Journal of Colloid and Interface Science 394 (2013) 26–35

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Electrostatically driven adsorption of silica nanoparticles on functionalized surfaces

Xue Li, Olivia Niitsoo, Alexander Couzis [*]

Department of Chemical Engineering, The City College of New York, NY 10031, United States

ARTICLE INFO

Article history:
Received 11 June 2012
Accepted 19 November 2012
Available online 13 December 2012

Keywords:
Electrostatic adsorption
Silica
Nanoparticles
Coatings
Solid–liquid interface
Amino-functionalized substrate

ABSTRACT

Adsorption of nanoparticles on solid supports is a scientifically interesting and technologically important phenomenon that has been attracting ever-increasing attention. Formation of particle-based films onto surfaces from stable suspensions is at the center of the development of new devices that utilize the plethora of newly synthesized nanoparticles with exciting properties. In this study we exploit the attractive electrostatic interactions between silica (SiO_2) nanoparticles and functionalized substrates that display an amine termination in order to devise a simple method for the fabrication of SiO_2 nanoparticle films. Electrostatically controlled adsorption allows for uniform coverage of nanoparticles over large areas. The Stöber method (a sol–gel approach) was employed to prepare uniformly sized SiO_2 nanoparticles with a diameter of 50–80 nm. Native oxide-covered silicon wafer substrates were amino-functionalized utilizing the self-assembled monolayer of 3-aminopropyltrimethoxysilane (APS). The adsorption of SiO_2 nanoparticle film onto the silicon wafer substrate was controlled by modulation of the electrostatic interaction between nanoparticles and the substrate. Modification of surface charge of either the SiO_2 NP or the substrate is a crucial step in the process. Thus the effect of APS adsorption time on the surface energy of the substrate was investigated. Also, process parameters such as NP concentration and solvent composition were varied in order to investigate the extent of NP adsorption. Moreover, NaCl was introduced to the SiO_2 suspension as a charge-screening agent to reduce the inter-particle repulsion in the suspension as well as interaction of the particles with the surface. This resulted in denser/thicker films.

Published by Elsevier Inc.

1. Introduction

The continuing expansion of synthetic methods for nanoparticles has brought to the forefront the need to form structures using these nanoparticles as building blocks. Many material properties related to nanoscale that once were only accessible through expensive semiconductor type processing are now accessible because of the nanoparticles. However, as complex structures are required to exploit these properties and build devices, assembly of these materials becomes crucial. Technological applications of such approaches include catalysis [1,2], sensors [3], photonics [4], antireflection [5], antifogging [6], self-cleaning [7,8] and so on. For applications in electronic and optical devices, most often films (coatings) of well-ordered closely packed nanoparticles over large areas are needed. A number of methods have been developed to achieve that. In this manuscript we briefly discuss the methods where nanoparticles are prepared prior to film deposition (“bottom-up” approach), leaving aside the approaches where the NP are formed in situ during the deposition process (some sol–gel techniques, spray pyrolysis, (electro) chemical deposition and physical vapor deposition methods with bulk precursor).

Spin-coating is well established in the electronics industry for depositing thin films of polymers for lithography [9]. It has also been used for depositing nanoparticle films [10]. Ogi et al. [11] have coated films of submicron-sized SiO_2 particles from aqueous suspensions on sapphire substrate with high surface coverage. While spin-coating enables good control of film thickness by adjusting the spin rate, the morphology and uniformity of the film is highly sensitive to ambient conditions and the solvent used to disperse the nanoparticles in. Controlled atmosphere (clean-room) fabrication conditions are likely to upset the costs – especially when NP-based materials are pursued as a more economical alternative to their bulk counterpart.

Dip-coating is relatively simple and easily automated [12]. It can be adjusted for coating almost any substrate size [13]. Widely used for 3D-assembly of photonic crystals, and referred to as vertical evaporation, is a process related to dip-coating. In vertical evaporation [14], instead of withdrawing the substrate from the NP suspension at controlled velocity, the substrate (placed vertically or at a fixed angle in the deposition vessel) is stationary and the solvent is allowed to evaporate, leaving behind a NP film. Just as dip-coating, also vertical evaporation can be performed repeatedly to increase film thickness.

In electrophoretic deposition (EPD) charged particles are attracted onto a conducting substrate by applying electric field to

---

[*] Corresponding author. Fax: +1 212 650 6660.
E-mail address: couzis@ccny.cuny.edu (A. Couzis).

0021-9797/$ - see front matter Published by Elsevier Inc.
http://dx.doi.org/10.1016/j.jcis.2012.11.042

the suspension [15,16]. EPD cannot be used for depositing NP films on insulating substrates (with the exception of porous membranes when placed in front of the electrode). Magnetic field has also been used for NP film deposition, but this approach is limited to magnetic NP [17].

Spray deposition has been successfully applied for many commercial coatings for decades [18]. However, it is difficult to obtain uniform thin (<2 μm) continuous films by spraying. Screen-printing and doctor blading are both simple and cheap, but do not offer very precise control on film thickness [19].

Langmuir–Blodgett (LB) technique entails self-assembly of NP at the gas–liquid interface, followed by compression by mechanical barriers and transfer of the NP film onto a solid substrate. The method is best suited for NP monolayer preparation, and can be applied on large surfaces [20]. Similarly to LB, NP can also be assembled at liquid–liquid interface and transferred to a solid substrate. Different methods can be combined to obtain the desired NP film, e.g. by Tsai et al. [21] who successfully coupled LB and electrostatic assembly by introducing a low dielectric constant solvent (ethanol) as a driving force for Au NPs to assemble from a suspension onto a monolayer of octadecylamine at air–water interface.

