Flame Deposition of Superhydrophobic and Superhydrophilic Nanoparticle Coating on Paperboard Materials

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ABSTRACT

In this paper, we have synthesised superhydrophobic and superhydrophilic nanoparticle coatings on paper board materials. The Liquid Flame Spray method was used in nanoparticle synthesis. The nanoparticles were continuously deposited directly from the flame onto the paper board in a pilot scale paper converting machine. The speeds for the substrate used in the experiments were up to 150 m/min. The TiO_2 coatings have superhydrophobic properties and the SiO_2 coatings have superhydrophilic properties. The reason for the different behaviour with water was studied using water contact angle measurements, scanning electron microscopy and transmission electron microscopy. The amount of material to produce the properties is significantly low, around tens of mg/m^2

Keywords: Nanoparticles, Functional coatings, Flame synthesis, Liquid Flame Spray, Titanium dioxide

1 INTRODUCTION

Flame methods in nanoparticle production can be easily scaled-up [1]. Previously, Liquid Flame Spray (LFS) has been used in many nanoparticle applications. The nanoparticles can be deposited directly on a surface to create functionality [2]. The parameters in the LFS process can be tuned in order to control the particle size [3].

Paper and paper board materials are widely used in packaging industry. The complete utilization of the good properties of paper like biodegradability, renewability, flexibility and affordability, demands the control of the surface properties. There are various techniques available to control the properties. Fluorinating or silane coating of the paper or board are conventionally used in superhydrophobisation of the surface [4]. Also, plasma techniques are used [5]. The manufacturing and converting processes use high volumes, are continuous and operate at high speeds. It sets limitations to the techniques that are used in the surface functionalisation.

We have recently developed a method of coating paper and paper board with nanoparticles using the LFS process [6]. The Liquid Flame Spray coated paper board can have superhydrophobic or superhydrophilic properties depending on the coating material. Titanium dioxide is used in synthesis of superhydrophobic coatings and silicon dioxide coatings in superhydrophilic coatings. The amount of the coating is only in the order of tens of milligrams per square meter, which is several orders of magnitude lower than with conventional coatings.

Here, we focus on the difference in coating materials. Silicon dioxide and titanium dioxide are both hydrophilic by nature [7]. This would indicate similar wetting properties but it is not the case. The formation of the coating seems to be the key reason for different behaviour of the two coating materials [8].

2 EXPERIMENTAL

In the Liquid Flame Spray process, precursor solution for the nanoparticles is atomized into a high-temperature H_2/O_2 flame. The material is evaporated and after decomposition the material condenses to form nanoparticles. The nanoparticles are then deposited on the surface or collected from the aerosol phase. Here, we deposited the nanoparticles directly from the flame onto the surface. Titanium dioxide nanoparticles are synthesised from titanium (IV)isopropoxide (TTIP) dissolved in isopropanol and silicon dioxide from silicon (IV)ethoxide (TEOS) dissolved in isopropanol. The concentration for both liquids are 50 mg(atomic metal)/ml and the feed rate into the flame 32 ml/min. The substrate speed through the LFS flame for deposition was between 50 and 150 m/min for various samples. The deposition process is already described in the references [6] and [8].

The deposited coatings are studied with water contact angle measurement device (CAW), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Detailed structural analysis is also presented elsewhere [9]. The amount of material was analysed with Inductively coupled plasma – mass spectrometry (ICP-MS).

