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Hydroxylation of Organic Polymer Surface: Method and Application

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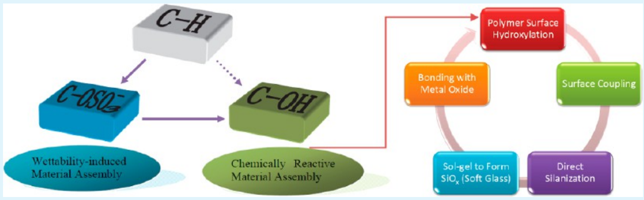


ABSTRACT: It may be hardly believable that inert C−H bonds on a polymeric material surface could be quickly and efficiently transformed into C−OH by a simple and mild way. Thanks to the approaches developed recently, it is now possible to transform surface H atoms of a polymeric substrate into monolayer OH groups by a simple/mild photochemical reaction. Herein the method and application of this small-molecular interfacial chemistry is highlighted. The existence of hydroxyl groups on material surfaces not only determines the physical and chemical properties of materials but also provides effective reaction sites for postsynthetic sequential modification to fulfill the requirements of various applications. However, organic synthetic materials based on petroleum, especially polyolefins comprise mainly C and H atoms and thus present serious surface problems due to low surface energy and inertness in reactivity. These limitations make it challenging to perform postsynthetic surface sequential chemical derivatization toward enhanced functionalities and properties and also cause serious interfacial problems when bonding or integrating polymer substrates with natural or inorganic materials. Polymer surface hydroxylation based on direct conversion of C−H bonds on polymer surfaces is thus of significant importance for academic and practical industrial applications. Although highly active research results have reported on small-molecular C−H bond activation in solution (thus homogeneous), most of them, featuring the use of a variety of transition metals as catalysts, present a slow reaction rate, a low atom economy and an obvious environmental pollution. In sharp contrast to these conventional C−H activation strategies, the present Spotlight describes a universal confined photocatalytic oxidation (CPO) system that is able to directly convert polymer surface C−H bonds to C−OSO_3^- and, subsequently, to C−OH through a simple hydrolysis. Generally speaking, these newly implanted hydroxyl groups preserve their own reactivity toward other complementary compounds, thus creating a novel base with distinct surface properties. Thanks to this functionalized platform, a wide range of organic, inorganic and metal materials have been attached to conventional organic polymer substrates through the rational engineering of surface molecular templates from small functional groups to macromolecules. It is expected that the proposed novel CPO method and its versatile usages in advanced material applications will offer new opportunities for a variety of scientific communities, especially for those working on surface/interface modulation.

KEYWORDS: *Surface modification, hydroxylation, photochemical reaction, polymer functionalization, patterning, organic−inorganic hybrid material*

1. INTRODUCTION

The hydroxyl group is one of the simplest molecular structures in chemical fields, and functions as a basic unit in biomolecules such as carbohydrates, amino acids and phospholipids. The appearance of this functional group often imparts the system with some of the reactive and interactive properties of water, e.g., ionizability, hydrogen bonding, etc. (Figure 1). These functional interactions become important chemical platforms in organic synthesis,[1] enzyme catalysis and inhibition[2,3] as well as in the formation of biological structures.[4]

Although the hydroxyl group plays a key role at a molecular interface, similar even more important contributions could be addressed for those hydroxyl groups spread at heterogeneous surfaces/interfaces. For example, polysaccharide-based bulk biomaterials show promising applications in biomedical realms because of their good biocompatibility on the hydroxyl-enriched material surfaces. Silica-based substances (mica, glass, silicon, etc.) as well as some other metal oxides express a hydroxyl-enriched boundary on surfaces, which could further be chemically derivatized through silanization to construct self-assembling monolayers with various distal groups for surface property tailoring.[5,6]

The success of these inorganic and metallic materials naturally draws our attention to synthetic polymeric substrates because these petroleum-based materials provide unique advantages over conventional metals and inorganic substrates when it comes to lightness, flexibility and recyclability. Because the number of synthetic polymers having reactive hydroxyl groups on their surfaces is limited,[7,8] an efficient functionalization for converting inert C−H as a major composition of

Received: December 19, 2013
Accepted: February 24, 2014
Published: February 24, 2014

Figure 1. Schematic description of the important properties of hydroxyl groups in homogeneous/heterogeneous systems.

synthetic polymers to C−OH (alkyl C−OH) without damaging the bulk properties is extremely important. Nonetheless, this topic is continuously challenging because of the following reasons. First, the conventional harsh hydroxylation strategies used on inorganic substrates, mainly involving Piranha solution (98% H_2SO_4/H_2O_2 = 7:3, *v*/*v*), are obviously unsuitable for soft polymer substrates due to the significant corrosiveness. Second, the classical organic synthetic chemistry for the conversion from C−H to C−OH might not to be good for polymer substrate because the undesired overoxidized products such as olefins, ketones and esters cannot be separated from the modified surface. Third, the recently emerging C−H activation strategies, such as transition metal-catalyzed reaction,[9] cannot be applied for heterogeneous C−H transformation on polymer surfaces due to reaction restrictions such as too few activation sites on inert alkyl C−H bonds, slow reaction speeds, a low atom economy/efficiency and the obvious environmental pollution. Fourth, physical strategies commonly used for polymer surface modification, such as plasma[10] and UV photooxidation,[11] normally involve high forces on soft polymers, often creating undesirable physical and chemical changes on the exposed soft surface, e.g., cracks, pitches and overoxidized products.

Aiming to solve this problem, our group has continuously worked on the development of a novel kind of chemistry for fast and simple C−H hydroxylation on arbitrary synthetic polymeric substrates containing C−H bonds, termed as confined photocatalytic oxidation (CPO).[12] The core of this newly developed method is a sequential surface chemical derivatization from an original C−H via an intermediate C−OSO_3^- to a final C−OH structure.[13,14] Specifically, we found that in a confined microscale space under strong UV irradiation, the conventional oxidation route by persulfate on a polymer surface could be adjusted and directed to a new route, probably a more controllable means to form a C−OSO_3^- surface. The resultant C−OSO_3^- surface could subsequently be hydrolyzed to create a more stabilized C−OH surface by simple hydrolysis in water.

