DOI: 10.1002/chem.200601340

Unusual Kinematics-Driven Chemistry: Cleaving C−H but Not COO−H Bonds with Hyperthermal Protons To Synthesize Tailor-Made Molecular Films

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Abstract: Unconventional reaction-design strategies have been developed to exploit the intriguing kinematics that occur when adsorbed organic molecules are bombarded by a beam of hyperthermal protons: kinematic energy transfer is only effective in H→H collisions and thus only C−H bonds are cleaved. This process yields a cross-linked molecular film with its chemistry governed by the selection of appropriate precursor molecules. Unlike the conventional wet-chemistry synthesis of cross-linked polymeric films, this new route uses no chemical initiators, additives, nor catalysts, and only requires a proton beam with a kinetic energy of a few electron volts in a dry-process mode compatible with molecular-device fabrication. The reaction designs are expressed unconventionally: reaction energy is tuned by the kinetic energy of the proton beam and reactant supply is controlled precisely by the proton fluence. However, conventional considerations such as bond-strength effects on kinematic outcomes and branching-ratio statistics are also important and they can extend the reaction applicability of the kinematics concept. For example, taking advantage of the fact that COO−H bonds are stronger than C−H bonds, we show, with practical reaction conditions, synthesis results, and surface analysis using X-ray photoelectron spectroscopy and atomic force microscopy, that we can break C−H bonds without breaking COO−H and other bonds, in the production of cross-linked molecular layers with any desirable COOH concentration and with no ester nor other chemical contaminations. The new reaction-design strategies are also applicable to the synthesis of molecular layers with other functionalities such as OH, and to the synthesis of a mixture of functionalities, such as OH/COOH, with a controllable concentration ratio.

Keywords: carboxylic acids · polymers · protons · surface analysis · thin layers

Introduction

The production of polymeric molecular devices[1] and biomedical devices[2] both demand the synthesis of thin layers of cross-linked molecules with specific chemical and mechanical properties, in addition to being able to manipulate electrons and photons in the former devices, and capture/release proteins and biological species in the latter. Driven by these demands, various molecular layers with specific chemical functionalities have been developed by a number of innovative chemical synthetic approaches that include, for example, forming carbon–carbon bonds by taking advantage of xanthates and related derivatives;[3] the application of organo-lithium compounds containing protected functional groups;[4] polymer grafting of molecular segments that have the required functionalities;[5] and addition of self-assembled monolayer (SAM) molecules with appropriate tail groups.[6] Although the latter approach gives precise control of molec-

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ular density, lattice structure, layer thickness, and chemical functionality, SAMs are delicate because their nature is governed by a balance of adsorption forces against very weak van der Waals bonds. In fact, many SAMs have relatively labile surface dynamics such that small perturbations in their chemical/physical environments can lead to phase changes or desorption. To circumvent this limitation, surface-initiated atom transfer radical polymerization (ATRP)[7] has been employed for cross-linking SAM molecules and thereby enhancing their stability. Other issues common to the wet-chemistry synthesis of tailor-made molecular layers are the requirements of aggressive reactants, chemical additives, and catalysts. These conditions are not desirable in electronic/photonic device fabrication processes, which are better suited to dry reactions with the smallest set of chemical reactants to reduce the risk of undesirable impurity incorporation and to improve the precision of process controls. To achieve precise control of chemical functionalities in molecular layers with a dry-process approach, one can activate the surface/precursor with excited inert gases,[8] supply unusual reactants in the form of hyperthermal mass-separated ion beams,[9–11] and synthesize specifically functionalized precursors for chemical vapor deposition.[12] As new molecular and biomedical devices are drawing increasing attention in both research and business, further development to facilitate their fabrication is desirable.

