

Fabrication and Characterization of Tunable Wettability Surface on Copper Substrate by Poly(ionic liquid) Modification via Surface-Initiated Nitroxide-Mediated Radical Polymerization

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ABSTRACT: Poly(ionic liquid) surfaces with tunable wettability were successfully prepared on micro/nanoscale CuO/Cu composite substrates by a surface-initiated nitroxide-mediated radical polymerization technique. Various characterization techniques including X-ray photoelectron spectroscopy, cold field emission scanning electron microscopy, and static water contact angle measurement were used to characterize the surfaces for each surface modification step. Kinetic studies revealed that the polymer chain growth from the surface was a controlled/"living" polymerization process. The surface with tunable wettability, reversible switching between hydrophilicity and hydrophobicity can be easily achieved by sequential counteranion exchange. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: surface-initiated nitroxide-mediated radical polymerization; poly(ionic liquid); reversible wettability; copper; film materials

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INTRODUCTION

Metals, such as copper, as very important engineering materials, have had many practical and potential applications, for example, in architecture, auto, aviation, and power transmission fields. But, effective protection and anticorrosion of the material surfaces have been puzzling material researchers. As we know, surface properties of metals influence their applications. So, to search for a precise control technique of the surface properties is still challenging.

Because of the correlation with a surface tension gradient, wettability control provides a more flexible and efficient way for wide applications. Recently, wettability control has attracted extensive interests for the development of advanced devices, such as self-cleaning,¹ discrete liquid droplet manipulators,² and tunable optical lenses.³ This control relies on surface free energy and surface roughness. So, it is a key to construct an appropriate surface structure for wettability control. In many cases, tethering of polymer chains onto a solid substrate provides an expedient method for modifying the surface properties of the substrate.⁴ Polymer chains can be firmly covalently anchored to the substrate via either the "grafting to" or "grafting from" technique. "Grafting to" technique directly grafts end-functionalized polymer chains onto the solid substrate. Whereas in "grafting from" technique, the grafting reaction can proceed

by *in situ* polymerization from the surface. Because of high tethering density, the "grafting from" technique is more attractive. In this technique, initiator groups are first immobilized on the surface of the substrate, subsequent polymerization from the surface-immobilized initiator moieties leads to a growth of tethered polymers on the surface.

Compared with other surface assembly techniques such as plasma grafting,⁵ layer by layer self-assembly,⁶ and so forth., surface-initiated radical polymerization has more advantages, including high reaction activity, controlled polymerization, firm combination of the polymer film with the substrate, and ordered molecular assembly and high tolerance of functional groups.^{7,8}

Ionic liquids (ILs) are molten salts at ambient temperature with low melting point (<100°C) and low flammability. Recently room temperature ILs have been widely studied because of their remarkable properties including nonvolatility, chemical and thermal stability, and high ionic conductivity.^{9–11} Their polymeric form might constitute a new class of polymer material with exceptional properties, such as high thermal stability, excellent mechanical and electrochemical properties.^{12–15} Especially, convenient counter anion exchange provides a possibility for reversible control of the surface wettability.

We ever published a poly(allyltriphenylphosphonium) brush-initiated reversible wettability on silicon substrate.¹⁶ As a systematic study, it is very important and interesting to clarify the effect of modification of different poly(ionic liquids) on surface wettability of substrates. Herein, we reported a new, smart copper surface with tunable wettability, reversible switching between moderate hydrophilicity and hydrophobicity by modifying it with a new poly(ionic liquid). This surface can be obtained by *in situ* growth of poly[1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate] (PVBIIm-PF₆) on a CuO/Cu substrate via surface initiated nitroxide-mediated radical polymerization (NMRP). It was found that poly(imidazolium hexafluorophosphate) modified surface had a stronger hydrophobic property than that modified by poly(quaternary phosphonium hexafluorophosphate) reported in Ref. 16.

MATERIALS AND METHODS

Materials

Tert-butyl hydroperoxide (TBHP, chemical grade, Sinopharm Chemical Reagent, China), 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO, Alfa Aesar, 98%), 3-chloropropyltrimethoxysilane (Alfa Aesar, 97%), 2,6-di-*tert*butyl-4-methylphenol (DBMP, Aldrich, 98%), ammonium hexafluorophosphate (Aldrich, 98%), 4-vinylbenzyl chloride (Aldrich, 90%), K₂S₂O₈ (Laiyang Chemical Reagent Plant, analytical grade, China), KOH (Sian Chemical Reagent Plant, analytical grade, China), methanol (Tianjin Chemical Reagent Plant, analytical grade, China) were used as received. Xylene and dioxane (Tianjin Chemical Reagent Plant, analytical grade, China) were refluxed over sodium and distilled twice before use. Copper sheet (Tianjin Chemical Reagent Plant, 99.5%, China) were cleaned using 4 mol/L HCl for 15 min, then rinsed with distilled water several times and dried under a stream of clean nitrogen. Other reagents were of analytical grade and used as received. All aqueous solutions were prepared with the deionized water.