The two resultant surface types provide specific driving forces for further material self-assembly and growth (Figure 2). On the one hand, the high hydrophilicity on the C−OSO_3^- surface creates a significant wettability contrast with an unexposed hydrophobic plastic background, which offers a useful wettability pattern applicable in wetting/dewetting-, bonding strength- and affinity contrast-based material assembly. On the other hand, the chemical reactivity on C−OH surfaces affords a molecular reaction site on an inert polymer surface for further chemical derivatization and the subsequent chemically reactive material assembly including surface grafting of small molecules, synthetic and natural polymers, metal and inorganic oxides (Figure 2).[15−23]

This Spotlight primarily discusses the chemical reactivity-induced material synthesis on C−OH surfaces due to its importance for the formation of stable composite material films. The discussions on this topic are mainly based on the systematic explorations on the synthesis of organic, inorganic and metallic functional materials where C−OH surfaces have been used to initiate and control the add-on material nucleation and growth.[15−23] It should be noted that similar work has previously been performed on self-assembling monolayers (SAMs)-modified substrates,[24,25] specifically on OH-terminated SAMs.[26−30] However, one major limitation of SAMs is that it strongly relies on the use of inorganic and metal substrates where hydroxyl and metal coordination sites are abundantly available for the formation of SAMs. Although some innovative work have been developed to prepare (pseudo)SAMs on polymer surface[31] through the use of hydroxyl-enriched polyvinyl alcohol (PVA) substrate,[32−34] silica-like buffer layer[35−38] or surface-adherent polydopamine films,[39] the construction of SAMs is mainly limited to inorganic and metal materials. The methodology based on this newly developed chemistry thereby provides a promising and general means of polymer surface hydroxylation and subsequent fabrication of versatile materials and patterning on flexible plastic substrates.

2. FUNDAMENTAL METHOD FOR THE PHOTOTRANSFORMATION OF C−H TO C−OH

The approach involves phototransformation of C−H to C−OH through the combinational use of a persulfate salt solution and

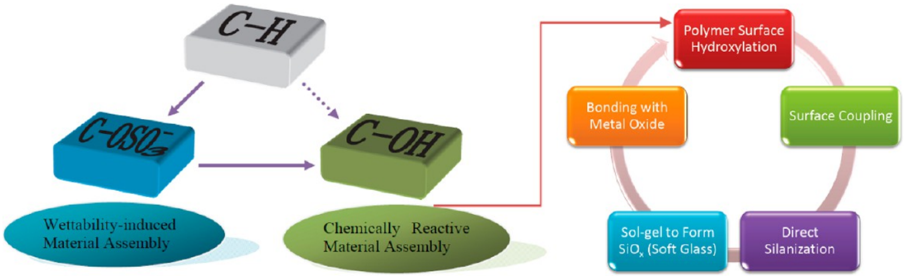
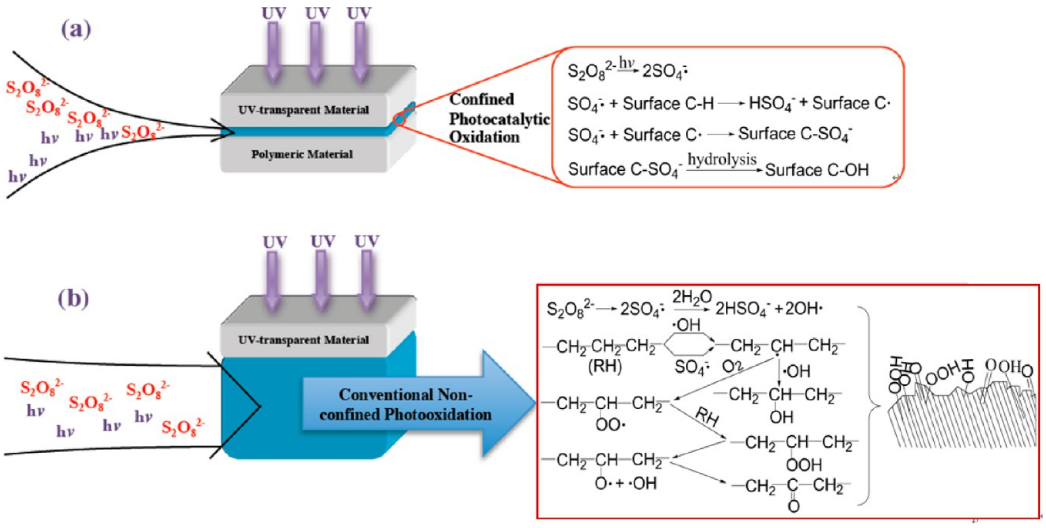


Figure 2. Schematic principle of material assembly on C−OSO_3^- and C−OH surfaces. On the right, the chemically reactive material assembly initiated by C−OH surface is further illustrated as four representative examples discussed in this Spotlight: surface coupling; direct silanization; sol−gel to prepare soft glass; supporting metal oxide deposition (bonding with metal oxide).

Scheme 1. Respective Reaction Models for CPO and Conventional Nonconfined Photo-Oxidation by Persulfates[a]



[a](a) CPO through a "sandwich" setup (thin persulfate solution layer as indicated in blue); (b) conventional nonconfined photo-oxidation through a conventional setup (thick persulfate solution layer as indicated in blue).

a confined photochemical reaction space (Scheme 1a).[13] Persulfate salt aqueous solution is a conventional oxidizing reagent capable of oxidizing organic substances under relatively mild conditions,[40] providing a moderate modification effect on the surface.[41−44] Although the mild oxidization effect can be promoted by heating,[41] addition of Ag^+ salt,[42] ultrasonication[43] and UV irradiation,[44] a slow oxidizing speed (hours) and a poor modification efficiency (a small increase in hydrophilicity) are typically obtained.

Scheme 1 shows the conventional oxidation route with the persulfate salt aqueous solution for a polymer surface, which results in the formation of heterogeneous functionalities, e.g., hydroxyl, ketone, aldehyde, carboxyl groups, etc., on the modified surface. In contrast to the conventional mechanism for obtaining a hybrid of groups on the surface, it is found that the formation of a very thin persulfate salt aqueous solution layer (μm) on substrates (organic polymers, glass or quartz) through specific technical methods (e.g., the sandwich setup shown in Scheme 1a), and strong UV light irradiating the assembly from the side transparent to UV light, lead to a fast surface hydrophilic modification method for most commercial polymeric materials (Figure 3).[13] Instead of hydroxyl and carbonyl groups expected in the conventional oxidation route, the main product on the modified surface with this new chemistry has been found to be sulfate anion groups (SO_4^-), as predominately demonstrated by static water contact angle (WCA) measurements and X-ray photoelectron spectroscopy (XPS). The change in the reaction product indicates the reaction path might be different from the conventional route.[13] As illustrated in Scheme 1a, the core feature of this newly proposed reaction mechanism is that the original oxidizing reaction of water by a sulfate anion free radical ($SO_4^{-\bullet}$) is suppressed, and alternatively, the direct oxidation (hydrogen abstraction and subsequent radical combination) on the polymer surface by $SO_4^{-\bullet}$ is significantly enhanced. During this process, the C−C bond that also widely appears on polymer surfaces would not be affected, because the hydrogen-abstraction-based oxidizing reaction of $SO_4^{-\bullet}$ is ineffective toward the C−C bond and thus could be negligible.[40]

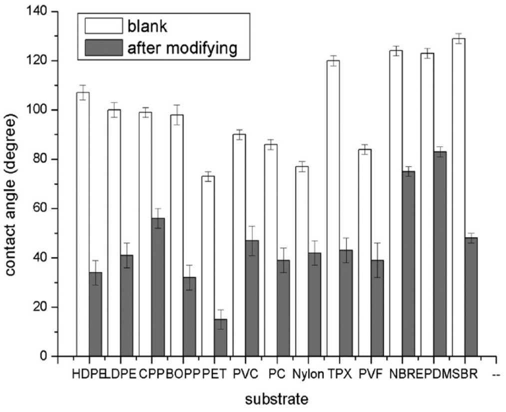


Figure 3. WCAs of the modified polymer surfaces. HDPE, high-density polyethylene; LDPE, low-density polyethylene; CPP, cast polypropylene; BOPP, biaxially oriented polypropylene; PET, polyethylene terephthalate; PVC, polyvinyl chloride; PC, polycarbonate; Nylon, polyamides; TPX, poly(4-methyl-1-pentene); PVF, polyvinyl fluoride; NBR, acrylonitrile−butadiene rubber; EPDM, ethylene−propylene−diene−terpolymer rubber; SBR, styrene butadiene rubber. Reprinted with permission from ref 13. Copyright 2003 Elsevier.

