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A directly patternable click-active polymer film via initiated chemical vapor deposition (iCVD)

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ABSTRACT

A new "click chemistry" active functional polymer film was directly obtained from a commercially available monomer of propargyl acrylate (PA) via easy, one-step process of initiated chemical vapor deposition (iCVD). Fourier transform infrared (FTIR) spectra confirmed that significant amount of the click-active acetylene functional group was retained after the iCVD process. The degree of crosslinking could be controlled by intentionally adding crosslinker, such as ethylene glycol diacrylate (EGDA) that was polymerized with PA to form click-active, completely insoluble copolymer. The formed iCVD polymers could also be grafted on various inorganic substrates with silane coupling agents. These crosslinking and grafting techniques give iCVD polymers chemical and mechanical stability, which allows iCVD polymers applicable to various click chemistry without any modification of reaction conditions. Pre-patterned iCVD polymer could be obtained via photolithography and an azido-functionalized dye molecule was also successfully attached on iCVD polymer via click chemistry. Moreover, pPA film demonstrated sensitivity to e-beam irradiation, which enabled clickable substrates having nanometer scale patterns without requiring the use of an additional e-beam resist. Direct e-beam exposure of this multifunctional iCVD layer, a 200 nm pattern, and QD particles were selectively conjugated on the substrates via click chemistry. Thus, iCVD pPA has shown dual functionality as of "clickable" e-beam sensitive material.

1. Introduction

Well-defined functional surfaces can serve as platforms to explore various interfacial interactions, in particular for biological components with the synthetic surfaces. Therefore, well-defined, stable, and biologically active interfaces can be utilized for various applications such as controlled drug release, biosensors, and artificial skins [1]. All of the applications suggested above require high selectivity and strong binding of biological component onto the synthetic surface. A number of immobilization schemes have been suggested including silane and thiol chemistry [2] and biotin–streptavidin binding [3]. Conversely, physisorption of biomaterials to the surface is undesirable because it is generally nonspecific to the binding site [3]. Therefore, high contrast of adhesion strength and site-selectivity are of great importance. Currently, the immobilization schemes combined with micropatterning techniques [4] provides a variety of opportunities of investigation into how the specifically immobilized biological components interact with their environment [5].

Currently, a new organic synthesis method termed "click" chemistry has attracted many researchers' interest. The "click" chemistry quickly and selectively creates covalent linkages between molecular building blocks. One of the most efficient and versatile click reactions is Huisgen 1,3-dipolar cycloaddition suggested by Sharpless and coworkers [6] in which the reaction of azides and terminal acetylene functionalities are catalyzed by Cu(I). The Sharpless-type click reactions are known to be i) highly efficient with fast reaction rate when the reaction is catalyzed by Cu(I), ii) highly regioselective without any side products and tolerant to various other functionalities, iii) bio-favorable because the reaction can be performed in various solvents, including water at mild temperature (25–70 °C) [7].

Click active surface have been synthesized via multistep processing comprised of either i) forming a protected functional surface followed by conversion of the protected surface functional groups to reactive azides/acetylenes or ii) synthesis of azide/acetylene terminated monomer and polymerizing the monomer to form functionalized coatings [8,9]. For example, Rozkiewicz et al. prepared the click-active surface by applying bromo-terminated self-assembled monolayer (SAM) and converting the bromo-termination to azido-terminated functionality afterward [10]. On the other hand, Nandivada et al. firstly synthesized acetyl-functionalized paracyclophane monomers and then applied a CVD process to obtain clickable surface [9]. Similarly, Sumerlin et al. also synthesized azido-functionalized methacrylate and applied atom transfer radical polymerization (ATRP) process with this clickable monomer [11]. These approaches are necessary because of the chemically vulnerable characteristics of azides/acetylenes and/or the lack of commercially available monomers able to form stable coatings in which the azides/acetylene functionalities are maintained [11]. Herein,

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we introduce a click chemistry active polymer coating prepared by the simple one-step synthetic process of initiated chemical vapor deposition (iCVD) using the commercially available monomer propargyl acrylate (PA). The iCVD can offer a variety of advantages including highly conformal coverage on the substrates with complex geometries such as electrospun fiber mat [12], and carbon nanotubes [13,14], and trenches, non-destructive coatability on various fragile substrates such as paper [15,16]. The iCVD process does not alter the micro- and/or nanostructure of the substrates and various kinds of reactive functional group can be easily introduced on the surface utilizing a number of different monomers containing reactive functionalities [13,17,18].

