



# Antifogging and anti-frosting coatings by Dip-layer-by-layer self-assembly of just triple-layer oppositely charged nanoparticles



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## ABSTRACT

Transparent stable antifogging (AF) and anti-frosting (AFR) coatings were fabricated via layer-by-layer dip coating self-assembly (Dip-LbL self-assembly) of just triple-layer oppositely charged nanoparticles (NPs) followed by calcination. The nanoparticles we prepared naturally carried a certain electrical charge. The positively charged NPs (ZrO<sub>2</sub> or TiO<sub>2</sub>) and the negatively charged SiO<sub>2</sub> NPs were bound firmly together via electrostatic interaction. Morphologies and structures were observed by transmission and scanning electron microscopy. Transparency was examined using an optical clarity test and a UV-Vis transmittance test. AF/Superhydrophilic and AFR properties were studied using a water contact angle test, a constant temperature (100 °C) AF test, an AFR test and an aspirating test. Mechanical stabilities were investigated using a water-bath shaking test, an ultrasonic test and a pencil hardness test. The results showed that the TiO<sub>2</sub>/SiO<sub>2</sub>/ZrO<sub>2</sub>, ZrO<sub>2</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> and SiO<sub>2</sub>/ZrO<sub>2</sub>/SiO<sub>2</sub> coatings with the 3D micro- and nanometer-scale hierarchical structure on the surface had excellent AF and AFR properties, and presented high mechanical stability and durability. The high availability of the materials and the simplicity of this method for the coating preparation might make the low-cost, non-toxic and eco-friendly AF and AFR coatings potentially useful in optical and display devices.

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## 1. Introduction

Fogging is a common phenomenon which occurs when saturated water vapor condenses in the form of discrete tiny droplets which are capable of scattering light randomly on a surface with a temperature lower than the dew point of the vapor [1]. Frosting, however, is a thin layer of ice that forms on a surface of substrate when the air becomes cold [2,3]. Fogging and frosting can severely reduce visibility and may present a dangerous condition on vehicle windshields or on goggle lenses or any type of glass requiring good visibility at all times. Transparent stable antifogging (AF) and anti-frosting (AFR) coatings can be effectively used to provide resistance to fogging and frosting. They can eliminate ghost images on optical surfaces and maintain the optical clarity in daily life. For this reason, they are useful for maintaining optical clarity in optical lenses and devices such as eyeglasses, gas masks, mirrors and laparoscope lenses [4–9]. Many research studies have been carried out on the topic [1,10–12], and the strategies for AF coatings preparation fall mainly into two categories: (1) Superhydrophilicity/Ultra-hydrophilicity, meaning that coatings/films are wet by water

completely and instantaneously (water droplet contact angle < 5° within 0.5 s or less). (2) Superhydrophobicity/Ultra-hydrophobicity, meaning that coatings/films completely resist wetting by water (<6-μL droplet; water droplet contact angle > 150° and very low sliding angle < 5°). Various methods; layer-by-layer (LbL) self-assembly, spray-coating, dip-coating and chemical modification etc., are often adopted in building Superhydrophilicity [13–16] and superhydrophobicity [10, 17–19], as well as the preparation for anti-frosting [9,11,20].

LbL self-assembly technique of oppositely charged particles was first reported by Iler in 1966 [21], it was subsequently further developed with significant improvement by Decher [22] and Zhang and Shen [23] in the late 1990s. Previous studies have shown that it is a simple, effective and inexpensive way to fabricate various kinds of coatings [4,9, 14]. Up to now, the main driving force for LbL self-assembly has been to employ electrostatic interactions, hydrogen bonding, van der Waals forces, hydrophobic interactions, molecular recognition, host-guest interactions, electron donor-acceptor interactions, coordination interactions and charge-transfer interactions [24–31]. Multiple substrates were selected as building blocks. These have included polyelectrolytes, nanoparticles (NPs), organic polymers, dendrimers, colloid particles, clay minerals, carbon materials, dyes, DNA, peptides, viruses, enzymes, proteins, chitosans and combinations thereof [32–41]. In this study, we used nanoparticles as building blocks. Nanomaterials are of great importance due to their widespread applications in almost all fields of

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industry.  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  are drawing more and more attention thanks to their stable, non-toxic and eco-friendly properties. The fact that they are inexpensive and abundant in the nature makes them a good choice. They are currently used in practically all fields of science and engineering.

In this work, we attempt to demonstrate that transparent stable AF and AFR coatings can be easily and quickly created via Dip-LbL self-assembly of NPs such as  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{ZrO}_2$ . The layers are bound firmly together via electrostatic interaction of oppositely charged NPs. In addition to a rough surface with high porosity, calcinations at high temperature can promote the formation of stable siloxane bridges, which endows the AF and AFR coatings with high mechanical stability and excellent adhesion to the substrates. This guarantees long-term stability in daily life. As investigated in previous studies, such a transparent film with just triple-layer oppositely charged NPs, which exhibits excellent stable superhydrophilic/AF and AFR properties has not yet been reported.