Recently, a new dry-process approach to synthesize molecular layers with tailor-made functionalities[13] was developed by using the concept of collision kinematics. Whereas a proton projectile of 10 eV hitting an adsorbed hydrocarbon precursor can transfer energy to a hydrogen target atom to break a C–H bond, the energy transfer to other heavier collision target atoms is ineffective and causes no further bond cleavage. Therefore, cross-linking the precursors by using this method preserves their chemical functionalities, while the mechanical properties of the resultant molecular film can be tuned by the proton fluence. More importantly, this proton-collision-induced cross-linking (PCIC) method requires no cross-linking agents, chemical additives, or catalysts, except hyperthermal protons that can be generated in a gas plasma. The concept and applications of this PCIC method in synthesizing molecular films have already been demonstrated both with ab initio quantum chemistry calculations and actual experiments.[13,14] In this article, we aim to explain the problems and their solutions for the exploitation of the PCIC method in synthesizing molecular films with chemical functionalities containing hydrogen. The impact is high because COOH, OH, NH_x, and SH are among the most important chemical functional groups, and the kinematics considerations in the PCIC method expect the recoil of hydrogen from both C–H and these X–H groups. Whereas rupturing hydrogen from C–H gives the desirable C–C cross-linking, rupturing hydrogen from these X–H groups may cause undesirable changes that compromise the merit of the PCIC method in preserving the chemical functionalities of the precursor molecules during the cross-linking process. In this article, we exemplify the reaction-design strategies with which these problems can be overcome. Examples of design considerations and feasibility validations are taken from our research on the synthesis of molecular layers with pure COOH functionality and any desirable COOH concentrations, because COOH is a versatile and very important hydrogen-containing functionality. We aim to show that by enriching the kinematics considerations of the PCIC method with other chemical reaction design considerations, such as reaction probabilities and the bond energy differences between C–H and COO–H, one can design PCIC reactions to cleave C–H bonds without cleaving COO–H bonds of adsorbed precursor molecules containing COOH. In addition to explaining the reaction strategies for the production of molecular films that have desirable COOH concentrations, we will also briefly reveal our on-going work on expanding the applicability of this reaction-design approach to the synthesis of other molecular films with tailor-made functionalities.

Results and Discussion

Advantages and disadvantages of exploiting kinematics in chemistry: The PCIC method is attractive, not because it yields new materials, but because it enables synthetic chemistry to be carried out by using reaction-design parameters[13,14] that are rather unusual to most chemists, that is, parameters that include projectile energy and fluence, projectile-target kinematics, collision cross-sections, collision-cascade volumes, other properties of the projectile beam, and properties of the adsorbed precursors. In the first approximation, the tenet of the PCIC method is collision kinematics of the proton projectile in a hydrocarbon matrix. As such, if the kinematics is effective in transferring energy to the hydrogen of a C–H unit to cleave the bond, the same physical process should also apply to the hydrogen atom of any COO–H, O–H, N–H, and S–H unit with the result of bond cleavage. Such undesirable/uncontrollable cleavages will lead to functionality contamination, such as the conversion of an alcohol to an ether and of a carboxylic acid to an ester. By taking an RCOO–H molecule as an example, the cleavage of the COO–H bond induces the generation of a carboxyl radical ($RCOO^{\bullet}$). One possible subsequent reaction is hydrogen abstraction as shown in Equation (1):

$$RCOO^{\cdot} + R'R''R^{\#}C{-}H \rightarrow RCOOH + R'R''R^{\#}C^{\cdot} \tag{1}$$

With this reaction, the COOH functionality is recovered. However, with the following Kolbe reaction[15] [Eq. (2)] in which a CO_2 molecule is released, the COOH functionality is destroyed:

$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2 \tag{2}$$

In addition, the recombination of carbon radicals can lead to either the formation of a C–C cross-link or the following ester formation in which the COOH group is also consumed

[Eq. (3)]:

$$RCOO^{\cdot} + R'R''R^{\#}C^{\cdot} \rightarrow RCOOCR'R''R^{\#} \qquad (3)$$

The occurrence of these reactions in the PCIC process was indeed confirmed by the PCIC of a ≈15 nm-thick poly(acrylic acid) (-$(CH_2CHCOOH)_n$-) film by using 10 eV protons. Poly(acrylic acid) was chosen as the model precursor because the COOH concentration is extremely high meaning that the degradation and loss of COOH can be measured with a high level of confidence. In fact, the X-ray photoelectron (XP) C 1s spectrum of the virgin film (Figure 1a) can be fitted, in accord with the well-accepted interpretation in the literature,[16] with three spectral components that can be assigned to $C^1H_2CHCOOH$ at 285.0 eV, CH_2C^2HCOOH at 285.5 eV, and CH_2CHC^3OOH at 289.2 eV. Any ester formation is easily tracked by using the XP C 1s spectrum of a poly(methylmethacrylate) (-$(CH_2CHCOOC^4H_3)_n$-) film as a reference (Figure 1b), because the ester is conspicuously shown by the spectral peak (C^4) at 286.6 eV, which is well resolved from the spectral peaks of the other three carbon atoms (C^1, C^2, and C^3) present in the poly(acrylic acid) film. The X-ray photoelectron spectroscopy (XPS) data also show that the carboxyl carbon in acrylic acid and in the ester are indistinguishable with both having a peak corresponding to C 1s at 289.2 eV (C^3 spectral peak).