In this report, poly (propargyl acrylate) (pPA) film was successfully prepared via iCVD and click chemistry was demonstrated utilizing the pendant acetylene functionalities of the pPA. By adding a proper crosslinking agent, pPA can be effectively crosslinked to form a copolymer which is insoluable in most of common organic solvents [19]. In spite of the importance of patterned bio-functional surfaces, bio-functionalizable materials compatible with conventional patterning techniques in nanometer scale are hardly found because dissolution or delamination often occur when the layers are exposed to the solvents used during the patterning process [20] or the reactive pendent functionalities do not survive the pattern steps. Using the proper surface treatment, iCVD pPA can be chemically grafted onto the substrate, which provides sufficient stability to enable the clickable iCVD polymers to be patterned via capillary force lithography [21] to achieve micron scale features. Alternatively, the iCVD pPA itself exhibits e-beam sensitivity and hence can be directly patterned via electron beam (e-beam) lithography without requiring a conventional resist layer. Thus, iCVD pPA has showed dual functionality as of "clickable" e-beam sensitive material. Negative-tone patterns on the nanometer scale were directly obtained by direct e-beam exposure and solution development of iCVD pPA. These patterned surfaces enabled selective functionalization with click chemistry. Thus, the iCVD technique enabled bio-functional surfaces patterned on the nanometer scale.

2. Experimental

2.1. iCVD polymerization

The procedure of iCVD process was described in detail elsewhere [19]. PA (Aldrich, 98%) and tert-butyl peroxide (Aldrich, 98%) was purchased and used without further purification. PA and initiator were vaporized at room temperature and introduced into the iCVD chamber at a flow rate of approximately 10 sccm and 2 sccm, respectively. For cross-linked pPA, EGDA (Aldrich, 90%) was used as a crosslinker. The polymerization reaction was initiated by heating up the hot filament at $T = 280$ °C. The process pressure was maintained at 1 Torr – controlled by PID controllable butterfly valve. Film thicknesses were monitored *in situ* by interferometry; approximately 100 nm of the pPA film was deposited in 12 min and 150 nm of crosslinked pPA film was obtained in 6 min.

2.2. Plasma polymerization

Plasma polymerized pPA film was obtained in parallel plate chamber with 150 mm diameter electrodes. The process pressure was 100 mTorr and PA was introduced at a flow rate of 5 sccm. 5 W of 13.56 MHz power source was applied with continuous RF discharge. After 10 min, plasma polymerized pPA film was obtained at the thickness of 100 nm.

2.3. Silane treatment

For surface grafting, 0.5 ml of trichlorovinyl silane (TCVS) (from Aldrich, 97%) was placed in the dessicator. Oxygen plasma treated Si wafer was exposed to TCVS vapor at 25 °C for less than 5 min. The process pressure in the dessicator was 100 mTorr. Exactly same iCVD process was applied on the silane treated Si wafer for grafted pPA on Si wafer.

2.4. Click functionalization

4 mM of N_3-coumarin (AnaSpec Inc., 97%), 1 mM of copper(II) sulfate, and 2 mM of sodium ascorbate were solubilized in 10 ml of DMF. A piece of grafted p(PA-co-EGDA) films (100 nm thick) on Si wafer was placed into the solution and stirred by magnetic bar at 25 °C for 16 h. After the reaction, the sample was rinsed with DMF several times and dried with nitrogen purge. Maintaining the same reaction conditions of N_3-coumarin except for replacing the N_3-coumarin with azido–biotin (Aldrich Inc.), resulted in biotin-functionalized pPA surface. The QD conjugation was achieved by soaking biotin-functionalized substrates in 1.0 mM of streptavidin-derivatized QD particle (Qdot® 605 streptavidin conjugate, Invitrogen) in water solution for 30 min. Afterward, the physically attached QD were rinsed with excessive water.