Characterization

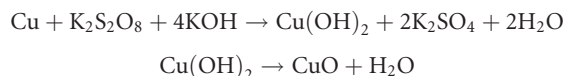
The static water contact angles were determined using a DSA100 contact angle goniometer (KRÜSS, Germany). Images of polymer-grafted flower-shape micro/nanoscale CuO surface were obtained with a JSM-6701F cold field emission scanning electron microscopic (JEOL, Japan). The X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI-5702 multifunctional XPS, using Al K α radiation as an exciting source (Electrophysics). The binding energies of the target elements were determined at a pass energy of 29.35 eV, with a resolution of ± 0.3 eV, using the binding energy of the gold (Au_{4f}: 84.0 eV) as a reference. Hydrogen and carbon nuclear magnetic resonance (¹H-NMR and ¹³C-NMR) spectra were measured with a MERCURY 400 MHz spectrometer with DMSO-*d*₆ or D₂O as a solvent (VARIAN). Crystal structure of the monomer was measured with a Smart APEX X-ray single crystal diffractometer with Mo K α radiation as an exciting source, 3 KW (Bruke, Germany). Gel permeation chromatography (GPC) was used to measure molecular weights and molecular weight distributions using poly(ethylene glycol) as a standard. GPC experiments were performed at 70°C in *N,N*-dimethylformamide (DMF) (with 0.05 mol/L LiBr to suppress interaction with column packing) using a GPC2000 instrument fitted with a differential refractometer detector (Waters). The attenuated total reflection infrared spectroscopy (ATR-FTIR) was

recorded on a Nicolet 870 infrared spectrometer equipped with a smart ATR accessory with 300 scans and a resolution of 4 cm⁻¹.

Methods

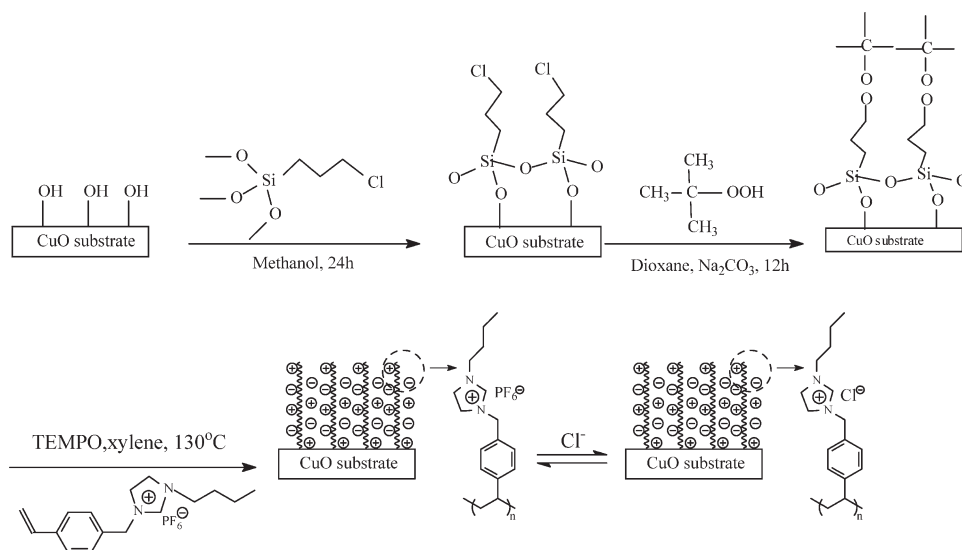
Synthesis of the IL Monomer 1-(4-Vinylbenzyl)-3-butylimidazolium Hexafluorophosphate. The synthesis of the IL monomer 1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate (VBIIm-PF₆) was performed according to a slight modification reference method.⁴ To a dried flask was added 3.1 g of *N*-butylimidazole (25 mmol), 4.2 g of 4-vinylbenzyl chloride (27 mmol) and 0.05 g of the inhibitor DBMP. The mixture was magnetically stirred at 42°C under N₂ atmosphere for 48 h to obtain a viscous liquid 1-(4-vinylbenzyl)-3-butylimidazolium chloride. The rough product was washed with an excess of ethyl ether and dried overnight under vacuum at room temperature to obtain a transparent viscous liquid with a yield of 84%. Target product was obtained through an anion exchange process between 1-(4-vinylbenzyl)-3-butylimidazolium chloride and ammonium hexafluorophosphate. The product was a waxy solid. The solid was recrystallized with a methanol and ethanol mixed solvent to obtain needle-like crystals. mp: 87–89°C. ¹H-NMR[400 MHz, δ , ppm, DMSO-*d*₆]: 0.88 (3H, t, -CH₃), 1.24 (2H, m, N-CH₂CH₂-CH₂-CH₃), 1.78 (2H, m, N-CH₂-CH₂-CH₂-CH₂CH₃), 4.15 (2H, t, N-CH₂-CH₂CH₂CH₃), 5.29(1H, d, CH₂=CH-), 5.40 (2H, s, Ph-CH₂-N-), 5.86 (1H, d, CH₂=CH-), 6.71 (1H, m, CH₂=CH-), 7.38 (2H, d, Ph), 7.52 (2H, d, Ph), 7.81 (2H, s, N-CH=CH-N), 9.27 (1H, s, N-CH-N). ¹³C-NMR (400MHz, δ , DMSO-*d*₆): 138.2 (N-CH-N), 136.7 (CH₂=CH-), 136.6 (Ph), 134.9 (Ph), 129.3 (Ph), 127.3 (Ph), 123.4 (N-CH=CH-N-Bu), 123.2 (N-CH=CH-N-Bu), 115.9 (CH₂=CH-), 52.4 (Ph-CH₂-N-), 49.3 (N-CH₂-CH₂CH₂CH₃), 31.9 (N-CH₂-CH₂-CH₂CH₃), 19.4 (N-CH₂CH₂-CH₂-CH₃), 13.9 (N-CH₂CH₂CH₂-CH₃).

