chemical structure of a surface modified TiO_2- nanoparticle

For the preparation of the inkjet inks the functionalized particles or the pristine TiO_2-particles are dispersed in a pure solvent or a binary solvent mixture. The solvents 1,5-Pentandiol (PEN, $C_5H_{12}O_2$) and Dimethylacetamid (DMAc, C_4H_9NO) are purchased at Merck KG, Germany and Sigma Aldrich Co. LLC., US respectively. The dispersion time is 5 minutes using an ultrasonic device.

Rheological Measurements

Rotatory viscosity measurements as well as rheological oscillation measurements are carried out with a cone and plate rheometer MCR 301 from Anton Paar GmbH, Austria. The dynamic viscosity is measured in dependence of the shear rate in the range between 0.1 and 10,000 1/s. The loss modulus and the storage modulus are determined at a frequency of 1 Hz in the strain amplitude range between 0.01 and 100 %.

These measurements are carried out for suspensions based on a binary solvent mixture of 50 wt.-% PEN and 50 wt.-% DMAc. The solids content is 15 wt.-% for the suspension based on functionalized TiO_2-particles and 15, 22.5 and 30 wt.-% for the suspension based on pristine TiO_2-particles.

Stability Measurements

The long term stability against sedimentation and the electrical properties of the particle inks are measured via an impedance-based sedimentation analysis. Here, a test setup consisting of a conductivity cell LTA 1 by WTW Wissenschaftlich-Technische Werkstätten GmbH, Germany and a LCR-meter 2826 by Sourcetronic GmbH, Germany is applied. A detailed description of the measuring principle can be found in [14].

Inks based on the solvent DMAc and solids content of 1 wt.-% are measured for both functionalized TiO_2-particles and pristine TiO_2-particles.

First, a steady-state measurement of the AC ohmic resistance against the solids content is performed at a frequency of 1 kHz. After that, the ohmic resistance of the ink is measured time-dependent at a frequency of 1 kHz. To eliminate the effects of possible interactions between the current and the functionalized semiconductor particles, single measurements in certain time intervals are performed. The intervals of the single measurements are 1, 2, 3, 4, 5, 6, 24, 48 and 120 h after the first measurement. The measuring electrodes are mounted at a height of 75 % of the total sample height. After 120 h the sample is inspected and the resistance is also measured as a function of the position of the measuring electrodes.

Inkjet Printing and Characterization

Photo electrodes for the photo assisted water splitting are inkjet printed. A dispenser head MD-K-140 from Microdrop Technologies GmbH, Germany in combination with a self-engineered traversing unit is applied. A detailed description of the system can be found in [15].

The printed ink is based on a binary solvent mixture of 50 wt.-% PEN and 50 wt.-% DMAc. The solids content of the surface modified TiO_2-particles is 5 wt.-%.

The photo electrodes are printed on a 30 × 30 mm soda-lime glass substrate coated with a conductive FTO-layer. The substrates are purchased from Solaronix SA, Switzerland. The area of the printed circular photo electrodes is 2.54 cm².

The layer thickness is determined with a laserscanning microscope VK X-200 from Keyence Corp., Japan. The photocatalytical performance of the electrodes is determined with a test setup consisting of a solar simulator, a photo electrochemical test cell and a potentiostat, a detailed description can be found in [11].

Results and Discussion

Rheology

In **figure 2** the results of the shear rate dependent viscosity measurements are shown. While the viscosity of suspensions based on pure particles moderately declines with an increasing shear rate, the suspension based on surface modified particles shows a strong shear thinning effect and a significantly elevated viscosity. Increasing the solids content of the pristine particles also induces a more shear thinning behavior as well as a general rise of the viscosity, but compared to the surface modified particles the effect here is an order of magnitude smaller.