Capillary force lithography: The detailed procedures are described elsewhere [22]. PS ($MW_n = 40{,}000$ and PDI = 1.03, PolySciences) was spin-coated to form 140 nm thick film on top of iCVD p(PA-co-EGDA) films grafted onto Si wafer. Pre-patterned poly (dimethylesiloxane) (PDMS) mold was applied on the p(PA-co-EGDA) film and pressed at the temperature of 100–110 °C for 30–60 min to force PS siphoned into the capillary of patterned mold, formed the pattern. Oxygen plasma etching was utilized to transfer the positive tone pattern to the p(PA-co-EGDA) layer.

2.5. e-beam lithography

e-beam was directly irradiated on top of iCVD p(PA-co-EGDA) films, and Negative tone patterning was obtained at a dose of 50 mC/cm^2. Developing for 90 s with DMF completes 200 nm feature size of p(PA-co-EGDA) pattern.

2.6. Characterizations

FTIR spectra were obtained via Nexus 870, Thermo Electron Corporation. XPS was done on a Kratos Axis Ultra spectrometer equipped with a monochromatized Al K α source. The e-beam pattern was examined by optical microscopy (Olympus, Model CX41) with the maximum magnification of ×1000. Fluorescence images were also gathered using AxioSkop 2 MAT, Zeiss with the excitation wavelength of 365 nm for N_3-coumarin and 605 nm for red QD. AFM image was obtained using DI3100, Digital Instruments.

3. Results and discussion

Fig. 1 represents the Fourier transform infrared (FTIR) spectrum of PA monomer (a) and iCVD pPA (b), respectively. In FTIR spectra, a characteristic band for the acetylene C–H stretch around 3200 cm^{-1} was observed both in PA monomer and polymer film (pPA). The peak around 2100 cm^{-1} represents the carbon–carbon triple bond stretch, which could also be detected in iCVD pPA [23]. The FTIR spectrum distinctly indicates that the pendant acetylene functionalities were retained during the iCVD polymerization process. The C=C stretch around 1600 cm^{-1} observed in PA monomer disappeared in iCVD pPA, which represents that polymerization reaction is driven to near completion by iCVD process, as observed previously for the iCVD of other vinyl monomers [24]. The slight increase of sp^3 C–H peak intensity around 3000 cm^{-1} also supports that the C=C group in PA monomer is converted to polymerized –CH_2– chain via iCVD process. A cross-linker such as ethylene glycol diacrylate (EGDA) was intentionally added in iCVD process to increase chemical stability of pPA polymer film. The degree of cross-linking can be controlled by the

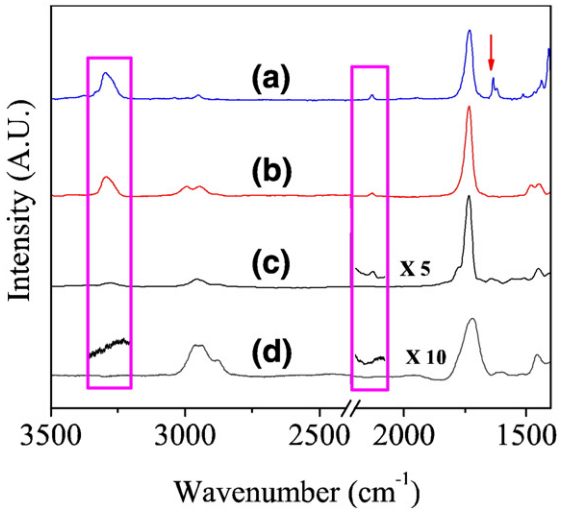


Fig. 1. FTIR spectra of (a) PA monomer, (b) iCVD pPA, (c) iCVD p(PA-co-EGDA), and (d) plasma polymerized pPA. Rectangular regions represent C–H stretch in acetylene group (around 3200 cm^{-1}) and C≡C stretch in acetylene group (around 2100 cm^{-1}) and arrow represents C=C stretch in acrylate (around 1600 cm^{-1}).

