Plasma polymerization of sulfur-rich and water-stable coatings on silica particles

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ABSTRACT

The plasma polymerization of thiophene has been applied to develop sulfur-rich coatings on silica particles. A range of plasma input energies (0.06–2.4 kJ·cm^{-3}) and deposition times (2–30 min) were applied in the plasma polymerization process. The surface chemistry of plasma polymerized thiophene (PPT)-coated particles was evaluated via X-ray photoelectron spectroscopy (XPS), while the distribution of sulfur-containing groups was studied by time of flight secondary ion mass spectroscopy (ToF-SIMS). Washburn capillary rise measurements quantified the hydrophobicity of uncoated and PPT-coated particles. The stability of PPT-coated particles in water was evaluated for immersion durations of 5 min to 24 h. Surface chemistry analyses showed a rapid and homogenous formation of sulfur-rich PPT layers on particles at a low plasma input energy of 0.06 kJ·cm^{-3}. ToF-SIMS results suggested the formation of high density thiol functionalities on surfaces. PPT coatings demonstrated high stability in water, which was attributed to their highly hydrophobic character. The deposition rate of PPT on particles and planar surfaces has also been compared in this investigation. It has been shown that the plasma polymerization of a monomer on a 2-D surface produces significantly thicker coatings in comparison to a 3-D surface. The plasma polymerization of thiophene via a rotating reactor was found to be an effective method for the fabrication of sulfur-rich coatings on particulate surfaces.

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1. Introduction

Surface functionalized particles have recently attracted attention in a wide range of applications from water purification [1,2] to immobilization of enzymes and proteins [3,4]. Among surface functionalities introduced on particles, sulfur-containing groups are of particular interest for the encapsulation of nanoparticles, protein separation, and water treatment [5–7]. The efficient removal of heavy metals such as Hg, Cd, and Pb via sulfur-functionalized particles has been well documented in the literature [7–10]. Silica particles are generally considered as ideal substrates for these applications as they are low-cost and demonstrate superb chemical, thermal, and mechanical stability [11].

Sulfur-containing functionalities are conventionally grafted onto silica substrates through a silane chemistry route. In this method, silica particles are dispersed in a solvent containing the functionalizing agent, often 3-mercaptopropyl trimethoxysilane (MPTMS) [12]. Functionalized surfaces are achieved as a result of a covalent bond between a silane coupling agent and silanol groups present on the substrate [13]. Such a wet-chemistry process is however complex

and highly time consuming with stirring times as long as 16–72 h in organic solvents [11,14,15]. The wet-chemistry process also has low efficiency due to the low sulfur atomic concentrations obtained on the surface as well as inhomogeneous distribution of sulfur-containing functionalities [5,16]. More importantly, the silane chemistry method is highly substrate dependent and therefore only applicable for the modification of particles with a high concentration of silanol ($-$Si-OH) groups. For example, polymeric and metallic materials cannot be modified as readily as silica particles via this method [14].

Plasma polymerization is an alternative to wet-chemistry routes, which can overcome the hindrances mentioned earlier. In contrast to wet-chemistry methods, plasma polymerization is a room-temperature, one-step, and solvent-free approach that can rapidly deposit plasma polymer (PP) layers on almost any solid substrate [17,18]. In this technology, the desired monomer is initially converted into vapor under a low pressure, while it is subsequently excited into the plasma state through an electric field. Plasma, also referred to as the fourth state of matter, is the partially ionized gas consisting of freely moving species, i.e., electrons, ions, neutrals, and radicals. The produced low-temperature plasma carries an overall neutral charge. The recombination of active species takes place on any surface exposed to the plasma. Thus, a thin layer of PP coating is gradually deposited on the targeted substrate [19–21]. Both the chemical and physical properties of PP coatings, e.g., the surface chemistry, thickness, and aqueous stability are governed by plasma polymerization parameters. The most

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influential parameters in this process are plasma energy (W), precursor monomer flow rate (F), and deposition time (t) [22]. Specific plasma energy, defined as the power (W) to monomer flow rate (F) ratio (W/F), demonstrates the available energy per unit volume of the monomer [23]. The chemical composition of the coating and the degree of cross-linking are highly associated with the W/F parameter, whereas the thickness of PP layer is mainly linked to the deposition time [24].

Although a large number of investigations have been carried out in the field of plasma polymerization on planar substrates, limited research has been devoted to particulate substrates. The plasma–surface modification of particulate surfaces is not as simple as planar substrates due to the larger surface area exposed to plasma [25]. To deposit a uniform PP layer on the entire surface of particles, specific plasma reactor designs and geometries are required. Such designs must result in a continuous exposure of entire surfaces to the plasma; otherwise, agglomerated particles become partially coated [26,27]. A number of designs including rotating [26,28], circulating fluidized bed [25,29], particle injection [30], magnetic stirrer [31], and retrofitted loudspeaker [32] reactors have been utilized to overcome such problems. A combination of arc evaporation of nano particles and in-flight deposition of a plasma polymer layer has also been utilized for the plasma modification of nanoparticles [33].

The plasma polymerization of sulfur-based monomers on planar substrates has been previously reported in the literature [34,35]. The deposited coatings were mainly applied as conductive PP layers [36] and corrosion protective coatings [35]. We have also recently reported the deposition of plasma polymerized thiophene on silicon wafers for subsequent $SO_X(H)$ functionalization [37]. Sulfur-functionalized plasma polymer coatings have however only been deposited on planar surfaces, while their deposition on particulate surfaces and their stability in aqueous solutions has not yet been investigated.