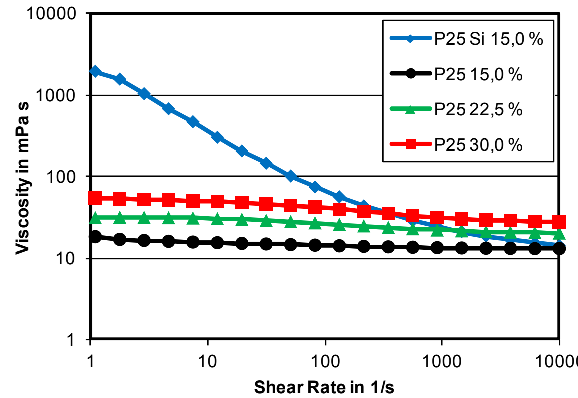

***Figure 2**. Dynamic viscosity of suspensions on the basis of surface modified particles (P25 Si) or pure particles (P25) with different solids contents in PEN/DMAc; temperature 20 °C.*

In **figure 3** oscillatory rheological measurements of the suspensions are shown. Loss modulus and elastic modulus are plotted against the amplitude of strain.

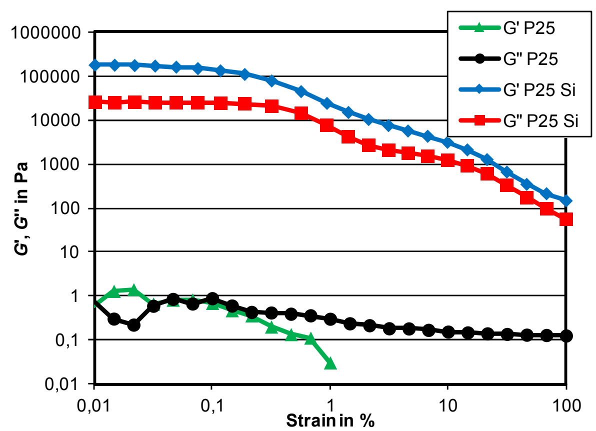

***Figure 3**. Storage modulus and loss modulus of the suspension based on surface modified particles (P25 Si) or pure particles (P25) in PEN/DMAc; solids content 15.0 wt.-%; temperature 20 °C.*

For the ink based on surface modified particles a viscous as well as an elastic part are observed, whereat the latter is clearly predominating. Both moduli decline monotonously with rising strain amplitude. For the ink based on pure TiO_2-particles the elastic part is close to zero for strain amplitudes greater than 1 %. For strain amplitudes smaller than 1 % both G' and G'' are in the same order of magnitude.

Several mechanisms come into consideration for explaining the observed characteristics. A change of the effective mean particle diameter can cause a change of the run of the shear rate dependent viscosity [16, 17]. However, the influence of this phenomenon is typically significantly smaller than the rise of the viscosity measured here for the surface modified particles. Thus, an impact of the particle diameter cannot be excluded but is most probably not the main reason for the observed characteristics.

A stabilization of suspensions by steric repulsion is possible by adding certain polymers in a proper concentration encasing the particles [18, 19]. This effect induces a decreased viscosity at low shear rates, a less pronounced shear thinning behavior and a lower elastic modulus [20]. Obviously none of these characteristics occur in the case of the surface modified particles examined here.

Furthermore, at low shear rates, the functional groups at the particle surface can cause a higher resistance against movement due to the chain structure. In the rheology of polymer melts, strong shear thinning is observed for entangled as well as for non-entangled polymer chains, whereat the viscosity tends to increase with the chain length [21, 22]. A further lead is the disproportionately strong increase of the storage modulus *G'* due to the surface modification. This also indicates an increased inter-particulate interaction.

Stability

In **figure 4** the resistance of the ink based on pristine TiO_2-particles is plotted against solids content for the steady-state case. During the measurement, a stable, homogeneous state can be assumed.

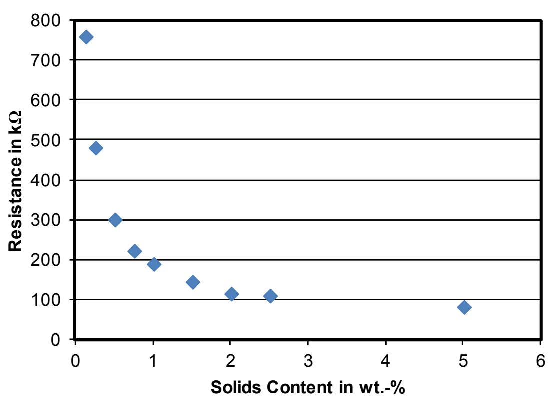

Figure 4. Resistance against solids content of suspensions based on pure TiO_2-particles and DMAc.