Preparation of Flower-Shape Micro/Nanoscale CuO Surface. Previously cleaned copper sheets were immersed in a mixed solution of K₂S₂O₈ solution (0.065 mol/L, 20 mL) and KOH solution (2.5 mol/L, 40 mL) and maintained at 65°C for 1 h. The sheets were removed from the solution and rinsed with distilled water several times and then dried in air. The dried sheets were heated to 180°C for 2 h in an oven to get the flower-shape micro/nanoscale CuO surface. Relative chemical reaction equation was follows:



Immobilization of 3-Chloropropyltrimethoxysilane onto the Micro/Nanoscale CuO Surface. The treated sheets were immersed in a solution of 3-chloropropyltrimethoxysilane in methanol at room temperature for 24 h without stirring. The sheets were removed from the solution and rinsed orderly with acetone and methanol and then dried in a stream of nitrogen. The sheets were directly used for the next step.

Introduction of Peroxide Groups onto Micro/Nanoscale CuO Surface. Dioxane (14 mL), TBHP (4 mL) and Na₂CO₃ (0.05 g) were sequentially added to a dry Bunsen flask of 100 mL equipped with a magnetic stirrer. After the 3-chloropropyltrimethoxysilane modified copper sheets were placed, the flask was degassed and backfilled with nitrogen three times and left under a nitrogen atmosphere. After slowly stirred for 12 h under nitrogen at 20°C in the dark, the copper sheets were removed from the



Scheme 1. Preparation process of tunable wettability surface by poly(ionic liquid) film modifying.

flask and rinsed with toluene and alcohol several times, and then dried in a stream of nitrogen. The sheets were also directly used for the next step.

Synthesis of PVBIIm-PF₆ Film Via Surface-Initiated NMRP. The prepared IL monomer VBIm-PF₆ (1.928 g, 5.0 mmol), xylene (15 mL) and TBHP (0.075 mL) were added into a dry Bunsen flask of 100 mL which had been degassed and backfilled with nitrogen three times. After the mixed solution was slowly stirred several minutes at 80°C until the solution became homogeneous, the peroxide group-immobilized copper sheets were placed, and then 23.4 mg of TEMPO was added. The flask was degassed and backfilled with nitrogen three times again. The reaction was performed in an oil bath at 130°C for various reaction times, and then, the copper sheets were removed from the flask and rinsed with DMF for several times to remove physically absorbed polymer chains and then dried in a stream of nitrogen.