For the optimal performance of plasma polymerized thiophene (PPT)-coated particles in the applications previously mentioned, the deposited sulfur-containing functionalities on the surface must demonstrate three crucial properties: high density, homogenous distribution, and high stability in aqueous media. The aim of this investigation was to plasma polymerize thiophene coatings on particulate surfaces, which demonstrate these three properties. X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectroscopy (ToF-SIMS) provided information on the chemical composition, density, and distribution of functional groups on silica particles. The water stability of PPT coatings was evaluated in water for up to 24 h. A systematic study was also conducted to compare the deposition rate of plasma polymers formed on planar and particulate surfaces under the same conditions. The plasma polymerization of thiophene by a rotating reactor has shown to be a promising method for the fabrication of sulfur-rich particulate surfaces.

2. Experimental

2.1. Materials

Quartz silica particles with a size range of 200–300 μm (BET surface area ≅ 0.5 m^2/g) and liquid monomer thiophene (C_4H_4S) (purity > 99%) were purchased from Sigma Aldrich and used as received. Silicon wafers (MMRC Pty. Ltd.) were cut into 1 cm × 1 cm squares, ultrasonicated in acetone (Merck Pty. Ltd.), and dried under the flow of nitrogen prior to the coating deposition.

2.2. Plasma polymerization

Plasma polymerization was conducted in a custom-built inductively coupled plasma reactor fitted with a rotating chamber, which has been previously detailed [38]. The reactor was powered via a 13.56 MHz radio frequency (RF) power generator and a matching network (Coaxial Power Systems Ltd.) run in continuous wave mode. The Pyrex glass chamber was equipped with a mixing paddle in order to keep the particles well dispersed during the plasma polymerization. A base pressure of ≈ 7×10^{-3} mbar (0.7 Pa) was applied using a rotary vacuum pump, while 50 g of silica particles were loaded into the chamber. The liquid monomer thiophene was applied as the precursor and was degassed via at least three freeze–pump–thaw cycles using liquid nitrogen. The monomer flow rate was controlled by a needle valve. Plasma powers of 2–80 W and thiophene flow rates of 1–10 sccm (standard cubic centimeter per minute) were accordingly adjusted to achieve specific energies in a range of 0.06–2.4 kJ·cm^{-3}. Samples deposited at different energies were produced at a constant deposition time of 5 min. The deposition time was also varied from 2 to 30 min at the optimized W/F value of 0.08 kJ·cm^{-3}, while a silicon wafer was attached onto the mixing paddle to be coated along with particles. The PPT-coated silicon wafers were employed for film thickness comparison studies. The chamber rotation speed of 14 rpm was kept constant during all experiments.

2.3. X-ray photoelectron spectroscopy

XPS survey spectra (0–1000 eV) of uncoated and PPT-coated particles were acquired using a SPECS SAGE at a takeoff angle of 90° relative to the sample surface and a non-monochromatic MgK$_\alpha$ (hv = 1253.6 eV) radiation operating at 200 W (10 kV, 20 mA). The hemispherical analyzer (Phoibos 150) with an MCD9 electron detector was operating at a pass energy of 30 eV and a resolution of 0.5 eV. Samples were mounted onto the sample holder using 1 cm circular carbon tape pieces with a circular analysis area of 3 mm in diameter. Multiple layers of particles were applied to avoid the contribution of carbon tape in the collected data. S 2p and C 1s high-resolution (0.1 eV) spectra were obtained at a pass energy of 20 eV. The recorded survey spectra were utilized to calculate the surface atomic concentration by CasaXPS software, while high-resolution spectra were employed to determine carbon- or sulfur-containing moieties. A linear background was applied in calculations. Systematic errors related to experimental settings and calculations were assumed to be less than 10% of the concentration values [39]. The effect of surface charge was neutralized by calibrating all the binding energies in reference to 285.0 eV, the binding energy of aliphatic C 1s component (C-H, C-C). All spectra were recorded no later than one day after deposition or stability tests.

2.4. Time of flight secondary ion mass spectroscopy

A physical Electronics Inc. PHI TRIFT V nano TOF equipment (Physical Electronics Inc., Chanhassen, MN, USA) was utilized to undertake ToF-SIMS measurements. The pulsed liquid metal $^{79+}$Au primary ion gun was functioning at 30 kV energy, while keeping the base pressure at 5×10^{-6} Pa or lower for all the samples. An electron flood gun and 10 eV Ar$^+$ ions yielded dual charge neutralization. "Unbunched" Au$_1$ instrument settings were employed to achieve images with maximum spatial resolutions. The silica particles were gently pressed into indium foil, which resulted in a relatively flat sample, considering sample morphology, as well as a constant background signal from the substrate. Secondary ion counts were collected for at least 6 areas of 400 × 400 μm per sample to ensure a representative data set. "Region-of-interest" analyses were performed on the collected raw image data. This involved the extraction of mass spectra specifically from within the boundaries of the particles of interest, which allowed the surface chemistry of only the particles of interest to be extracted from the background indium signal as well as avoiding any effects from the voids between particles. Integrated peak values of selected ions were normalized to the total selected secondary ion intensities, to correct for differences in total ion yield between analyses and samples. Spectra analyses and processing