The resistance decreases with increasing solids content nearly following an 1/x law. This corresponds to a nearly linear increase of the conductivity with the solids content which was also the result of a former study [14].

Figure 5 shows the time dependent measurement of the inks based on pure particles or surface modified particles. The measured resistance of the suspension based on functionalized particles is of the same order of magnitude as the resistance of the suspension based on pure particles. However, larger values are measured for the modified particles in almost the entire time range.

For both suspensions the resistance decreases with time nearly following an 1/x law. This observation seemingly contradicts the fact, that after 24 h a subsidence of the particles as well as a brightening of the suspension at the location of the measurement electrode becomes clearly visible. Hence, the solids content at the position of the measuring electrode decreases with time due to sedimentation of the particles. According to figure 4, a rise of the resistance would therefore be expected.

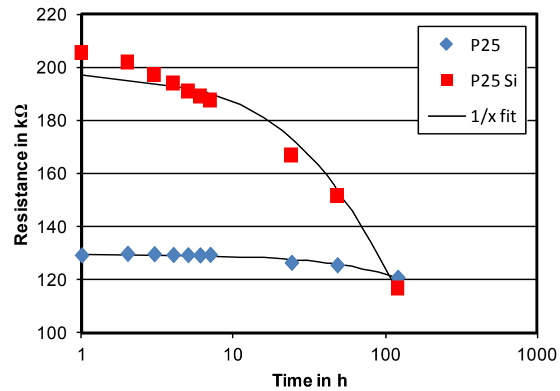

Figure 5. Time dependent measurement of resistance for inks based on DMAc and pure particles or surface modified particles.

Attempting to resolve these contradicting observations, we have calculated the corresponding conductivities from the measured resistances shown in figure 5 and then computed the first time derivative for the discrete time steps. These results are shown in **figure 6**.

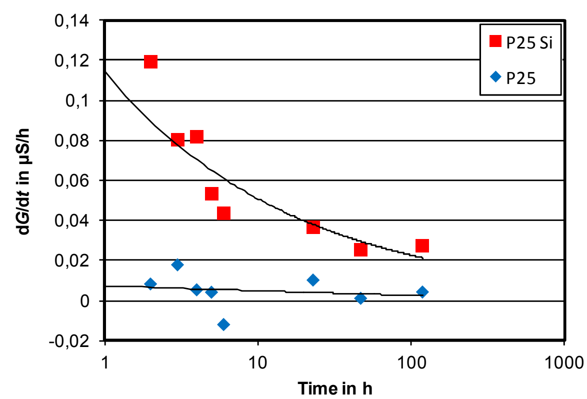

Figure 6. Time derivative of conductivity of suspensions based on surface modified particles (P25 Si) or pure particles (P25)

In both cases, the time derivative tends to decrease with time, thus the observed growth of the conductivity decreases with time. This effect is stronger for the suspension of surface modified particles; here the final value is about 20 % of the initial value, whereas we find a decrease of about 50 % for the pure particle suspension.

After 120 h the suspensions are inspected. Both have a dim, almost transparent supernatant, a thin layer with increased solids content due to capillary forces at the reservoir wall at the top of the sample as well as distinct sediment at the bottom of the sample. **Figure 7** shows the steady state resistance measurement after 120 h for both inks in dependence of the sample height. For both suspensions, the resistances increase at the top and at the bottom of the sample, where increased solids concentrations are observed optically. In between, the values are nearly constant.

structures. The connection of functional groups to the surface of the particle can strongly impact on the flow characteristics and the

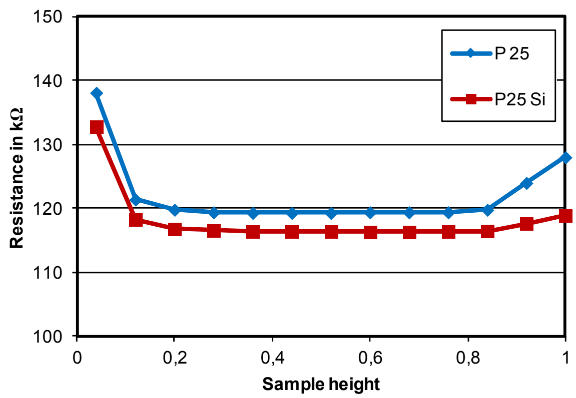

Figure 7. Steady state resistance measurement after 120 h, variation of the position of the measuring electrode.