## 2. Experimental section

### 2.1. Materials

Tetraethyl orthosilicate (TEOS, 98+%), aqueous ammonia ( $\text{NH}_3$ , 28%), concentrated sulfuric acid (95–98 wt%), hydrogen peroxide (30%), titanium tetrachloride ( $\text{TiCl}_4$ , 98%), zirconyl oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , 99%), and anhydrous ethanol (99.80%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. Ultrapure water with a resistivity higher than  $18.2 \text{ M}\Omega \cdot \text{cm}$  was used in all experiments, and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

### 2.2. Preparation of monodisperse silica NPs

Monodisperse silica NPs of ca. 42 nm were prepared as follows [42]. 50 mL anhydrous ethanol (99.80%) and 1.5 mL aqueous ammonia (28%)

were mixed with stirring in a round-bottomed flask at room temperature in a water bath, then 1 mL of TEOS was added dropwise to the solution under stirring at 1500 rpm for 10 min. Afterward, the temperature was increased to  $30^\circ\text{C}$  and kept at this temperature under magnetic stirring at 500 rpm for 48 h. Finally the ethanol suspension of silica NPs of ca. 42 nm in size was obtained. The as-prepared nano-silica was diluted with ethanol and ultra-sonicated before use. The concentration of silica ( $\text{SiO}_2$ ) was 1.5 mg/mL, and the silica NPs had a  $\zeta$ -potential of  $-30.7 \text{ mV}$  and 42.3 nm in size [polydispersity index (PDI) = 0.050] measured by Malvern Zetasizer Nano-ZS.

### 2.3. Synthesis of $\text{ZrO}_2$ NPs

$\text{ZrO}_2$  NPs were prepared using a modified hydrothermal method as described in previous reports [43,44]. 45 mL  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (0.1 M) and 30 mL anhydrous ethanol were mixed in a beaker by magnetic stirring for 10 min at room temperature. The solution was then transferred into a Teflon-lined stainless-steel autoclave (100-mL capacity) and heated at  $198^\circ\text{C}$  for 15 h. After the autoclave was cooled down to room temperature naturally, the product was purified by centrifugation and re-dispersed in ethanol via an ultra-sonication assisted process. The  $\text{ZrO}_2$  was diluted in ethanol to a final concentration of 1.5 mg/mL. Afterward, the zeta potential was measured using a Zetasizer Nano ZS, and it had a  $\zeta$ -potential of  $+57.5 \text{ mV}$ .

### 2.4. Synthesis of $\text{TiO}_2$ NPs

$\text{TiO}_2$  NPs were prepared as follows [45]: 4 mL  $\text{TiCl}_4$  were added into a Teflon-lined stainless steel autoclave (200-mL capacity) loaded with 156 mL ice water (ca.  $0^\circ\text{C}$ ) under nitrogen at room temperature. It was then sealed and maintained at  $160^\circ\text{C}$  for 8 h. After the autoclave was cooled down to room temperature naturally, the product was purified by centrifugation and re-dispersed in ethanol via ultra-sonication several times to remove impurities. Finally, the  $\text{TiO}_2$  was diluted in

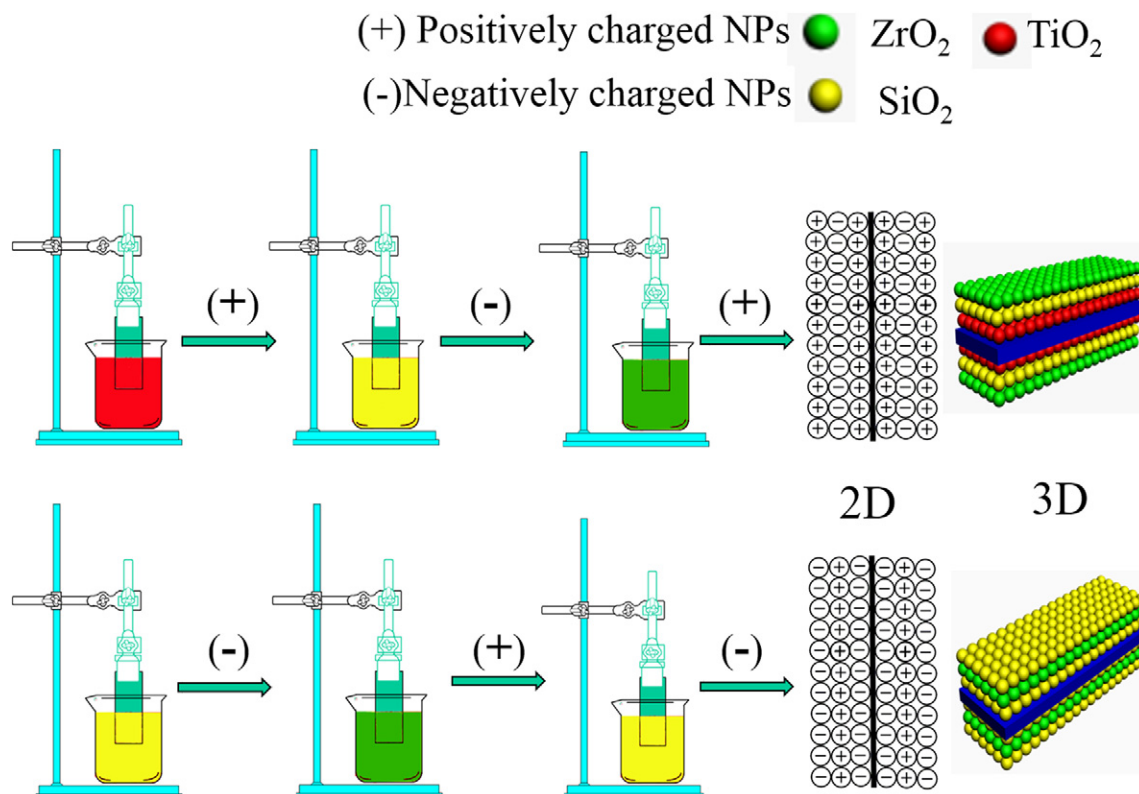


Fig. 1. Schematic of Dip-LbL self-assembly process to create transparent antifogging and anti-frosting films on a substrate.

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