Hence, in the presence of a mixture of acrylic acid and ester, the amount of acrylic acid can only be deduced by subtracting the C^4 spectral intensity from the C^3 spectral intensity because acrylic acid has C^3 but no C^4 whereas acrylic ester has an equal amount of C^3 and C^4. On the other hand, the total amount of COOH and COOR in such a mixture can be correlated to the C^3 spectral intensity. With this reference clarified, the ester formation in the poly(acrylic acid) film induced by PCIC with 10 eV protons as a function of proton fluence is clearly seen from the XP spectra of these PCIC-treated films as shown in Figure 1c–f, particularly with the films receiving high fluences of 1×10^{16} cm^{-2} (Figure 1e) and 2×10^{16} cm^{-2} (Figure 1f), both of which undoubtedly have the C^4 peak at 286.6 eV. In addition, the retention of COOH and the emergence of COOR as a function of proton fluence is shown in Figure 2. Clearly, the decrease in the concentration of COOH (referred to as [COOH] thereinafter) cannot be totally accounted for by the rise in [COOR], which indicates the loss of COOH by means of the Kolbe process.

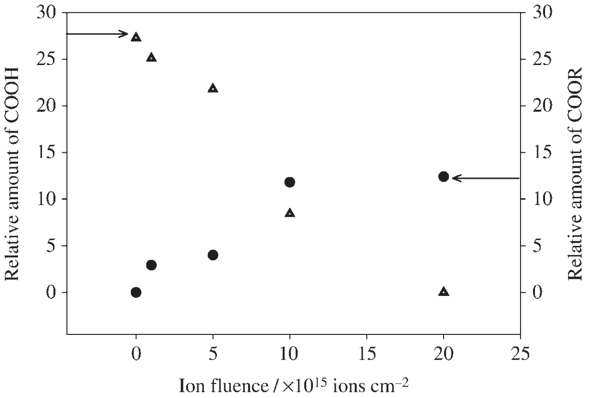

Figure 2. Consumption of carboxylic acid (▲) and formation of ester (●) as a function of fluence for PCIC with 10 eV protons.

Optimizing reactant supply: The first strategy to minimize COOH loss was proposed with the recognition that the bond strength[17] of COO–H (≈440–450 kJ mol^{-1}) is considerably higher than that of C–H (<400 kJ mol^{-1}). It is thus conceivable that the probability of breaking the COO–H bond is lower than that for C–H, and that the probability of recovering a broken COO–H bond by hydrogen abstraction is higher than that for C–H. As such, by controlling the supply of the proton projectiles, which is easily carried out by controlling the proton fluence in the PCIC method, one can have enough reaction products with cross-links without a significant loss of the COOH functionality. The effectiveness of this "reactant supply" strategy is demonstrated in Figure 1c and d in which the C 1s spectra of the films subjected to 10 eV proton bombardment show the retention of almost 100% of the COOH functionality after a proton fluence of 1×10^{15} cm^{-2} (Figure 1c) and more than