Tuning of the Wettability of Poly(ionic liquid) Modified Surfaces by Counter Anion Exchange. The PVBIIm-PF₆ modified copper sheets were immersed in 0.2 mol/L NaCl aqueous so-

lution for 6 h. The sheets were removed from the beaker, rinsed with distilled water some times and then dried in a stream of nitrogen. The reversibly altered wettability from moderately hydrophilic to hydrophobic can be easily achieved by re-immersing PVBIIm-Cl modified sheets into 0.1 mol/L NH₄PF₆ aqueous solution for 2 h.

RESULTS AND DISCUSSION

Tunable wettability surface was prepared according to the Scheme 1.

Characterization of the Crystal Structure of the Monomer VBIm-PF₆

Single crystal of the monomer molecule suitable for X-ray diffraction study was obtained in methanol and ethanol mixed solvent. We measured the crystal and molecular structure of the monomer molecule. Its molecular structural formula is shown in Figure 1 and the selected bond lengths and angles are given in Table I. Crystallographic data and refinement detail are listed in Table II.

The C13, C9 are almost in imidazole ring plane of the molecule (vertical distance of 0.017 and 0.007 Å, respectively). The N—C

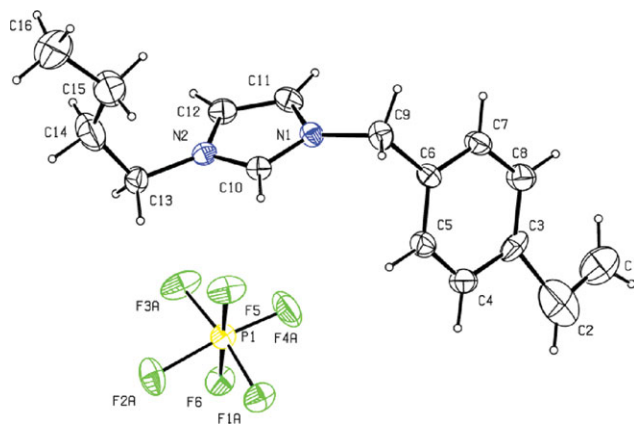


Figure 1. The molecular structure of VBIm-PF₆. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

Table I. Selected Bond Distances (Å) and Bond Angles (°) for VBIm-PF₆

Bonds	Bond lengths (Å) ^a	Bond angles	Bond angles (°) ^a
N(1)—C(9)	1.446(6)	N(1)—C(10)—N(2)	109.6(5)
N(1)—C(11)	1.354(7)	C(10)—N(2)—C(13)	125.7(5)
N(2)—C(10)	1.293(6)	C(9)—N(1)—C(10)	137.82(9)
N(2)—C(13)	1.456(6)		
N(1)—C(10)	1.325(6)		
N(1)—C(2)	1.409(5)		
N(2)—C(12)	1.351(6)		

^aThe numbers in parentheses stand for absolute errors.

Table II. Crystallographic Data and Refinement Details for VBIm-PF₆

Empirical formula	Fw	Crystal system	Space group	a (Å)	b (Å)	c (Å)	β (°)
C ₁₆ H ₂₁ F ₆ N ₂ P	386.81	Triclinic	P-1	9.695(3)	12.176(4)	16.597(6)	78.22(2)
V (Å ³)	Z	D _{calc} (g cm ⁻³)	Crystal size (mm ³)	F (000)	μ (mm ⁻¹)	θ range	Reflns collected
1906.1(12)	2	1.341	0.38 × 0.33 × 0.29	794	0.200	1.25–25.50	10202
Independent reflns	R(int)	Observed reflns [I > 2σ(I)]	R ₁ ; wR ₂ [I > 2σ(I)]	R ₁ ; wR ₂ (all data)	GOF (F ²)		
6950	0.0954	3097	0.0818, 0.2270	0.1442, 0.2693	0.998		

bond length in imidazole ring is 1.325(6), 1.354(7), 1.293(6), and 1.351(6) Å, respectively. The N1—C10—N2 bite angle is 109.6(5)°.

Silane Coupling Agent Monolayer Characterization

Introduction of 3-chloropropyltrimethoxysilane layer onto the micro/nanoscale CuO surface is very important to graft polymer chains from the surface as a linker between the substrate and polymer chains.