This noticeable change was considered to come from the space confinement occurring during the photochemical reaction. The above reaction route has been found to occur only when the reaction system is largely constrained in a confined microscale space. For example, if the sandwich setup is changed to a conventional thick solution layer system while keeping other irradiation parameters (UV intensity, persulfate concentration) unchanged (Scheme 1b), the surface hydrophilicity of the samples enhances only to a little extent even after prolonging the irradiation time. For example, the minimum WCAs for cast polypropylene (CPP) and low density polyethylene (LDPE) modified by a conventional thick solution layer system are significantly higher than those obtained by the "sandwich" setup (Table 1). These results reflect that the reaction extent (also possible reaction routes) is largely retarded after replacing the sandwich setup with the conventional thick solution layer system.

Table 1. WCAs of Polymer Films Modified by Conventional (Nonconfined) and Confined Photo-Oxidation[a]

substrate	setup	reaction time (s)	WCA (deg)
LDPE	Scheme 1b	90	76
LDPE	Scheme 1b	240	75
CPP	Scheme 1b	90	83
CPP	Scheme 1b	240	76
LDPE	Scheme 1a	90	44
CPP	Scheme 1a	90	56

[a] Reaction conditions: 6500 μw/cm^2; $(NH_4)_2S_2O_8$, 30 wt %.

On the basis of the above experimental results and the established knowledge on the effect of media confinement on photochemical reaction,[46] it is thus hypothesized that the confined space (~2 μm) determined by the specially designed "sandwich" setup provides the reaction with enhanced light distribution and simultaneously affords limited mobile fluctuations of reactive species. These factors facilitate that the overall reaction route changes to a new direct surface ionization route from the conventional complex path. Specifically, the solution sandwiched between the two polymer films cannot diffuse into the substrates but remains a continuous phase with μm thickness because of the space confinement and great polarity difference between the persulfate salt aqueous solution and polymeric substrates. On the one hand, such an ultrathin solution layer induces the intimate contact between the solution layer and target substrate and, on the other hand, causes the continuous aqueous phase to lose its flowing ability due to the thinness. Both these effects finally lead to a relatively concentrated C−H bond array on the organic substrates available for photo-oxidation in the adjacent solution. Thinning the solution layer also largely decreases the self-screening effect due to the photoabsorption in a thick solution layer, and much more $SO_4^{-\bullet}$ can be formed rapidly under strong UV irradiation, and subsequently attack the concentrated C−H bonds on the surface. Because the reaction rate constant of $SO_4^{-\bullet}$ attacking the organic substrates is much higher than with H_2O, the reactions of $SO_4^{-\bullet}$ with the polymer surface would dominate the entire reaction course, finally resulting in the formation of surface SO_4^- groups (C−OSO_3^- surface). The abbreviation of this reaction as CPO was thus outlined to show the most typical feature of this reaction that the "confinement" from the special setup forced the oxidation reaction to proceed in a new direction instead of in the conventional way.

An important application of the C—OSO_3^- surface obtained by CPO is hydrolysis-mediated surface hydroxylation. It was found that the CPO chemistry in Scheme 1a did not end after the formation of C—OSO_3^- at the surface but continuously propagated into the second step as the hydrolysis of C—OSO_3^- led to the formation of a more stable hydroxylated (C—OH) surface. The hydrolysis is simply conducted by immersing and incubating the C—OSO_3^- surface in ultrapure water for determined time. The hydroxyl group on the hydrolyzed surface was qualitatively judged by incubating the hydrolyzed polymer surface in trifluoro acetic anhydride (TFAA),[47] because it was assumed that the hydroxyl groups on the surfaces could keep their reactivity toward TFAA through a well-established esterification and that the fluorine-containing product would be apparent and indicative in the XPS and ATR-FTIR spectra (Figure 4).[45] In XPS spectra, it was found that the characteristic F_{1s} signal, indicating the reaction product of a fluorine-containing ester, only appeared on the hydrolyzed surface, while the other two surfaces, i.e., unmodified and sulfated BOPP, displayed no detectable F_{1s} signal. Similarly, in the ATR-FTIR spectra (Figure 4D), neither the untreated pristine substrates (a) nor the modified surface before hydrolysis, i.e., the as-formed C—OSO_3^- surface before (b) and after soaking in TFAA solution (d) displayed the characteristic peaks for ester carbonyl and C−F bonds. In contrast, after the hydrolysis on the C—OSO_3^- surface, the spectrum of the resultant sample (c) clearly showed an ester carbonyl bond at 1789 cm^{-1} and a CF_3 group at 1222 cm^{-1}, strongly indicating the existence of isolated hydroxyl groups on the modified surface (C—OH surface) with a similar hydroxyl reactivity as that in solution. The comparison of the XPS

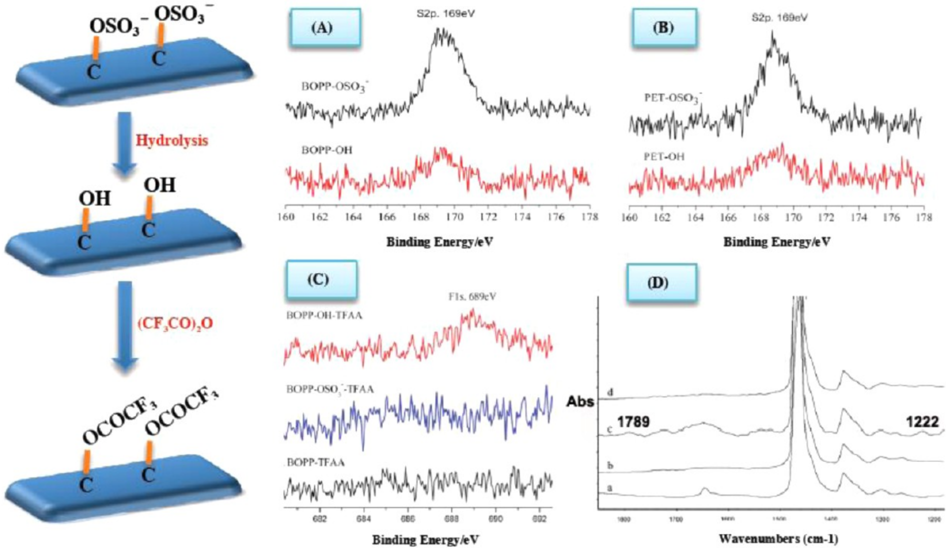


Figure 4. Chemical structure analysis on C—OSO_3^-, C−OH surfaces obtained by CPO reaction (A, B) and the resultant C—OSO_3^-, C−OH surfaces after the treatment in TFAA solution (C, D). (A−C) high-resolution XPS spectra for S_{2p}, F_{1s} elements on the surfaces; (D) ATR-FTIR spectra on the corresponding surfaces as the pristine LDPE (a), C—OSO_3^- LDPE (b), C—OH LDPE after the treatment in TFAA solution (c) and C—OSO_3^- LDPE after the treatment in TFAA solution (d).