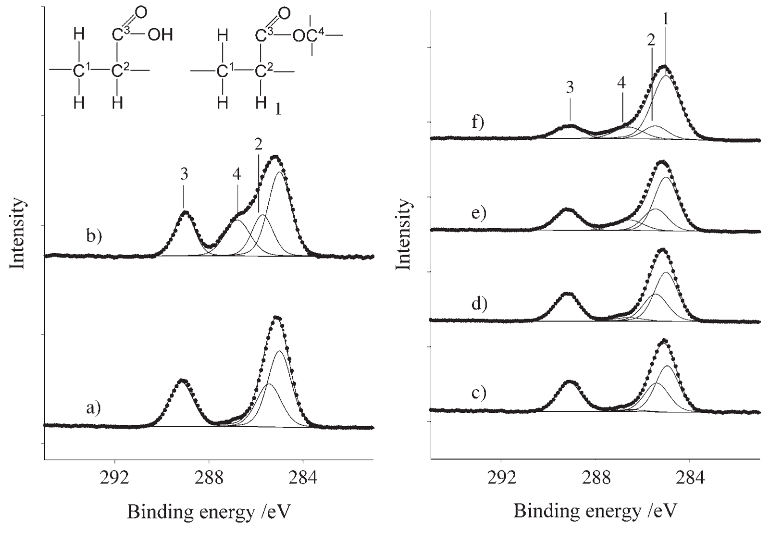

Figure 1. XPS C 1s core-level spectra of a) virgin poly(acrylic acid) film, b) virgin poly(methyl methacrylate) film, and poly(acrylic acid) films bombarded by 10 eV protons with different fluences: c) 1×10^{15}, d) 5×10^{15}, e) 1×10^{16}, and f) 2×10^{16} cm^{-2}.

80 % retention after a fluence of 5×10^{15} cm^{-2}. The degree of cross-linking is inevitably compromised in this reaction-design approach; but after the film dissolution test, which consists of soaking the bombarded film in organic solvents to remove any loosely bounded molecules, has been carried out, a coherent ≈8 nm-thick film is still obtained with the low proton fluence of 5×10^{15} cm^{-2}. Therefore, the formation of a stable cross-linked layer of poly(acrylic acid) with 80 % retention of the COOH functionality can indeed be achieved.

Optimizing kinetic energy: An alternative strategy was proposed to exploit the bond strength differences, with the expectation that lowering the proton projectile energy in the PCIC process may reduce the degree of COO–H cleavage more than that of C–H cleavage. The effectiveness of this second strategy is illustrated in Figure 3 in which the retention of the COOH functionality and the relative degree of cross-linking (% of film thickness after the film dissolution test) are plotted against projectile energy for a constant fluence of 2×10^{16} cm^{-2}.

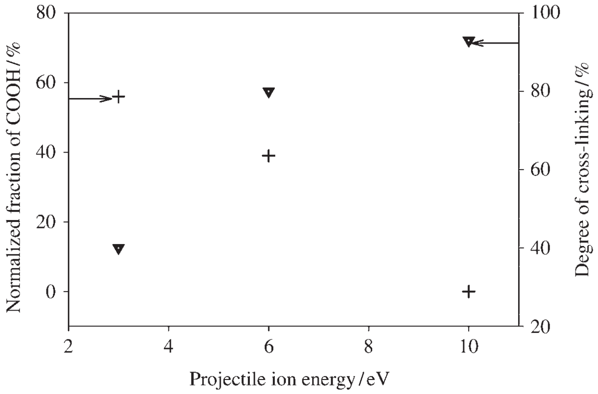

Figure 3. Effects of proton projectile energy on the retention of COOH (+) and the relative degree of cross-linking (▼) for PCIC of poly(acrylic acid) films with a proton fluence of 2×10^{16} cm^{-2}.

The results show that for PCIC with 10 eV protons at this fluence on a poly(acrylic acid) film that is ≈15 nm thick, a film of ≈11 nm thickness survives the film dissolution test but all COOH functionality is lost through the ester-formation pathway and the Kolbe reaction. In comparison, a reduction of the proton energy to 6 eV gave a cross-linked film that was ≈11 nm thick and with retention of 40 % of the original [COOH]. The results are thus far better than those with 10 eV protons. Although further reduction of proton energy can increase the COOH retention, the effectiveness of cross-linking becomes detrimentally compromised because the probability of C–H cleavage also drops rapidly when the proton energy is reduced below 5 eV, an effect that has already been illustrated in our earlier study[13] of PCIC of hydrocarbons.

In short, the strategy of "energy optimization" is indeed effective and the optimal proton energy for cross-linking the poly(acrylic acid) precursors is ≈6 eV. By further incorporating the strategy of optimizing reactant supply in the overall reaction design, we found that with a proton energy of 6 eV and a proton fluence of 5×10^{15} cm^{-2}, virtually all COOH functionality was retained and a coherent cross-linked film survived the dissolution test.