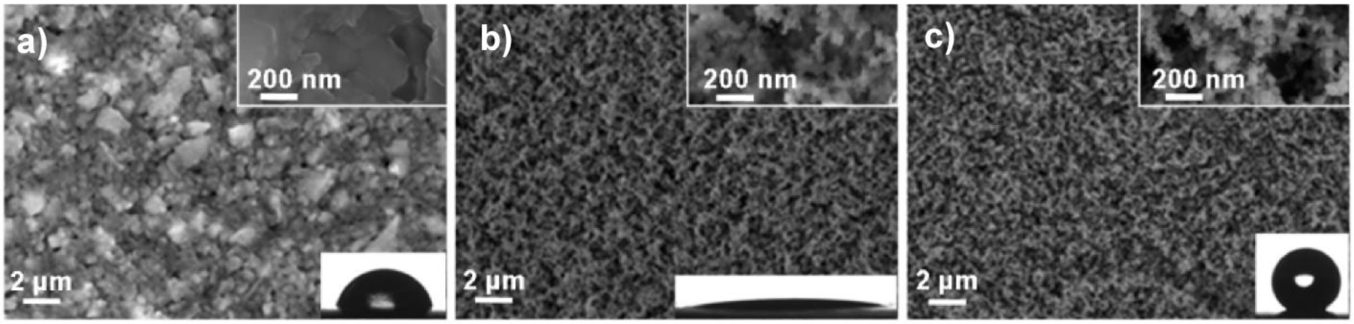

Figure 1. SEM images of the a) reference sureface b) silicon dioxide coated surface and c) titanium dioxide coated surface

3 RESULTS

The water contact angle for the different coatings (TiO_2 and SiO_2) were measured using a WCA measurement device. The WCA for a reference sample of paper board is 77 °. For SiO_2 coated paper board the WCA value is 12 ° and for TiO_2 coated paper board 161 °. There are some structural differences between the nanoparticle coated paper boards and the reference board as can be seen in figure 1. However, both of the coated samples look similar. There are also higher magnifications as inserts in the figure. The nanocoating produces a nanostructure on top of the microstructure which is in the substrate or here in the uncoated reference sample.

TEM images from the particle deposits differ from each other. The TEM grid was attached directly onto the surface, where the particles were deposited so that there was no need to prepare the sample otherwise. The TEM image for TiO_2 deposit shows that there is a tiny layer of light material on top of the particle deposit. As the material is quite light and there are excess peaks in the energy dispersive spectrometer spectrum than, it is believed to be carbonaceous. A TEM image of the TiO_2 particles is shown in figure 2. A TEM image of the SiO_2 deposits is shown in figure 3. The shape of the particles is very musch different when compared to figure 2. The particles do not have round shapes, which are typical for particles that are not single crystals and are formed in gas phase. There is no shell-like structure as there was for the TiO_2 particle deposits.

The deposits were analysed in ICP-MS in order to find out the amount of material needed to produce the superhydrophobic and superhydrophilic properties. The mass was between 35 and 75 mg/m^2 for various substrate velocities.

4 DISCUSSION

Even though both silicon dioxide and titanium dioxide are supposed to be hydrophilic materials, the coatings act differently. Mainly the titanium dioxide nanoparticle coating produced with the LFS method has superhydrophobic properties. The superhydrophobicity cannot be alone because of the lotus-like structure as the silicon dioxide coating looks similar, but is superhydrophilic.

The layer on top of titanium dioxide is believed to be carbonaceous. Carbon is highly hydrophobic. The layer is most likely formed because of a slight combustion of the substrate material. The combustion cannot be visually observed, but the simulations [10] show that the temperature would be optimal for combustion. The velocity of the substrate is quite high and the substrate cools down rapidly. Thus, the conditions for the combustion are developed. As there are fumes from combustion, the carbonaceous layer is a product of the fumes deposited on the particle layer as the substrate cools down.

TEM images reveal the difference between the silicon dioxide and titanium dioxide coatings as shown in figure 2 and 3. SiO_2 deposit looks very different from the TiO_2 particles. The particles do not look like they were born in aerosol phase, because of the shape. Usually, particles born from gas phase are round. Coagulation and sintering produce also round shapes, even though the sintering would not be complete. Thus, the shape strongly suggests that the particles are formed directly from the precursor liquid. TEOS is not as volatile material as TTIP is, which gives a possibility of liquid deposition on the surface. The precursor liquid will then decompose thermally or hydrolyze into silicon dioxide. The liquid deposition would prevent the combustion fumes to come out of the paper. Therefore, there is now carbonaceous layer on top of the silica particles. Also, the liquid deposition will decrease the temperature of the substrate slightly.