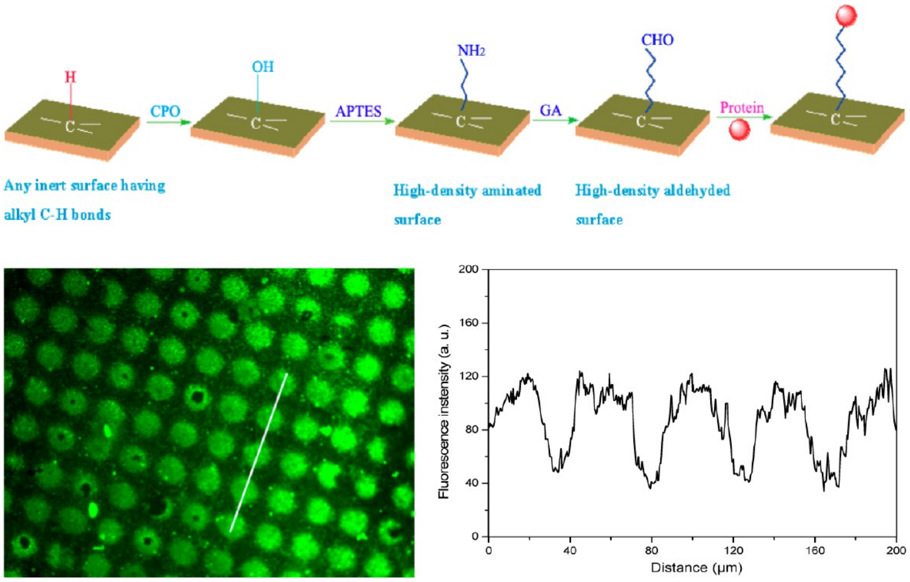


Figure 5. The proposed silanization strategy on a C−OH polymer surface and subsequent biomolecule (FITC-IgG) immobilization characterized by fluorescence microscopy. Adapted with permission from ref 15. Copyright 2009 American Chemical Society.

spectra of the C—OSO_3^- BOPP (biaxially oriented polypropylene) and PET (polyethylene terephthalate) surfaces before and after hydrolysis clearly reflected a nearly complete diminishing (>80%) of the S atom content after hydrolysis (Figure 4). The quantitative calculation based on the elemental analysis has shown the distribution density of sulfate anion across the modified surface around 37 groups/100 Å^2 with the assumption that the modification mainly takes place in a monolayer (S═O bond length 1.49 Å), and then the final functionality density of hydroxyl group on C—OH surface could be estimated around 30/100 Å^2.

It is worth noting that the etching or damage usually accompanied with polymer surface modification is avoided in this method, presenting a smooth and stable polymer surface with good integrity. The great polar difference between the salt aqueous solution and the organic substrate caused the oxidation reactions to take place solely at the outermost surface of the substrates. This limitation, in addition to short irradiation time and the moderate oxidizing ability of persulfates, was the reason that there was no observable etching or smoothing effect on the modified surface, as demonstrated by surface topography analysis by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

The CPO process is further compared with conventional widely employed surface modification methods including dry oxidation (e.g., corona, plasma, photooxidation, etc.) and chemical wet oxidation. In contrast to high capital, instrumentation requirement and poor stability of modification layers from dry oxidation, certain pollution and poor modification results as well as potential damage to substrates from wet oxidation; it has been shown that the CPO has exhibited some good features including rapidity, simplicity, low-cost, environmentally friendly and low damage to substrates. For example, the evaluation on the stability of a modification layer by hydrophobic recovery test showed that the WCAs on the modified CPP surface increased to 74° from initial 54° when incubated in an oven at 40 °C for 1 week. Such a recovery speed is obviously slower than the result obtained on plasma-oxidized PP surface.[47] Possible radical-induced photo-cross-linking[12] during the CPO process might be responsible for this stability improvement. This type of surface obtained by CPO thus stood out as a potential novel functionalized platform for further surface material assembly, as discussed below.

3. APPLICATIONS

The introduction of hydroxyl monolayer on polymer surface offers a great opportunity to directly tailor polymer surface property through engineered surface chemistry. The development of flexible chemical strategies to construct versatile functionalized surfaces provides an excellent foundation for the fabrication of polymer-supported hybrid materials, which could integrate a variety of building blocks on a polymer substrate, e.g., inorganic/organic/metal thin films, as exemplified in the following sections. One precondition to achieve the fabrication of polymer-supported hybrid materials was that the chemical reactivity of the hydroxyl groups implanted onto the heterogeneous C−OH surface could be as well-preserved as in a homogeneous solution. The results shown in Figure 5, describing the reaction between C−OH and TFAA, preliminarily reflect the good reactivity of the grafted hydroxyl groups. As described in the following sections, the grafted hydroxyl groups on the C−OH surface demonstrated a flexible and versatile reactivity toward a variety of building blocks for chemically reactive material assembly.

3.1. Application for Functional Organic Thin Film Fabrication. Functional organic thin films such as SAMs,[24,25] polymer coating[48] and polymer brush[49−51] as well as multilayer[52−54] have demonstrated their flexibly engineered functions to construct advanced materials. As described below, the incorporation of these building blocks on hydroxylated polymer substrate formed by our CPO method has been successfully developed, providing a possibility to construct all-organic functional material and devices.