Figure 2 shows a typical XPS survey spectrum and high-resolution elemental scan of C_{1s}, Cl_{2p}, and Si_{2p} which were recorded from 3-chloropropyltrimethoxysilane modified micro/nanoscale CuO surface. Curve splitting proved the C_{1s} core-level spectrum included three peak components, respectively, at 283.8, 284.8, and 286.4 eV, attributable to the C—Si, C—H/C—C, and C—N. The presence of the Cl_{2p} and Si_{2p} peaks at the BEs of about 200.3 and 102.3 eV indicated that the silane coupling agent species had been successfully immobilized on the micro/nanoscale CuO surface.

Characterization of PVBIIm-PF₆ Modified Micro/Nanoscale CuO Surface Via a Surface-Initiated NMRP Reaction

XPS, SEM and contact angle analysis were respectively used to monitor the formation of the PVBIIm-PF₆ modified surface.

Figure 3 shows a typical XPS survey spectrum and high-resolution elemental scan of F_{1s}, P_{2p}, and N_{1s} of the PVBIIm-PF₆ modified micro/nanoscale CuO surface. The peaks located at

686.5, 136.4, and 401.7 eV were respectively attributable to F_{1s}, P_{2p}, and N_{1s} species. The molar ratio of [N] : [F] : [P] for the PVBIIm-PF₆ modified CuO surface was about 2 : 6.2 : 1 which was in fairly good agreement with the theoretical result. After PF₆⁻ was replaced by Cl⁻, F_{1s} and P_{2p} peaks disappeared and Cl_{2p} appeared, indicating that the counter anion PF₆⁻ had been successfully exchanged by Cl⁻ (Figure 4).

Figures 5 and 6, respectively, show SEM morphologies of flower-shape micro/nanoscale CuO surface before and after PVBIIm-PF₆ modifying. Obviously CuO film is composed of a large number of micro/nanoscale composition structures and shows a flower petal-like morphology. This micro/nanoscale composition structure and appropriate roughness was a main reason to show superhydrophobic property.¹⁷

According to the Refs. 18–20, the mechanism of the formation of flower petal-like CuO surface with a micro-nanoscale composition structure was inferred. In the presence of KOH, CuO was at first oxidized to Cu(OH)₂, and then Cu(OH)₂ dehydrated to form CuO nuclei. Follow-up Cu²⁺ ions were adsorbed on the nuclei, which resulted in the formation of large nano-petals. Alkali played an important role in formation of CuO nano-flowers. It was reported that OH⁻ influenced the anisotropic growth of CuO nanocrystals.²¹ The preferential adsorption of molecules and ions from solution on different crystal faces directed the anisotropic growth of nanoparticles by controlling growth rate along different crystal axis and OH⁻ ions kinetically controlled

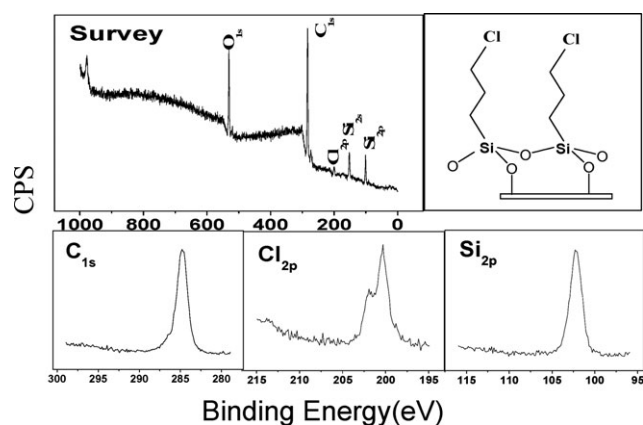


Figure 2. XPS survey spectrum and high-resolution elemental scan of Cl_{2p}, C_{1s} and Si_{2p} of 3-chloropropyltrimethoxysilane modified micro/nanoscale CuO surface.

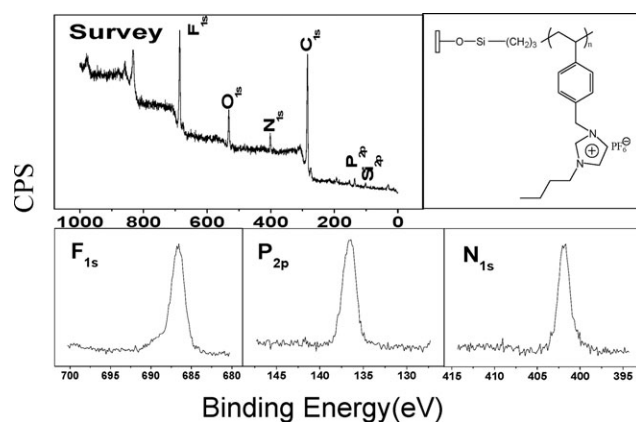


Figure 3. XPS survey spectrum and high-resolution elemental scan of F_{1s}, P_{2p}, and N_{1s} of the PVBIIm-PF₆ modified micro/nanoscale CuO surface.