flow rate of added EGDA in iCVD process [19]. A highly cross-linked pPA (p(PA-co-EGDA)) iCVD copolymer was successfully obtained and was completely insoluble to all organic solvents tested, including acetone, THF, methanol, 2-isopropanol, and DMF. The FTIR spectrum of the copolymer film demonstrates that considerable degree of the acetylene functional groups were retained, as was also the case for the pPA homopolymer films mentioned above (Fig. 1c). The intensity of acetylene C–H stretch around 3200 cm^{-1} and acetylene C≡C stretch around 2100 cm^{-1} were relatively decreased, which indicates that significant amount of EGDA was incorporated in cross-linked p(PA-co-EGDA) film.

Alternatively, the mechanical stability could also be offered by grafting the pPA film on Si wafer surface by using pre-treatment with silane coupling agent TCVS [22]. The surface grafted pPA was not dissolved in the organic solvents (THF, DMF, and acetone) and no distinctive change was observed in FTIR spectra. Ultrasonication and tape test showed highly enhanced adhesion of iCVD pPA on Si surface (data not shown) [22]. Compared with the FTIR spectrum of monomer, the intensities of acetylene C–H stretch peak around 3200 cm^{-1} and acetylene C≡C stretch peak around 2100 cm^{-1} were almost identical, which follows that the iCVD process retains the "click-active" side functionality. The film resulting from plasma polymerization of PA contains virtually no acetylene functionalities. (Fig. 1d). The contrast between Fig. 1b and d clearly displays the result obviously shows the non-destructive characteristics of iCVD process relative to plasma polymerization.

X-ray photoelectron spectroscopy (XPS) spectra also represent that well-defined pPA was obtained by iCVD (Fig. 2). The survey scan of pPA shows that only C and O elements were detected from XPS spectrum. The C 1s high resolution scan spectrum was non-linear least squares fit using four different peaks providing quantitative analysis that is well matched with the theoretical chemical composition of pPA [25]. Of particular interest for a "clickable" surface, is the intense peak at 285.0 eV corresponds to the carbons in acetylene group. Thus XPS confirms that the acetylenic groups identified in the bulk iCVD pPA film by FTIR, are also present at the surface where their reactivity is desired. The O 1s high resolution scan spectrum can be non-linear least squares fit to two independent peaks corresponding to the two distinct oxygen sites in acrylate group. Therefore, the XPS analysis distinctly displays that the surface composition of iCVD pPA film is fully consistent with the theoretically predicted molecular structure of pPA. Moreover, these XPS results corroborate the FTIR results and support the hypothesis that most of the reactive acetylene functionality survived the iCVD polymerization reaction.

The azido-derivatized fluorescent dye was applied onto iCVD polymerized pPA surface to assess the reactivity of pPA to heterogeneous click reaction. The Huisgen 1,3-dipolar cycloaddition between 7-methoxycoumarin-3-carbonyl azide (N_3-coumarin, peak emission = 488 nm) and iCVD pPA was performed with copper(II) sulfate and excess of sodium ascorbate. Sodium ascorbate reduces copper(II) sulfate to yield Cu(I) ions that catalyze the cycloaddition reaction to form triazole linkage between iCVD pPA and N_3-coumarin (Scheme 1). X-ray photoelectron spectroscopy (XPS) scan was applied on both iCVD pPA and the N_3-coumarin functionalized iCVD pPA surface via click reaction, which clearly showed that new nitrogen peak around 400 eV was formed at N_3-coumarin functionalized iCVD pPA surface via click reaction, which was absent in freshly prepared iCVD pPA (Fig. 3a). The presence of new nitrogen peak indicates that the cycloaddition of N_3-coumarin was successfully achieved. The N 1s high resolution scan XPS spectrum demonstrates the attachment of N_3-coumarin on iCVD pPA surface via click chemistry (Fig. 3b). Since N_3-coumarin does not contain any of nitrogen elements except for the azido group, the nitrogen at the surface of polymer surface solely comes from the "click"-linkage of