Optimizing precursor selection: In addition to these two strategies that take advantage of the bond strength differences, another strategy was proposed with the simple consideration of collision statistics. That is, if the precursor molecule in the PCIC process has a high number of C–H bonds per COO–H bond, the precursor can be cross-linked with a high probability of COOH retention. The effectiveness of this strategy is demonstrated in Figure 4 in which the C 1s spectra of a docosanoic acid ($CH_3(CH_2)_{20}COOH$) film before and after the PCIC treatment with 10 eV protons at 2×10^{16} cm^{-2} show no change in the COOH nature after being subjected to the PCIC treatment. Moreover, the film passes the dissolution test with nearly full retention of the original precursor film thickness.

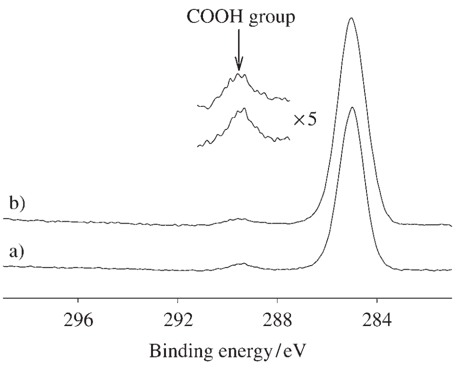

Figure 4. XPS C 1s core-level spectra of a docosanoic acid film a) before and b) after 6 eV proton bombardment with a fluence of 4×10^{15} cm^{-2}.

In this model analysis, there are 43 C–H bonds and only one COO–H bond in the precursor molecule. In comparison, the poly(acrylic acid) precursor has three C–H bonds per COO–H bond. Hence, by combining the three strategies proposed in this work, one can certainly design a viable PCIC process for the synthesis of cross-linked hydrocarbon films with any desirable concentration of COOH.

Synthesizing molecular films with low [COOH]: To further illustrate the applicability of the above reaction-design considerations, films with controllable COOH densities were synthesized and characterized. For example, docosanoic acid precursor molecules were spin-cast to a film thickness of ≈6.5 nm on a silicon wafer and then bombarded by 6 eV protons to a fluence of 4×10^{15} cm^{-2}. The PCIC-treated film survived the hexane dissolution test with a residual thickness of ≈6.0 nm, with no detectable XPS spectral change of the COOH signature. The contact angle of the virgin film was 83 ± 1° and that of the PCIC-treated film was 84 ± 1°; in comparison, the contact angle of the virgin and PCIC-treated films of dotriacontane ($CH_3(CH_2)_{30}CH_3$) were both 104 ± 1°. Hence, a cross-linked film was formed by using this PCIC reaction design, with full retention of the relatively low concentration of COOH functionality (1 COOH per 22 C atoms) and mild wettability. In addition, the virgin film was smooth (root-mean-square (rms) surface roughness of ≈1 nm) with a fractal morphology, and no changes to this nature were detected after the proton bombardment, as shown by the atomic force micrographs in Figure 5.

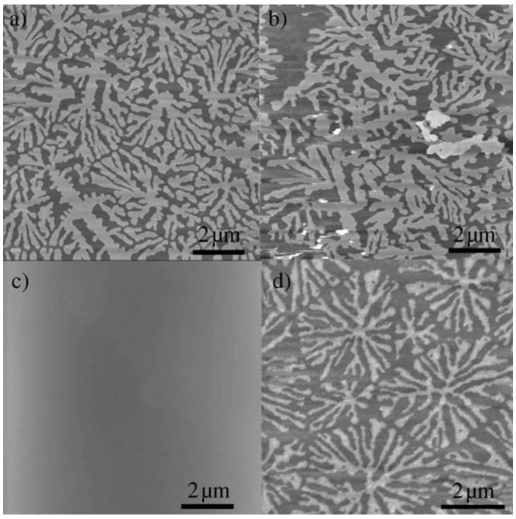

Figure 5. AFM images of docosanoic acid thin films showing: a) the morphology of the virgin film, b) shear tearing after repetitive AFM scanning, c) film dissolution by means of a hexane rinse, d) the morphologic and mechanical integrity of the film sequentially treated with 6 eV protons with a fluence of 4×10^{15} cm^{-2}, the hexane rinse, and repetitive AFM scanning.

One exception is that whereas the virgin film was mechanically weak to the extent that repetitive atomic force microscopy (AFM) scanning could tear the film (Figure 5b), the cross-linked film (Figure 5d) was mechanically strong enough to survive these shear perturbations even after the dissolution test. This gives qualitative evidence that mechanical properties can be tuned with the degree of cross-linking.