Unfortunately, these approaches are not always useful for practical applications and all have some drawbacks such as the requirement for specific equipment; not applicable to large area substrate; limited to a small set of surfaces (e.g. conducting or flat substrates); the morphology and uniformity of the film is highly sensitive to environmental conditions. Compared to these traditional strategies, the electrostatic adsorption technique offers an easy and inexpensive process for layer formation and allows a variety of materials to be incorporated within the film structures. Therefore, the assembly process based on adsorption can be considered as a versatile bottom-up assembly technique.

Adsorption (either by physisorption or chemisorption) of nanoparticles onto a substrate is the simplest method of fabricating self-organized 2D and 3D networks or arrays. One of the most prominent advantages of the electrostatic adsorption is its simplicity [22]. Electrostatic adsorption is mainly directed by electrostatic interactions between the particles and the substrate [23–25]. In the adsorption process, the substrate is immersed into nanoparticle dispersion for a time optimized for adsorption. It is then withdrawn, rinsed, and dried. Nanoparticles can be adsorbed and arrayed to the substrate to form ordered two-dimensional networks or three-dimensional arrays. For some applications a monolayer of NP is desired, and often the lengthy adsorption time is not of concern. For multilayer coatings repeated adsorption steps are usually implemented. This approach is referred to as the layer-by-layer (LbL) self-assembly technique [26–30]. Polyelectrolytes are often introduced into LbL self-assembly method in order to obtain opposite charged substrates and particles. Ahn [31] and co-workers made use of the electrostatic attraction and formed random close-packed polystyrene latex particle monolayers, which find uses as anti-reflection coatings. Qiu et al. [32] studied systematically the key parameters for controlling the quality of the self-assembled ceramic particle film. Tettey et al. [33] successfully showed that LbL assembly of oppositely charged particles could be performed in a nonpolar solvent, toluene, as a general film fabrication technique. Not only electrostatic attraction but also secondary bonding interactions, e.g. hydrogen bonding, are often employed in the LbL assembly [34]. Li et al. [35] successfully prepared asymmetrically functionalized Janus particles as well as hollow microcapsules by coating the particles with cross-linked hydrogen-bonded multilayers followed by polymer-on-polymer stamping.

In the absence of polyelectrolytes, LbL assembly can still be performed simply by taking advantage of the chemical nature of particles and substrates under certain process conditions. Lee et al. [7] reported ‘‘all-nanoparticle thin-film coatings’’ composed of only negatively charged SiO_2 and positively charge TiO_2 NP. Otherwise, when particles and substrates have the same surface charge, surface charge modification is necessary. Usually there are two different approaches to surface charge modification. The first one involves the self-assembly of a bifunctional monolayer onto a substrate (formation of a self-assembled monolayer, SAM) and then subsequent attachment of nanoparticles to the monolayers [36,37]. The other approach involves the surface charge modification of nanoparticles themselves by bifunctional molecules [38–42]. 3-aminopropyltrimethoxisilane (APS) is one of this kind of bifunctional molecule which is widely used and is also adopted in this research [43]. Lee and co-workers presented one-component all-nanoparticle multilayers assemblies comprising oppositely charged SiO_2 NP by sequential adsorption of negatively charged SiO_2 NP and amino-functionalized SiO_2 NP [44]. Applications related to the electrostatic adsorption have developed rapidly and there are a number of theoretical studies [45–47].

In this manuscript we report on the development of a framework of electrostatically driven nanoparticle adsorption utilizing a carefully selected set of experiments to test the impact of process variables and material properties. In our work we have used SiO_2 nanoparticles for the formation of electrostatically adsorbed films onto silicon wafer substrates. The unique component of this study is that by using APS monolayers to control the charge density on either surface or particle we can investigate the balance of the forces that direct the adsorption of particles onto a surface. We are not uniquely locked into one state of charge for surface or particle, and we can independently control that parameter from the ionic strength of the solution.

2. Materials and methods

2.1. Materials

3-aminopropyltrimethoxysilane (APS, 99%) was obtained from Gelest Inc., stored in a desiccator and used as received. Tetraethoxysilane (TEOS, 98%, from Gelest Inc.), ammonium hydroxide (Acros Organics), chloroform (HPLC grade, Spectrum), toluene (anhydrous, Alfa Aesar), acetone (ACS grade, Alfa Aesar), methanol (laboratory reagent, Sigma Aldrich), ethanol (200 proof, Decon Laboratories Inc.), diiodomethane (CH_2I_2, 99%, stabilized with copper, Alfa Aesar), sodium chloride (NaCl, Spectrum) were used without further purification. All water used was deionized water. Silicon wafers (p-type, $\langle 100\rangle$, from Silicon Quest) were polished on one side.

2.2. Preparation of silica nanoparticles

Silica particles were prepared by following the Stöber method. 0.31 M TEOS was added to a mixture of 0.51 M ammonium hydroxide, 15 M ethanol and 2.5 M deionized water. The resulting solution was kept stirring for 24 h. Monodispersed colloidal silica dispersion with narrow size distribution was formed. In order to purify the silica particles, the colloid was centrifuged and redispersed in ethanol for three times.

2.3. Preparation of APS coated silica nanoparticles (SiO_2/APS)

APS was used to functionalize SiO_2 NP surface with positively charged amino groups. The as-prepared SiO_2 NP were treated with APS by dispersing the vacuum-dried SiO_2 NP in 5 mM APS solution in toluene. The mixture was stirred from 0.5 h, 1 h to 1.5 h. The functionalized particles were then centrifuged and transferred back to ethanol.

Download English Version:

https://daneshyari.com/en/article/607740

Download Persian Version:

https://daneshyari.com/article/607740

Daneshyari.com