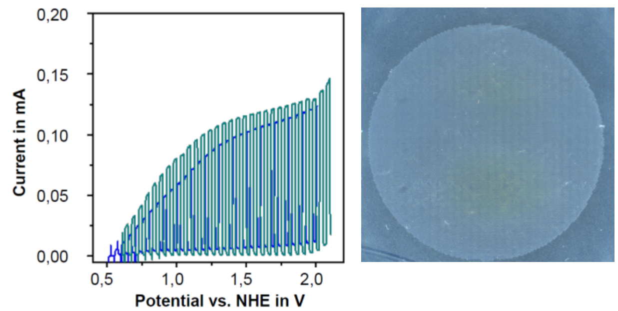

***Figure 8**. Digital-microscopic photograph und voltammetric diagram of inkjet printed photo electrodes based on surface modified TiO_2-nanoparticle; diameter of the electrode is 18 mm.*

The observed results can be explained as follows. It has to be taken into account, that after sufficient time has passed, the solids content is not any more the decisive impact on the measured resistances. Instead, the conductivity of the solvent itself determines the electrical properties of the suspension. As a probable reason for this, we suppose a possibly light driven chemical-catalytically reaction between the N- and OH- groups of the solvent and the TiO_2-particles, causing the formation of ions which merge in the solvent and increase its conductivity. Supportingly, numerous examples for reactions of nitrogen and hydrogen compounds with TiO_2 at room temperature can be found in literature [23-25].

A further lead can be read from figure 6. The decreasing growth in conductivity indicates, in our opinion, a process or a reaction that depends on the concentration of particles or a functional group of the solvent at the corresponding location. With decreasing material concentration due to sedimentation the output of the reaction decreases and so the conductivity grows in a smaller rate.

In this way, also the observations shown in figure 7 can be explained. Considering that the electrical behavior of the suspensions after 120 h is mainly determined by the ions in the solvent, it seems consequent that the measured resistance increases at the locations with greater solids content.

Inkjet Printing

Figure 8 shows an inkjet printed photo electrode and the corresponding voltammetric diagram of electrodes that were printed with surface modified TiO_2-nanoparticles. The measured area-related current in an order of magnitude about 0.1 mA/cm² corresponds to values that are achieved with other coating processes. For the spin coating we measured for the same particles at counter potential of 1 V a current of 0.1 mA/cm² [9, 11]. The high agreement of the two graphs indicates a good reproducibility of the procedure. We determine a mean layer thickness of 100 nm.

Conclusions

Surface modified nanoparticles can be applied in functional inkjet printing for tuning the characteristics of functional structures. The connection of functional groups to the surface of the particle can strongly impact on the flow characteristics and the stability of the corresponding inkjet inks. We show this effect using surface modified TiO_2-nanoparticles and discuss mechanisms as possible explanations.

By means of rheological measurements we show, that the inter-particulate interaction is altered by surface modification. We suspect that a greater resistance against movements between the particles is caused by the chain molecules at the particle surface.

By means of impedance-based measurements we show, that the conductivity of a suspension based on TiO_2-particles and DMAc increases nearly linear with the solids content for the steady-state case. The time dependent results indicate that a chemical-catalytically reaction occurs which influences the measured resistance. Thus, a dependence of the measured resistance on the solids content does not exist for the non-steady case.

On the basis of the results, no conclusion regarding the time dependent sedimentation characteristics can be drawn, though it is shown by means of optical inspection and a steady state measurement that after 120 h a nearly complete sedimentation has developed.

The method of impedance-based analysis is hardly suitable for the determination of solids contents of catalytically active suspensions, though in future it might be used as an indicator for the presence of a corresponding reaction in inkjet inks.

We show the successful application of an inkjet ink based on surface modified TiO_2-particles by printing photo electrodes for the photo activated water splitting. The printed electrodes have activities in the same order of magnitude as electrodes assembled in a spin-coating process.

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