Synthesizing molecular films with high [COOH]: In another trial test, poly(acrylic acid) precursor molecules were spin-cast on a silicon wafer to a film thickness of ≈15 nm and were then bombarded by 6 eV protons to a fluence of 4×10^{15} cm^{-2}. The PCIC-treated film survived the hexane dissolution test with a residual thickness of ≈6 nm, with over 95 % COOH retention as determined from the XPS spectra. The contact angle of the virgin film was 16 ± 1° and that of the PCIC-treated film was 20 ± 1°. Hence, a cross-linked film was formed by using this PCIC reaction design, with nearly full retention of the extremely high concentration of COOH functionality (1 COOH per 2 C atoms) and surface hydrophilicity. In comparison, if an excessively high fluence of 2×10^{16} cm^{-2} of 6 eV protons is employed, the COOH retention drops to about 40 % and the contact angle rises to 50°. The result is further compromised if the proton energy is raised to 10 eV: almost all COOH groups are lost and the contact angle rises to 72°.

Conclusion

A dry reaction approach for the synthesis of cross-linked molecular films with tailor-made chemical and mechanical properties has been developed by exploiting the intriguing kinematics of proton–hydrocarbon collision and by optimizing the synthetic process as a function of proton fluence, proton energy, and precursor selection. The performance of the kinematics-driven synthesis of cross-linked molecular films with a controllable density of COOH can be optimized to achieve ≈100 % COOH retention and adequate mechanical strength. In addition, this approach requires no chemical initiators, additives, nor catalysts, hence, it is compatible with most device-fabrication technologies. In fact, we have already initiated a research program to exploit this approach for the development of new organic semiconducting films and devices. As for further development of the PCIC method, the design strategy considerations of the "COOH" pilot project are expected to be applicable to harnessing the cleavage of C–H bonds without any degradation of other hydrogen-containing functionalities such as OH and NH_x. Indeed, we have already obtained some preliminary results on OH to support this expectation. We are currently working on the synthesis of molecular films with a controllable concentration ratio of OH to COOH. An extension of the study to NH_x will be even more exciting as the availability of molecular films that have a controllable concentration ratio of NH_x/OH/COOH may open up new opportunities in biomedical research.

Experimental Section

Synthesis: The precursors used in the present experiments were docosanoic acid and poly(acrylic acid) (with an average molecular weight of 2000 g mol^{-1}). The compounds, supplied by Aldrich, were dissolved in chloroform and 2-propanol, to a concentration of 0.1 wt % for docosanoic acid and 0.3 wt % for poly(acrylic acid). The films were then formed by spin-casting on p-type silicon wafers. The proton-collision-induced reactions were carried out in a mass-separated low-energy ion beam system with protons at ion energies of 3, 6, 10, and 50 eV. Briefly, a hydrogen plasma was generated in an ion source and ions (H^+, H_2^+, and H_3^+) were extracted and focused to a mass filter. The mass-separated proton beam was decelerated prior to its arrival to the sample surface. Energetic neutrals were filtered by ion-beam bending. The pressure in the target chamber was maintained below $\approx 2\times10^{-8}$ torr during ion bombardment.

Characterization: A Kratos AXIS-HS X-ray photoelectron spectrometer equipped with a monochromatic $Al_{K\alpha}$ source was employed in this work for both the chemical composition analysis and film thickness analysis. The latter was determined by measuring the XPS intensity ratio of the C 1s peak to the Si 2p peak, a method that has been recently defined as the most accurate method for determining the thickness of a hydrocarbon molecular layer on silicon.[18] The binding energy data were calibrated by setting the Au $4f_{7/2}$ peak to 84.0 eV. The samples were also characterized by using AFM with a Nanoscope III AFM system (Digital Instruments, Santa Barbara, CA, USA) in the contact mode. The contact-angle data of the samples were collected by using a CA-XP Contact Angle Meter (Kyowa Interface Science, Japan).

Acknowledgements

This work was partially supported by the Department of Physics, the Chinese University of Hong Kong, the Research Grant Council of Hong Kong (grant no. CUHK4106/98P, CUHK401303), the National Natural Science Foundation of China (grant no. 20574058), and Surface Science Western, the University of Western Ontario in Canada.

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Received: September 19, 2006