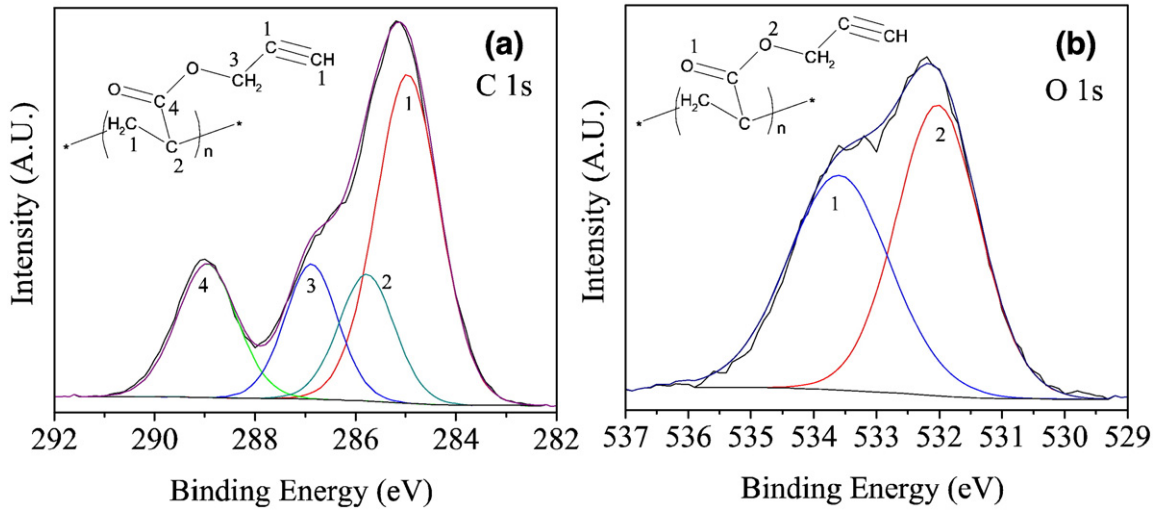
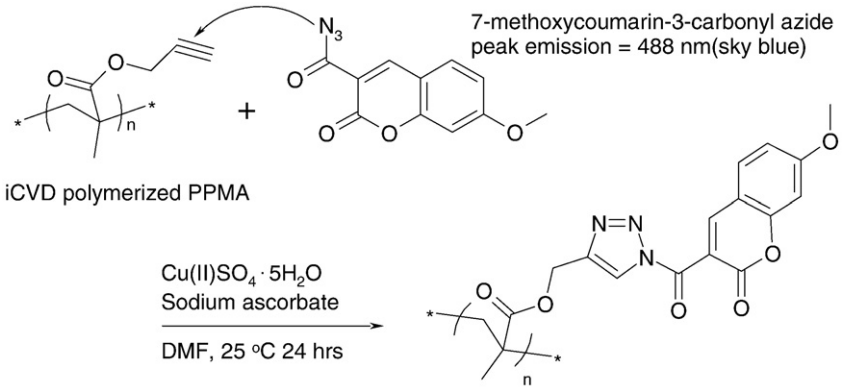


Fig. 2. XPS high resolution scan data of pPA; (a) C 1s and (b) O 1s, respectively.



Scheme 1. Click reaction between iCVD pPA and azido functionalized fluorescent dye, N_3-coumarin.

triazole group. The nitrogen peak were non-linear least squares fit to two peaks, which were assigned as the amide bond in triazole at 399.7 eV and two N=N bond in triazole at 400.2 eV [25]. The ratio of peak areas was calculated into approximately 1:2, which is consistent with the chemical structure N_3-coumarin functionalized pPA [26].