3.1.1. Single Layer as SAMs. An important application of the C−OH surface toward engineered surface functionalization was explored through the decoration of small functional groups. Inspired by classical silanization on hydroxylated silicon substrates for silane-based SAM construction,[5,6] a similar strategy for the direct formation of silane-based SAMs on a

C−OH polymer surface was developed. This strategy contributes to the realm of polymer surface modification because ideally, as already demonstrated on silicon substrates, the great design flexibility on silane-based SAMs imparts a well-controlled and versatile interfacial molecular engineering to inert synthetic polymers. For this aim, C−OH polymer substrates are incubated in a 3-aminopropyltriethoxysilane (APTES) solution (widely utilized as a model silane reagent for silanization-based SAM construction) (Figure 5). After a determined time, an APTES silane SAM with amine as the terminal group was found to be well-constructed on the C−OH surface.[15] This successful and direct formation of silanization-based SAM on inert polymer substrates excludes the use of other complex pretreatment procedures.[32−38]

It was further characterized that such a silanization SAM was actually not a monolayer in theory, because the atom ratio of N to O on the modified surface revealed by XPS was higher than this theoretical value that implied a possible formation of multilayer construct. By collecting the mass increment after the modification, the amine density along the surfaces could be calculated around 201 groups/nm^2. This was obviously too crowded for a monolayer distribution, further supporting the judgment that the multilayer structure was actually formed on the modified surface. The high amine density facilitated the sequential chemical reactions on the modified surface. For instance, the activation of these amines by a condensation reaction between glutaraldehyde (GA) and the amines made it possible to obtain an aldehyde-modified surface with CHO density ranging from 67 to 200 groups/nm^2. The formation of high density amine and subsequent aldehyde groups on polymer surface is beneficial for versatile practical biomedical applications.[12] A typical application is conceptually proved by utilizing such a surface as an effective platform for the patterned immobilization of proteins (Figure 5).[15]

The significance of this method is that it can directly benefit from the well-developed silane chemistry, thereby rendering grafting any functionalities on inert alkyl surfaces by changing the terminal groups in silanes possible, which should instantly stimulate the development of many domains such as microarrays, immunoassays, biosensors, filtrations and microseparation as well as fast-developing organic electronics. For example, the incorporated high-density amine groups on a silane SAM-modified polymer substrate was further used to support deposited gold nanoparticles. As shown in Figure 6, a regionally controlled deposition could be easily achieved thanks to a photomask, where the photoexposed areas, namely amine-modified surfaces, presented a densely packed gold film comprising agglomerated gold nanoparticles. In contrast, sparsely deposited gold particle aggregations were randomly dispersed on the unexposed original regions, indicating a poor adsorption and subsequent reduced ability of supporting gold nanoparticles due to the inert chemical nature of the unmodified polymer.

3.1.2. Single Layer as Polymer Brush Graft. The chemical reactivity of the surface hydroxyl groups was further utilized in a conjugation reaction with organometallic compounds to initiate surface graft synthesis of biodegradable polymers. For instance, the ring-opening polymerization of ε-caprolactone (ε-CL) from hydroxylated PP film (C−OH) modified by the CPO method was successfully achieved (Figure 7).[16] This method consists of the following two steps: (1) the exchange of stannous(II) octoate ($Sn(O(O)CCH(C_2H_5)C_4H_9)_2$ [$Sn(Oct)_2$] with the hydroxyl groups on the surface of the PP film, forming OSn(Oct) groups bonded to the surface; (2) a surface-initiated ring-opening polymerization of ε-CL with the OSn(Oct) groups. The resultant PCL graft chain clusters then grow into regular spheroidal particles, which can be transformed into other morphologies by treatment with various solvents.

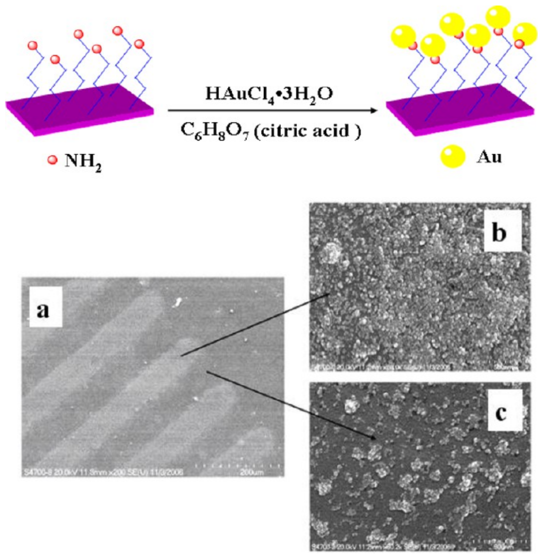


Figure 6. SEM images of the modified (b) and unmodified (c) regions on a patterned deposition of gold nanoparticles on a hydroxylated polymer surface (a).

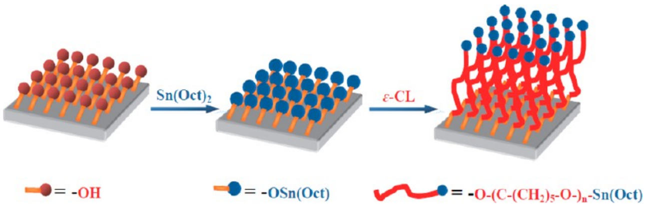


Figure 7. C−OH surface-initiated ring-opening polymerization of ε-CL on PP film.

3.1.3. Multilayer as Layer-by-Layer Deposition. Besides the above-mentioned single organic layer, a surface hydroxyl-initiated chemical bonding assembly was also developed toward the construction of multilayer organic films. This concept is demonstrated by the reaction between hydroxyl and carbonyl chloride. Typically, a chemical bonding assembly (CBA)[55] at a molecular level based on surface hydroxyl-initiated alternate reactions with the bifunctional linkers terephthalyl chloride (TPC) and bisphenol A (BPA) was successfully achieved on the C−OH surface to form self-assembled organic multilayers (Figure 8a).[17] As revealed by UV−vis spectra, such a step-by-step condensation polymerization afforded a stable and well-defined multilayer during strict LbL growth (Figure 8b). The resultant surface morphology exhibits a brush-like organic polymer graft layer (Figure 8c), probably due to intermolecular steric repulsion from grafted high-density chains. This study directly demonstrates that the grafted hydroxyl groups on the surface maintain their original reactivity toward specific chemical reactions.

3.2. Application for Functional Inorganic Thin Film Fabrication. A simple and efficient method to combine covalently functional inorganic/metal oxide thin film with polymer substrate is obviously important toward modern materials science and technologies, such as organic semi-