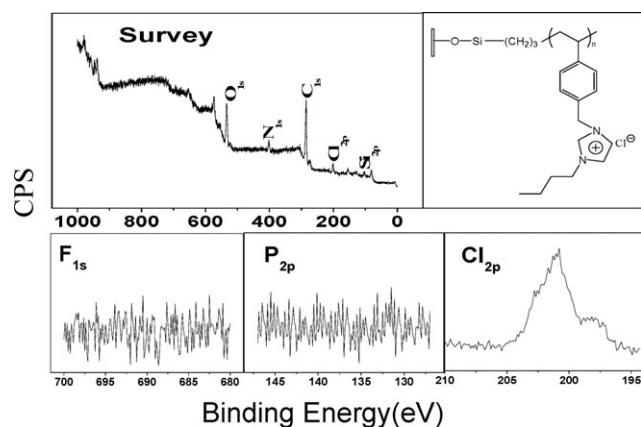


Figure 4. XPS survey spectrum and high-resolution elemental scan of F_{1s} , P_{2p} and Cl_{2p} of the PVBIm-Cl modified micro/nanoscale CuO surface.

the growth rate of specific faces through selective adsorption on these faces.^{22,23}

Figure 6 shows PVBIm- PF_6 film has completely and uniformly covered CuO nano-petals. Compared with bare CuO film the polymer-covered “flower leaves” became evidently thicker indicating that poly(ionic liquid) chains had been successfully grafted. It is just because of covering of PVBIm- PF_6 film of low surface energy that polymer modified CuO films show stronger hydrophobicity.

Figure 7 shows IR spectra of initiator and poly(ionic liquid) brush modified CuO surfaces. In the spectrum of the initiator modified substrate [Figure 7(a)], the peaks at 967 and 1192 cm^{-1} were attributed to Si—O stretching vibration. ATR-FTIR spectrum of PVBIm- PF_6 is showed in Figure 7(b). The strong peak appeared at 853 cm^{-1} was assigned to P—F stretching vibration and the peaks between 2800–3300 and 1554 cm^{-1} were characterization absorption peaks of the PVBIm cation. Compared with PVBIm- PF_6 modified surface, after PF_6^- ions were substituted by Cl^- ions an obvious change came from the disappearance of the characterization peaks of PF_6^- at 853 cm^{-1} .

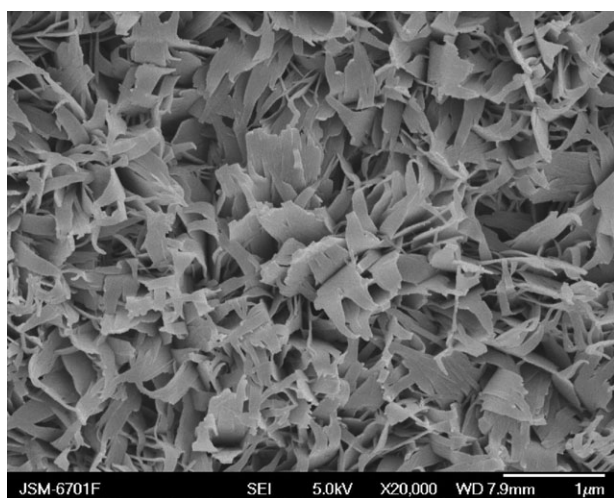


Figure 5. SEM image of the flower-shape micro/nanoscale CuO surface.

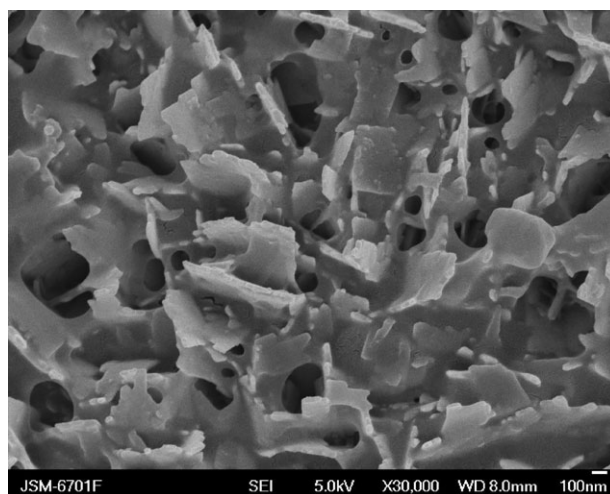


Figure 6. SEM image of the PVBIm- PF_6 modified micro/nanoscale CuO surface.