Chemical selectivity of click reaction with iCVD p(PA-co-EGDA) was assessed by applying click chemistry onto pre-patterned p(PA-co-EGDA). To pattern p(PA-co-EGDA), a non-conventional stamping patterning process of capillary force lithography was applied on p(PA-co-EGDA) [21,22]. With a pre-patterned PDMS stamp, a well-defined 3 μm size line pattern was easily obtained. The same click chemistry was applied on the patterned substrate to obtain a N_3-coumarin functionalized p(PA-co-EGDA). Fluorescence microscope image (inset in Fig. 3b) shows a sharp contrast of fluorescence from blue N_3-coumarin dye. The fluorescence image exactly overlapped with the area of patterned p(PA-co-EGDA) confirming that the N_3-coumarin was selectively functionalized only on p(PA-co-EGDA) regions and clearly illustrates that the terminal acetylene groups on p(PA-co-EGDA) were retained during the patterning process. This encouraging result demonstrates that the terminal acetylene groups are reactive to click chemistry and the reactive p(PA-co-EGDA) is applicable to various functional surface coatings.

Many acrylate polymers such as polymethylmethacrylate (PMMA), polyhydroxyethylmethacrylate, and polymethylmethacrylic acid are known to retain electron beam (e-beam) patternability [18,27,28]. Previously, negative-tone e-beam patterning of iCVD glycidal methacylate films was reported [18]. As one of the acrylate polymers, iCVD p(PA-co-EGDA) could also be expected to display e-beam sensitivity and indeed a well-defined pattern in nanometer scale was easily obtained with the e-beam irradiation directly onto iCVD p(PA-co-EGDA) film (Fig. 4). Fig. 4a through d show the e-beam patterned iCVD p(PA-co-EGDA) film. The optical microscope and AFM images clearly show that the e-beam irradiated area was developed out with *N,N′*-dimethylformamide (DMF) for 90–120 s. 200 nm stripe patterns were easily obtained with the dosage of 50 mC/cm^2 at 50 keV acceleration voltage. Compared with one of the standard e-beam resist, PMMA, p(PA-co-EGDA) requires about 10–50 times higher e-beam dose for the same level pattern resolution. We suspect that during e-beam exposure some, but not all, of the acetylene groups in p(PA-co-EGDA) cross-link simultaneous to the depolymerization of acrylate group and hence a higher dose of e-beam is required as compared with acrylate resist with inert side group.

On top of 200 nm line patterned iCVD p(PA-co-EGDA) surface using e-beam lithography, 10–15 nm fluorescent quantum dot (QD) particles (λ_{em} = 605 nm, ca 15 nm) were functionalized using click chemistry (Fig. 4). The fluorescent dye functionalized polymer film did not show sufficient spatial contrast in fluorescence microscope because of the small feature size of pattern. Hence, instead of N_3-coumarin dye, a larger particle was used to assess the pattern