The amount of material is relatively low compared to the conventional coatings that produce similar effects. Also another difference to conventional coatings is that conventional coatings need to be activated in order to get e.g. hydrophilic properties. The activation is usually done by corona or other methods and is based on electrical phenomena. As the wetting behaviour of the LFS coatings are based on chemistry, a similar decay of wetting properties, such as has been observed for conventional coatings, is not observed for our LFS-coating..

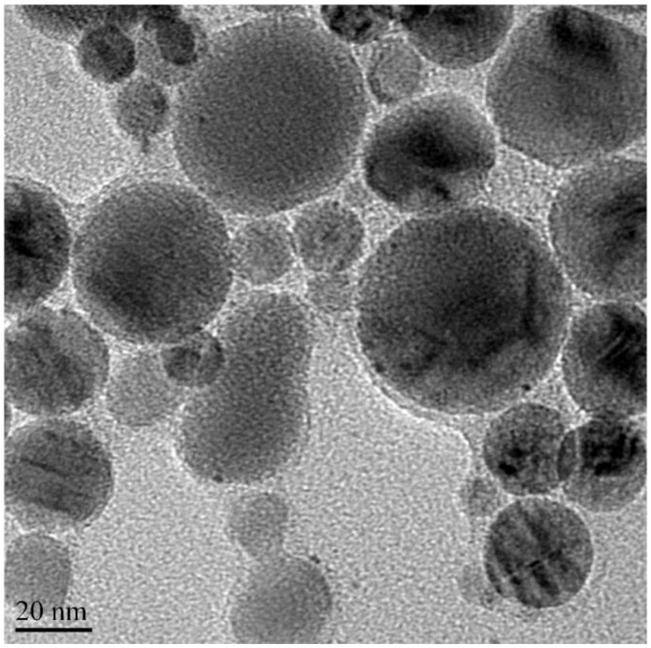

Figure 2. TEM image of the titanium dioxide particles as deposited on the paperboard substrate.

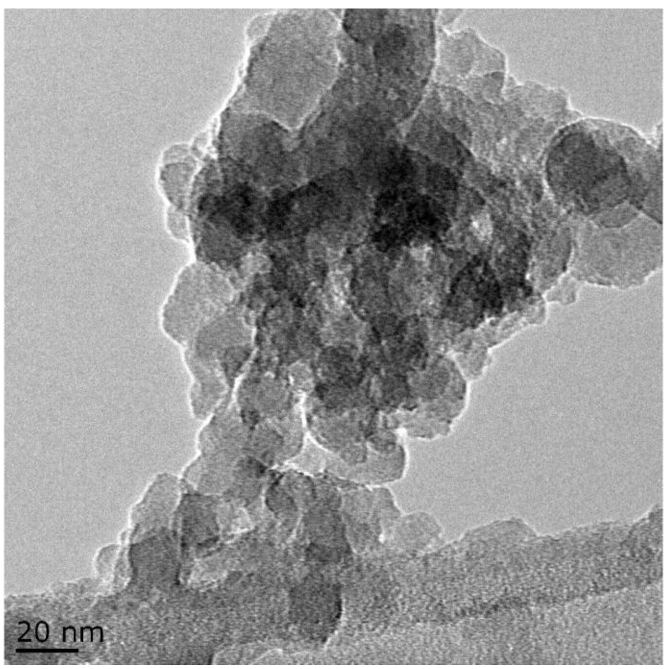

Figure 3. TEM image of the silicon dioxide particles as depositer on the paperboard substrate

5 CONCLUSIONS

The deposits of silicon dioxide and titanium dioxide show different wetting behaviour. The microscopy analysis reveal the major difference in the particle coatings. Silicon dioxide coating is formed as a result of liquid deposition and consecutive thermal decomposition or hydrolysis. Titanium dioxide particles have a carbonaceous layer on top, which promotes the hydrophobic behaviour.

The amount of material is relatively low for the LFS deposited nanoparticle coating. It is several orders of magnitude lower compared to conventional coating materials. Thus the LFS deposited nanocoatings show huge potential in replacing the conventional coatings. The properties are already demonstrated to work in a pilot scale. The flame methods are easily up-scalable into industrial scale.

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