To prove that the polymerization of the functional IL monomers was a controlled process, we added free initiator in solution and used the homopolymer formed by free initiator in solution to monitor the surface grafted polymerization process. Considering the fact that the free and surface-grafted polymer molecules have the same molecular weight and molecular weight distribution, this treatment is reasonable.^{24–27} Figure 8(a) shows the linear relationship between $\ln([M_0]/[M])$ and the reaction time, where $[M_0]$ was the initial monomer concentration and $[M]$ was instantaneous monomer concentration. Figure 8(b) shows the dependence of molecular weight M_n and polydispersity index (M_w/M_n) of “free” PVBIm- PF_6 on the conversion of the VBlm- PF_6 monomer. The M_n of the “free” polymer increased linearly with the monomer conversion increasing and the polydispersity index was less than 1.4. The above results revealed that the graft polymerization of PVBIm- PF_6 on CuO substrate via NMRP was a controlled/“living” polymerization.

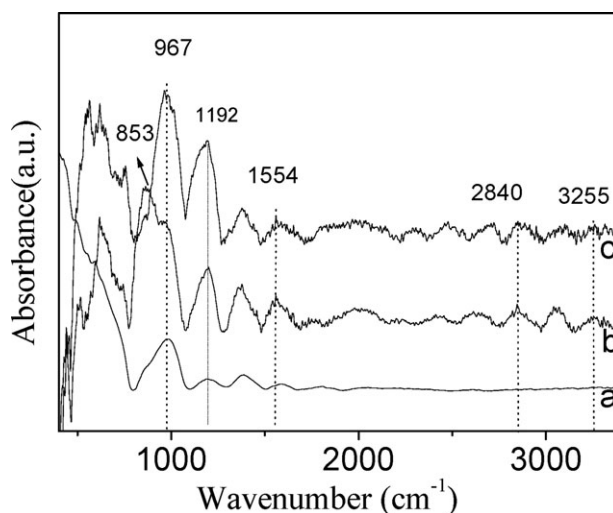


Figure 7. ATR-FTIR spectra of the initiator modified CuO surface (a), PVBIm- PF_6 modified CuO surface (b) and PVBIm-Cl modified CuO surface.

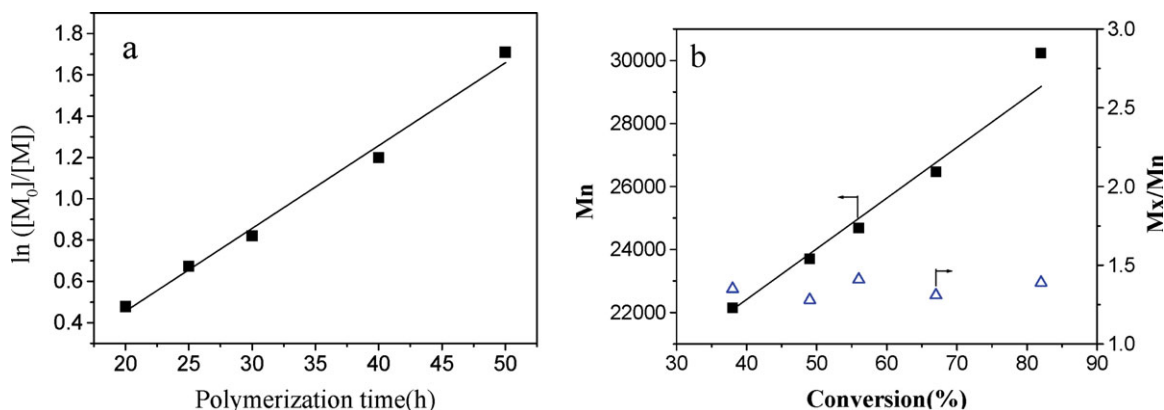


Figure 8. Relationships between $\ln([M_0]/[M])$ and the polymerization time (a) and between M_n of “free” PVBIIm-PF₆ formed in the solution and the monomer conversion (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Counter Anion Exchange and Reversible Wettability