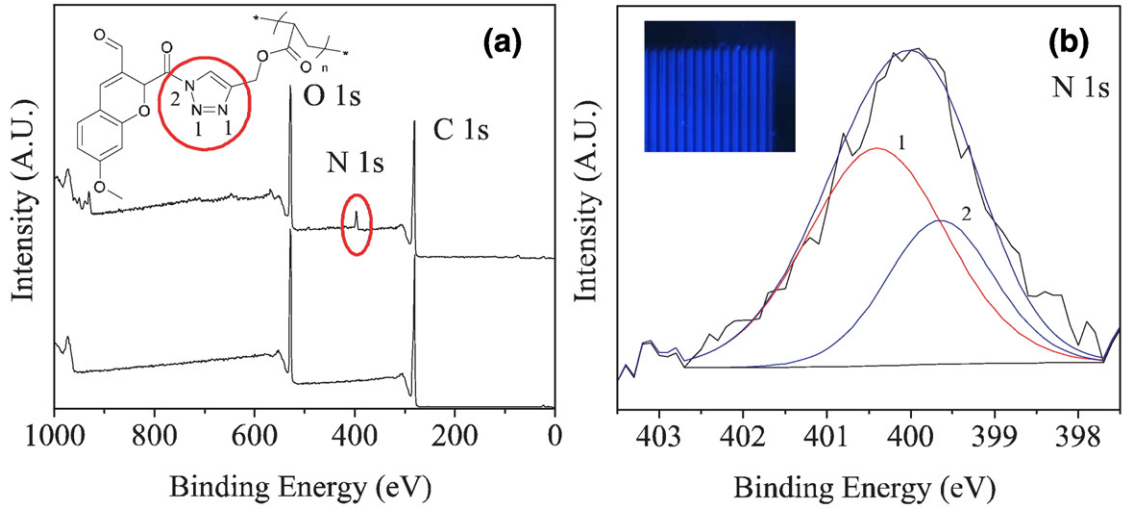


Fig. 3. XPS (a) Survey scan of pPA (bottom) and N_3-coumarin functionalized p(PA-co-EGDA) films (top) and (b) high resolution N 1s scan data of N_3-coumarin functionalized p(PA-co-EGDA) films via click reaction, respectively. Red circles in (a) highlight the newly formed N 1s peak by click addition reaction. Inset in (b) represents a fluorescence microscope image of patterned p(PA-co-EGDA) film click-functionalized with N_3-coumarin. Scale bar represents 20 μm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