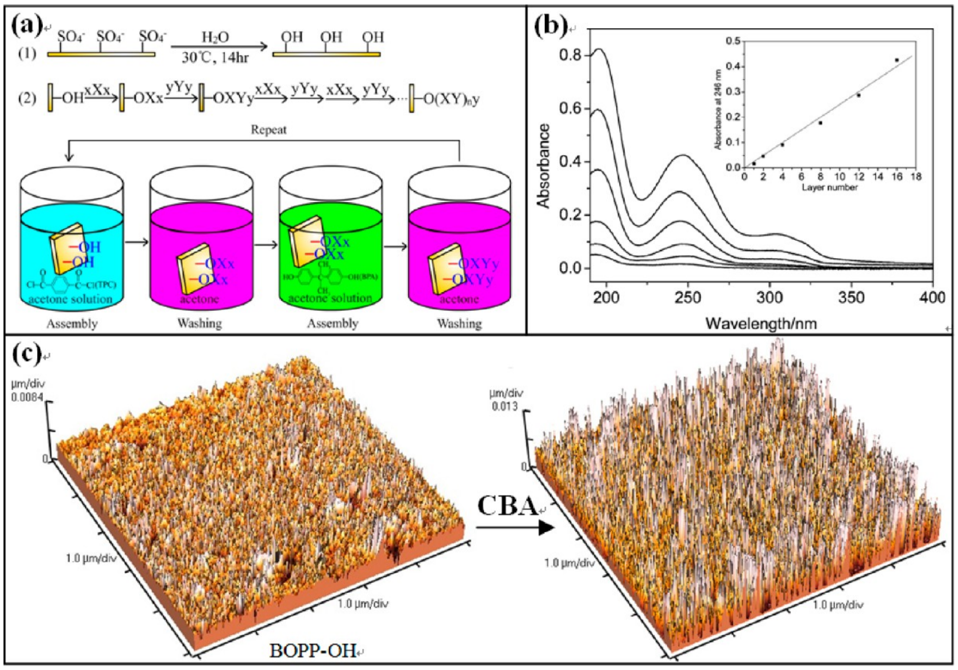


Figure 8. Surface hydroxyl group-initiated CBA LbL assembly. (a) The schematic CBA process; (b) the resultant UV−vis absorption spectra of the CBA films with varying numbers of layers; (c) the AFM images on BOPP−OH surfaces before and after modified by the CBA process (12-layer). Adapted with permission from ref 17. Copyright 2007 American Chemical Society.

conductor devices,[56,57] and polymer packaging materials.[58] As discussed below, the basement materials in these advanced applications such as silicon oxide, titanium dioxide and zinc oxide have been successfully integrated with hydroxylated polymer substrate obtained by CPO method, thus offering a promising method to fabricate organic/inorganic hybrid material (Figure 9).

3.2.1. Surface-Initiated Sol−Gel for Direct Covalent Bonding of Oxide Film and Patterning with High Quality. The reactivity of the surface hydroxyl groups was first utilized to initiate a sol−gel process to prepare a metal oxide film on a polymer substrate. Among various metal oxides, a silicon oxide-like (SiO_x) film on a polymer substrate is especially important because this semiconductor material can provide crucial properties in devices or serve as a base layer for further multilayer construction. We found that the C−OH surface could act as a nucleation-and-growth site for a subsequent sol−gel reaction on the surface.[18,19] Differing from commonly used sol−gel techniques where bulk sol−gel reactions occur simultaneously, surface hydroxyl-directed sol−gel reactions present the unique character of surface-initiated cascade growth (Figure 10). Recently, a similar method has been used for the fabrication of a TiO_2 film on a polymer substrate.[20]

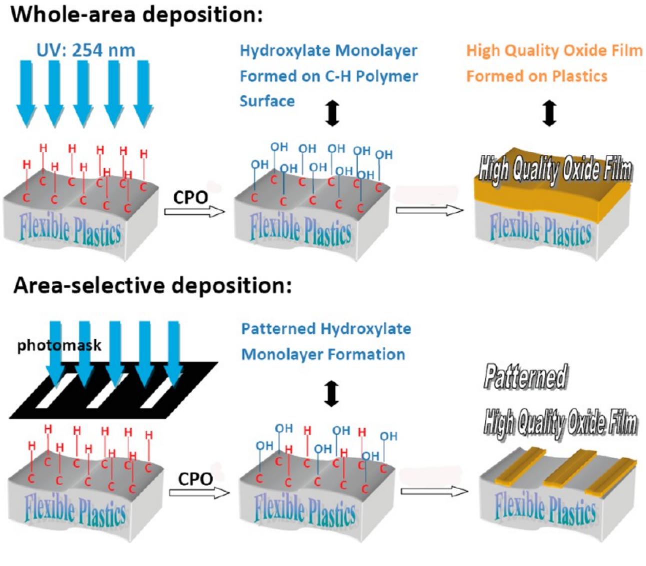


Figure 9. Schematic process to fabricate inorganic/metal oxide and its patterning on hydroxylated polymer surface.

Specifically, a standard sol solution (Si−Sol) was first prepared by dissolving certain amount of tetraethyl orthosilicate (TEOS) and HCl into a mixture of water and ethanol. After the Si−Sol was spin-coated on the C−OH polymer surfaces, the surface hydroxyl groups captured silanol groups to initiate surface gelation. Such a condensation reaction at the interface was possibly catalyzed by trace water and acidic molecules adsorbed onto the hydrophilic hydroxyl-modified surface. The latter physisorption could become energetically favorable through the possible formation of hydrogen bonds and/or protonation between trace water/acid and surface hydroxyl groups. This kind of surface condensation reaction seemed to express a higher reactivity than the Si-Sol condensation in the bulk, because the preferential surface growth without any obvious "off-plane" increase of the thickness was observed at the early deposition stage (i.e., 4−6 nm SiO_x layer after 10−40 min). The process lasted at least 40 min in order for enough reactive sites to form. After 40 min, the mature thin silica layer served as nucleation-and-growth templates to gradually thicken.

Figure 11 presented a typical cross-sectional image of a BOPP−OH/SiO_x film indicating that there was a clear and even interface between the SiO_x and BOPP phases. A homogeneous SiO_x surface was also partially revealed from this side-view observation. Accordingly, the thickness of the SiO_x layer could be directly obtained from these cross-sectional pictures. It was further found that the thickness could be

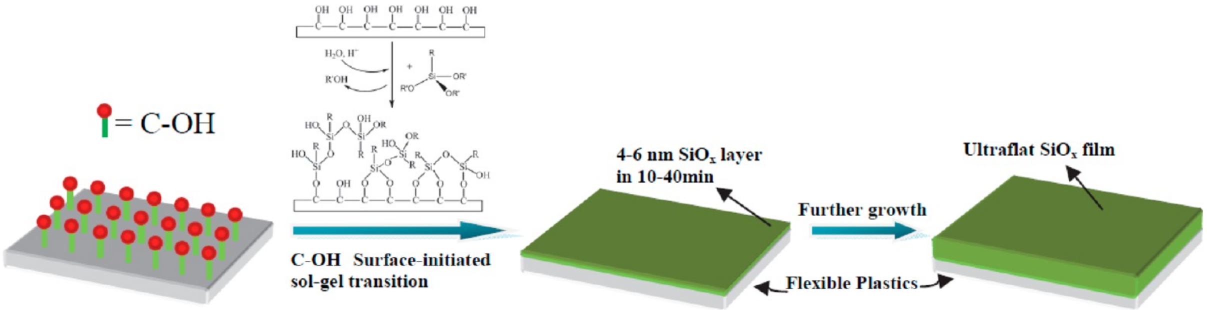


Figure 10. Tentative illustration of the interaction between hydroxylated BOPP and Si−Sol to describe C−OH surface-initiated sol−gel transition and further growth of a SiO_x film.