According to the Ref. 28 for imidazolium IL, PF₆⁻ salts are hydrophobic and Cl⁻ salts are hydrophilic. So Cl⁻ was selected to exchange PF₆⁻ to induce a reversal of the surface wettability. The counter anion exchange and resulting reversible wettability behavior of the poly(ionic liquid) modified surfaces were confirmed by XPS and contact angle analysis. Figure 4 shows the typical XPS survey spectrum and high-resolution elemental scan of F_{1s}, P_{2p}, and Cl_{2p} of the PVBIIm-Cl modified micro/nanoscale CuO surface. Disappearance of the F_{1s} (686.5 eV) and P_{2p} (136.4 eV) peaks and appearance of the Cl_{2p} component at the BE of 200.8 eV indicated that the PF₆⁻ has been exchanged with Cl⁻. Through XPS analysis, it was found that the [N] : [Cl] ratio for the PVBIIm-Cl modified silicon surface was about 1.6 : 1, which was also in agreement with the theoretical result.

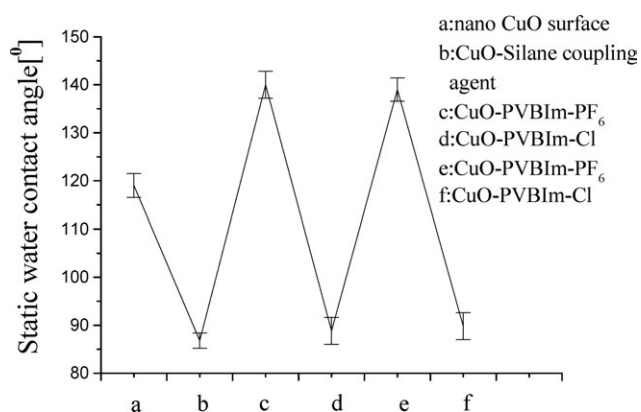


Figure 9. Changes of static water contact angles corresponding to various surfaces of copper substrates. The insets show six photographs of the shapes of water droplets on different surfaces.

Table III. Static Water Contact Angles Poly(ionic liquid) Modified CuO Surfaces

Samples	Reaction time (h)	Static water contact angle (°)
Bare CuO		120 ± 3
Silane coupling agent modified CuO		87 ± 3
PVBIIm-PF ₆ /CuO(1)	10	128 ± 3
		92 ± 3
PVBIIm-Cl/CuO(1)		
PVBIIm-PF ₆ /CuO(2)	20	132 ± 3
PVBIIm-Cl/CuO(2)		89 ± 3
PVBIIm-PF ₆ /CuO(3)	30	140 ± 3
		98 ± 3
PVBIIm-Cl/CuO(3)		
PVBIIm-PF ₆ /CuO(4)	40	139 ± 3
PVBIIm-Cl/CuO(4)		95 ± 3
PVBIIm-PF ₆ /CuO(5)	50	134 ± 3
PVBIIm-Cl/CuO(5)		91 ± 3

By contact angle analysis, we can find that the wettability can be easily reversed and tuned by simply counter anion exchange. When PF₆⁻ ions were substituted by Cl⁻ ions the static water contact angles changed from 140° to 98°.

Table III shows the changes of static water contact angles between PVBIIm-PF₆ and PVBIIm-Cl modified micro/nanoscale CuO surfaces at different time, it was clear that from 10 to 50 h, the changes were nearly the same (more than 40°). At 30 h, the water contact angle of PVBIIm-PF₆ modified surface was the biggest (about 140°). That is because the wettability depends on surface roughness and surface free energy. The water contact angle of unmodified flower-shape micro/nanoscale CuO surface was about 120°. With the polymerization time increasing from 10 to 30 h, the polymer chains gradually grew on the surface, which led to a decrease of the surface free energy and increase of the water contact angle. But, when the polymerization time exceeded 30 h, longer polymer chains would lay on the substrate surface to cause the surface roughness and water contact angle to reduce. Figure 9 shows when counter anions were sequentially exchanged again and again, the surface wettability maintained excellent reproducibility.

CONCLUSIONS

A double bond functionalized IL VBIIm-PF₆ was synthesized and its crystal and molecular structures were measured by X-ray single crystal diffraction method. Then, through a simple chemical oxidation procedure, micro/nanostructural flower-shape CuO surfaces were constructed on copper substrates. Finally, polymeric IL PVBIIm-PF₆ films were successfully grafted onto the micro/nanoscale CuO surfaces by a surface-initiated NMRP process using the newly synthesized IL as monomer. Kinetic studies revealed that the polymer chain growth from the surface was a controlled/"living" polymerization process. The surface with tunable wettability, reversible switching between hydrophilicity and hydrophobicity can be easily achieved by sequential counteranion exchange.

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