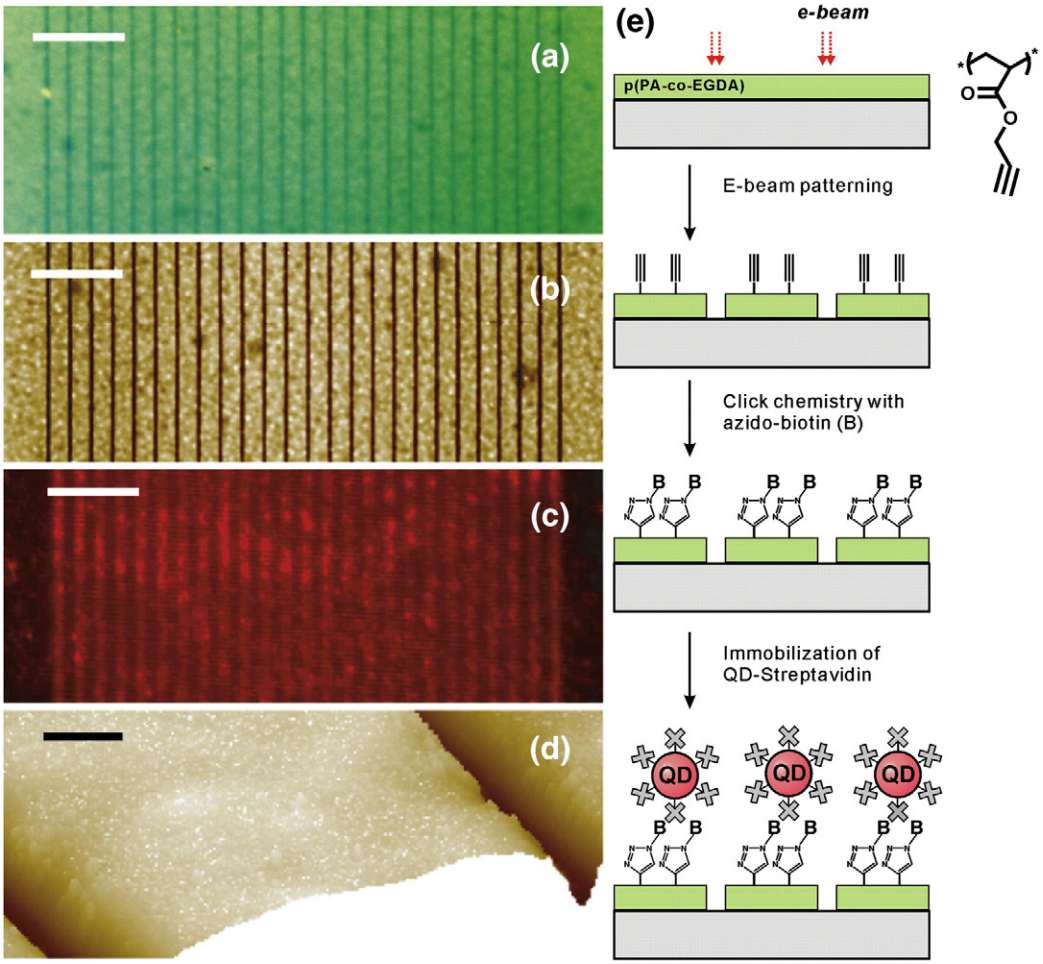


Fig. 4. (a) Optical microscope image, (b) AFM image, and (c) fluorescence microscope image of e-beam patterned p(PA-co-EGDA) film conjugated with QD particles via click chemistry, respectively. Each scale bars represents 10 μm. (d) Enlarged 3-D AFM image of e-beam patterned p(PA-co-EGDA) film conjugated with QD particles via click chemistry. Scale bars of a through represents 500 nm. (e) Schematic procedure of direct e-beam lithography of p(PA-co-EGDA) film and subsequent QD-streptavidin immobilization onto the patterned polymer film by biotin–streptavidin binding via click reaction.

fidelity in click chemistry, which could be clearly observed by using AFM image (Fig. 4d). First of all, azido-derivatized biotin was conjugated on pre-patterned iCVD p(PA-co-EGDA) substrates by click chemistry. Afterward, streptavidin-functionalized QD particles are spread onto the biotin-functionalized p(PA-co-EGDA)film and strong biotin-streptavidin binding was successfully formed in 30 min. Since the fluorescence image is isotropic and the spatial resolution of fluorescence microscope was less than for the optical and AFM images. However, the obtained fluorescence image distinctively suggests that nano-patterned, clickable surface can be achieved without using any a conventional resist material. The AFM image of QD-functionalized substrate shows that the surface of unexposed area has a high surface density of QDs, which appear shown as white dots in Fig. 4d. On the other hand, negligible amount of QD particles were observed on the etched out area. This obvious contrast in QD particle density on the surface is totally consistent with the fluorescence microscope image. The dual functionality of iCVD p(PA-co-EGDA) can offer a powerful tool for various selective surface modification applications. Since the developer is totally compatible with the click chemistry and the developer does not destroy the patterned surface any further, a variety of click reaction can be directly applied on the e-beam irradiated surface, which can minimize the impurity incorporation during the patterning step. The mechanical and chemical stability gifted by cross-linker and grafting agent ensures the use of very strong solvent without any constraints. Combined with the advantages of CVD process, such as conformal coverage, non-sensitiveness to the substrates, and ability to be grafted on various substrates, the clickable iCVD polymer e-beam sensitive layer can be utilized to various applications, such as biosensors, microfluidic devices, and tissue engineering [1].

4. Conclusion

In conclusion, a new rapid synthetic pathway for depositing the click chemistry active polymer coating of pPA was obtained via a one-step vapor-phase iCVD process utilizing a commercially available monomer. The pendent acetylene groups in pPA were clearly observed in FTIR and XPS spectra. By introducing cross-linking agent and surface grafting agent to the iCVD process, the mechanical and chemical stability of iCVD clickable layer was greatly enhanced. The improved stability of the iCVD polymer film enabled the micron-scale patterning of pPA film by capillary force lithography without any modification of patterning process. The well-defined acetylene surface functionality enables click chemistry through selective reactivity with azides. pPA film demonstrated sensitivity to e-beam irradiation, which enabled clickable substrates having nanometer scale patterns without requiring the use of an additional e-beam resist. Direct e-beam exposure of this multifunctional iCVD layer, a 200 nm pattern, and QD particles were selectively conjugated on the substrates via click chemistry. Combined with the advantages which iCVD can provide, the functional pPA films can be utilized in various surface modification applications. Especially, current research progress has reported various azido-derivatized ligands for biointerfaces and the functional pPA films can

be a design platform for immobilized bio-devices including biosensors, bio-assays, drug discovery, and bio micro-electro-mechanical systems (bio-MEMS).

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