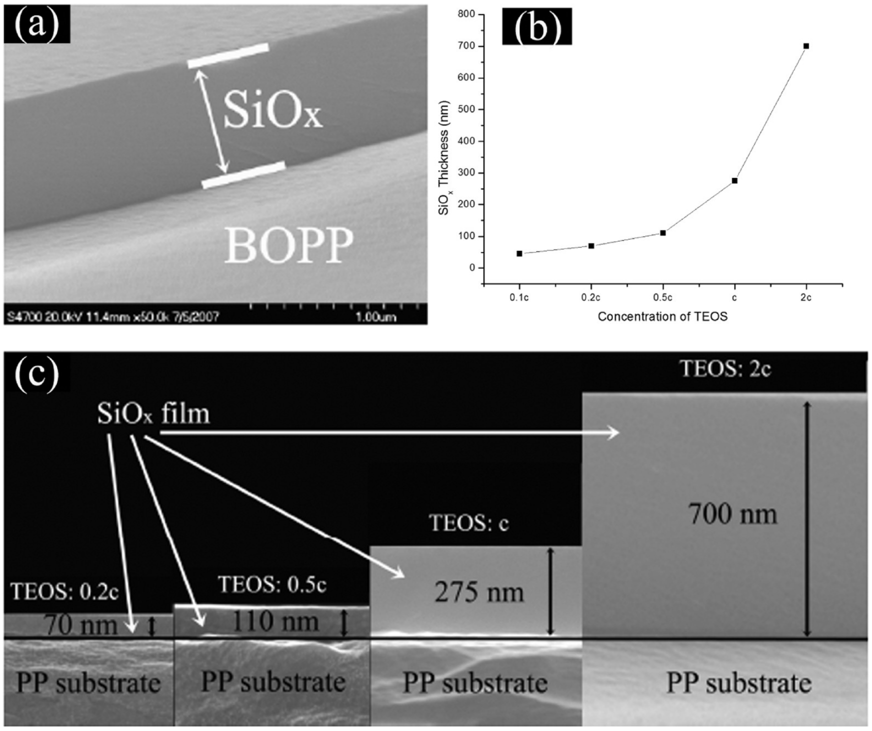


Figure 11. Typical cross-sectional FE-SEM image (a) of SiO_x deposition on a BOPP−OH surface (BOPP−OH/SiO_x). The deposition thickness was facilely controlled by changing the TEOS concentration, as plotted in (b) and visualized in (c). The c in TEOS concentration represents the following solution parameters: water, 2 mL; TEOS, 5 mL; HCl, 1 mL; ethanol, 12 mL. Reprinted with permission from ref 18. Copyright 2010 Springer.

flexibly tuned by simply changing the sol−gel condition from nanometer to micrometer, which is crucial for practical applications. The effect of the TEOS concentration on the thickness increase was not linear but one typically observed in inorganic oxide sol−gel processes.

The BOPP−OH/SiO_x surface showed a very even and homogeneous morphology in the large scale compared with pristine BOPP and BOPP−OH films (Figure 12a). Defects such as cracks and pinholes commonly observed in other methods did not appear, and a porous morphology was also did not appear. Further measurements illustrated that an ultrasmooth surface with extremely low root-mean-square (RMS) (∼8 Å) over a large area (25 μm^2) was obtained after the formation of the SiO_x layer on the BOPP−OH surface. The RMS value on such an ultraflat surface was lower than on BOPP and BOPP−OH surfaces before the deposition and even better than that on commercial quartz surfaces (around 10 Å). Because such an ultrasmooth surface was obtained using only the well-developed sol−gel technique and universal CPO reaction on the polymer surface, this method constitutes a very simple and scalable approach to quickly fabricate ultraflat oxide films on polymeric materials. The ultraflat BOPP−OH/SiO_x film showed a WCA similar to that obtained on a pristine quartz surface, further indicating that the BOPP−OH/SiO_x film surface possessed a similar surface distribution density of hydroxyl groups as that on the quartz surface. The resultant film also had a superior optical transparency (Figure 12b). Compared with the blank BOPP film, the BOPP−OH/SiO_x films of varying thicknesses only presented a very small decrease (<3%) in the transmittance at 600 nm, even when the thickness of SiO_x increased to 300 nm. The micropatterning of SiO_x films on a modified substrate was expected to be easily achievable thanks to the high coating adhesion difference that exists between hydroxylated (covalent bonding) and unmodified (physisorbed) regions. Toward this aim, patterned hydroxylated surfaces were first fabricated by CPO under the

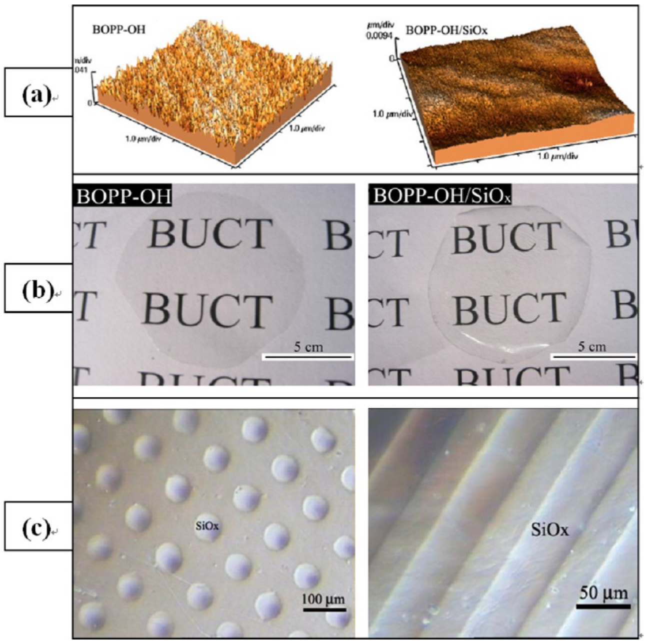


Figure 12. Surface morphology, optical transparency and micropatterning of BOPP−OH/SiO_x film. (a) Surface roughness evaluation by AFM; (b) the optical image after putting a BOPP−OH or BOPP−OH/SiO_x film on a paper with "BUCT" characters on it; (c) optical images of patterned SiO_x layers on a BOPP−OH surface fabricated by adhesive tape peeling (left) and ultrasonic agitation (right). Adapted with permission from ref 18. Copyright 2010 Springer.

control of a photomask. After sol−gel deposition on these patterned hydroxylation surfaces, the SiO_x pattern was finally formed through mechanical destabilization from either ultrasonic washing or 3 M adhesive tape peeling to remove weak depositions on unmodified regions. As a result, clear patterns with extremely low line edge variation and good consistency with the photomask were obtained (Figure 12c).

The feature size of such patterns was found to be homogeneous with few defects. A large-area homogeneous pattern (cm^2) with good fidelity was also obtained. Thanks to strong interfacial bonding and low internal stresses, no discernible cracks were observed on the SiO_x layer when the BOPP−OH substrate was mechanically bent even though cracking of an inorganic layer during deformation of organic substrates is a common problem when preparing hybrid composite films. The presented strategy provides a simple and effective way to fabricate high-quality SiO_x on polymer substrates without the requirements of a clean room and vacuum devices so as to fulfill low-cost and fast fabrication demands.

The application examples for high-quality SiO_x layers on plastics has been conceptually explored including packaging materials and protein microarray. It is found that the oxygen permeation rate of SiO_x-deposited polymer films is 25 times lower than for the pristine polymer substrate (Figure 13a).[18] Classical APTES-based SAM could be conveniently implanted onto the resultant SiO_x layer through the well-established silanization procedures, which subsequently supported the immobilization of the model protein IgG onto a plastic substrate with an effective signal-to-background ratio (Figure 13b).[18] Recently, it was further demonstrated that the SiO_x film-coated polymeric substrate could support a high quality ink pattern printed by a common official inkjet printer, and the resulting ink pattern with high fidelity could be employed as flexible polymeric photomask in the spatially controlled surface photochemical modification of planar and curved subjects[21] and subsequent simple fabrication of polymer surface with the gradients of surface energy, graft layer thickness and graft polymer chain density by using a polymeric flexible photomask with printed inkjet color gradation.[22]

3.3. Surface-Templated Liquid Phase Deposition For Direct Deposition of Metal Oxide Film and Patterning.

The sol−gel process often requires a gelation process at relatively high temperatures for the material to crystallize. This is not an atom-saving economy or beneficial to soft polymer substrates. It is thus necessary to develop a mild liquid phase deposition (LPD) process with the purpose of directly growing crystallized metal oxide films on the hydroxylated polymer substrates at low temperatures.[14] For this, the hydroxylated BOPP surface was first fabricated by CPO, and subsequently the C−OH surface was incubated in a solution mixture of $(NH_4)_2TiF_6$ and H_3BO_3 at a specific values of (low) temperature, molar ratio of reactants and incubation time. Under the determined deposition conditions, an anatase TiO_2 film could be selectively deposited on the hydroxylated region while the original hydrophobic regions were undisturbed (without deposition) (Figure 14).[14] Under similar conditions, a TiO_2 film could not be effectively deposited onto a sulfated surface before hydrolysis (i.e., C-OSO_3^- surface). The formed hydroxyl groups were thus considered more favorable to the deposition of the TiO_2 layer than the sulfate groups since hydroxyl groups are known to favor TiO_2 deposition whether on silicon or polymer surfaces. A possible reason for this is that surface hydroxyl groups can take part in the condensation

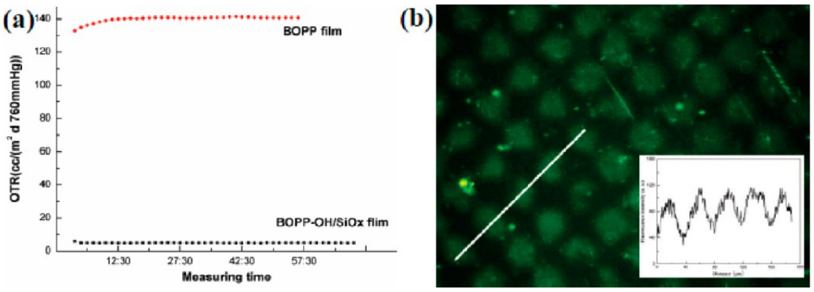


Figure 13. Application examples on BOPP−OH/SiO_x samples. (a) The oxygen permeability of BOPP−OH film with only 150 nm thick SiO_x could get 25 times the decrease than that of pristine BOPP; (b) the fluorescence microscope image demonstrated that patterned FITC-IgG immobilization could be easily achieved on BOPP−OH/SiO_x. The profile intensity on selected region (inset picture) showed around 3:1 signal-to-background ratio. Reprinted with permission from ref 18. Copyright 2010 Springer.

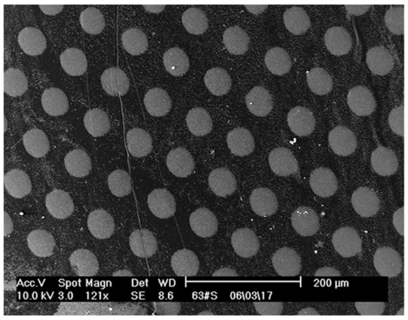


Figure 14. FE-SEM photo of patterned TiO_2 deposition on hydroxylated polymer surfaces. Reprinted with permission from ref 14. Copyright 2007 American Chemical Society.

polymerization among $Ti(OH)_6^{2-}$ to form a supported Ti−O−Ti network structure. In contrast, it is probable that the affinity between the sulfate anion groups and the TiO_2 particles was poor due to an electrostatic repulsion force.

Not at all limited to TiO_2 films, this method actually also opens the door to a direct fabrication of various functional inorganic (especially metal oxide) films and micropatterns on macromolecular substrates. For example, patterned ZnO deposition, similar to patterned TiO_2 deposition, showing densely packed vertical ZnO microrods has also been achieved on hydroxylated polymer substrates.[23]

4. SUMMARY AND OUTLOOK

The research described herein consists in a novel organic surface C−H hydroxylation chemistry to easily produce hydroxyl monolayers on synthetic polymeric substrates. The superior ability of the resultant C−OH polymer surfaces for templating inorganic and metal oxide micropatterning as well as organic/inorganic hybrid film arrays on soft matter has been explored, and will contribute to the current fast development of flexible polymer-based biomedical, energy and optical sensors. We propose that our systematic explorations of the fabrication of functional materials mediated by surface-immobilized organic molecular templates could find potential in fundamental and engineering research on polymer-supported advanced technologies, biomineralization, inorganic nanocrystals and macroelectronics. For example, the very recent examples developed by our group proved the innovative usages of this method on the intelligent water droplet transportation,[59] direct photolithographic micropatterning of silane SAMs on silicon oxide surface[60] and micropatterned deposition of versatile conductive materials including carbon nanotube, reduced graphene oxide and Ag nanowires on flexible plastics.[61]

The future direction of this field could be based on the following four aspects: (1) metal deposition with good bonding strength with the polymer substrate requires more attention than is currently given; (2) the fabrication of more complex integrated materials/devices is highly desirable; (3) areas such as hydroxyl-specific reactions, other building blocks for material assembly should be explored, e.g., the deposition of functional carbon materials including graphene/graphene oxide, carbon nanotube/nanfibers and fullerene on CPO-modified surfaces; (4) the transfer of a material and its pattern from the primarily nonconductive polymer platforms used today to conductive substrates would be useful for practical device fabrication.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

P. Yang thanks the Grant 21374057 and Grant 51303100 from National Natural Science Foundation of China (NSFC), the funding from Changjiang Scholars and Innovative Research Team in University (IRT 1070) and Fundamental Research Funds for the Central Universities (GK201301006) for financial support. W. Yang gratefully acknowledges funding from the Major Project (Grant 51033001) and the Fund for Creative Research Groups (Grant 51221002) from the National Natural Science Foundation of China (NSFC) as well as the Major Project (Grants XK100100433 and XK100100540) for Polymer Chemistry and Physics Subject Construction from the Beijing Municipal Education Commission (BMEC).

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