

Self Assembled Monolayer Films of C₆₀ on O,O'-Bis(2-aminoethyl)dithiophosphate Modified Copper

Xiao Yu CHEN, Yu HAN, Ling QI, Zheng XU*

Coordination Chemistry Institute, the State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093

Lan Sun ZHENG

Department of Chemistry, Xiamen University, Xiamen, 361005

Abstract: On the surface of O,O'-bis(2-aminoethyl) dithiophosphate modified copper C₆₀ forms self-assembled monolayer films (SAMs) through the chemical bond. The film was characterized by contact angle, X-ray photoelectron spectroscopy, electrochemistry, TOF Mass Spectropy.

Introduction

Fullerene films exhibit a wide variety of interesting properties such as electronic conductivity¹, electrochemical and optical response². The first step of designing new fullerene based materials with novel and potential useful properties is rational organizing C₆₀ into well designed two- or three-dimensional films. Caldwell et al³ reported the self-assembly of C₆₀ onto Au surfaces with a preadsorbed monolayer of NH₂CH₂CH₂SH as a molecular tether. To strengthen the intensity of fullerene monolayer we use the O,O'-bis(2-aminoethyl) dithiophosphate as the molecular tether to modify the copper surface. The monolayer was characterized by contact-angle, X-ray photo electron spectroscopy, electrochemistry, TOF Mass Spectroscopy. These data confirm the formation of a tightly packed monolayer of fullerene on O,O'-bis(2-aminoethyl) dithiophosphate modified copper.

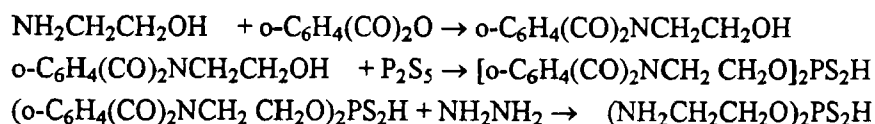
* To whom correspondence should be addressed.

Experiment

The treatment of copper: Polished copper was oxidized into black by H_2O_2 at the acid environment. The oxide surface was washed off in 10% H_2SO_4 , then washed with water and acetone.

The synthesis of O,O'-bis(2-aminoethyl) dithiophosphate:⁴

$\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ (1 mole) and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ (1 mole) were mixed and heated at 100°C to get $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NCH}_2\text{CH}_2\text{OH}$ (I). To 20 g I in 60 ml hot C_6H_6 was added 5.8 g P_2S_5 , the mixture was refluxed 3 hours and then 200 ml of dry ether was added to get $[o\text{-C}_6\text{H}_4(\text{CO})_2\text{NCH}_2\text{CH}_2\text{O}]_2\text{P(S)SH}$ (II), 84% yield, m.p. $123\text{-}4^\circ\text{C}$. To a suspension of 38.1 g II in 200 ml MeOH was added 24.5 g 98% hydrazin hydrate to get a solid mass which was dissolved in 1.8L hot MeOH, then filtered into 25 ml of piperidine and cooled to get 10.5g of O,O'-bis(2-aminoethyl) dithiophosphate, m.p. $173\text{-}4^\circ\text{C}$. Anal.: $(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{PS}_2\text{H}$. Calcd: C, 22.58; H, 6.24; N, 12.66. Found: C, 22.22; H, 6.02; N, 12.96.



Instrument and Measurement: The surface contact angle was measured with Rame Hart A-100 goniometer. X-ray photoelectron spectra were obtained with an MK-2 X-ray photoelectron spectrometer. Cyclic voltammetry was recorded with a BAS-100 electrochemical analyzer. TOF-MS measurement: The desorption and ionization were made by laser, detected by ion detector. TOF-MS spectrograph is consisted of accelerating potential, ion focusing potential, ion focusing lens and electronic multiplier. When the sample is put in high vacuum and exposed to focused laser pulse, a variety of positive and negative ion cluster are yielded. The laser's wavelength is 532nm with pulse width 7 ns and power density $10^7\text{W}/\text{cm}^2$. The system works in 10^{-6} torr vacuum and accelerating voltage is 1 KV. The yielded positive and negative ion cluster are detected by ion detector and treated by computer.

Results and Discussion

After a series of treatment, copper plate was washed with acetone and dried to get substrate A. The hydrophilicity of substrate A is obtained via contact angle measurement which is $\theta(\text{H}_2\text{O}) = 53^\circ$. Substrate A is soaked for 72 hours in a 1.0 mM ethanol solution of $(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{PS}_2\text{H}$. The resulting substrate is repeatedly washed with ethanol, dichloromethane and benzene to get substrate B, the contact angle of substrate B is θ

$\theta(\text{H}_2\text{O})=68^\circ$. X-ray photoelectron spectroscopy shows the signals of S(2p) and N(1s). The ratio of atoms for S and Cu is approximately 1.2:1, and for N and Cu is about 1.5:1. The TOF-MS of substrate B appears two peaks at m/e 16 and 139. The former is attributed to NH_2 fragment and the latter is attributed to the $\text{CH}_2\text{CH}_2\text{OPS}_2$ fragment. Based on above results and considered that dithiophosphate has strong coordination capacity with copper, we may suggest that $(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{PS}_2\text{H}$ coordinated to the surface of copper as a bidentate ligand and formed a monolayer film. As well know dithiophosphate usually acts as a bidentate ligand⁵ in the dithiophosphate metal coordination compound.

Substrate	$\theta(\text{H}_2\text{O})$	C(1s):S(2p)	E _{binding} (e)	E _{1/2} (V) _a	M+
A	53				
B	68	5.7	286.30		16,139
C	80	87	285.10	-1.16,-1.56	720

a:vs Fe/Fe⁺

Because fullerene reacts readily with primary and secondary amine⁶, the substrate B is soaked in a 1.0 mM benzene solution of C_{60} for 72 hours at room temperature. The resulting substrate was rinsed with benzene and dichloromethane thoroughly to remove residual physisorbed C_{60} to get substrate C. Due to the hydrophobicity of C_{60} , the contact angle $\theta(\text{H}_2\text{O})$ of substrate C increases to 80° . The X-ray photoelectron spectrum exhibits a large increase in the ratio of C(1s) to S(2p) upon C_{60} bonding which is from 5.7 (substrate B) to 87 (Substrate C). It is obvious that the carbon ratio in substrate C increases largely. The C(1s) electron binding energy is 286.30eV for substrate B and 285.10eV for substrate C. The later is close to that of C_{60} (285.14eV)⁷. The cyclic voltammetry of Substrate C exhibits two pairs of oxidation-reduction peaks. The two reduction peaks are at -1.16V and -1.56V (vs. Fe/Fe⁺). Compared with the $E_{1/2}$ of the first two reduction for unmodified C_{60} (-0.98V and -1.38V vs Fe/Fe⁺)³, substrate C's two reduction waves move toward negative 0.18V. The shifts of -0.18V respectively are consistent with a bond forming reaction between the self-assembled C_{60} and the underneath amine layer; With the addition of NH_2 to C_{60} , the negative charge increase on C_{60} leads to the negative moving of reduction wave of C_{60} . The TOF-MS of substrate C presents a strong peak at m/e 720. All above experiment results confirm that C_{60} has been tethered onto the surface of copper to form a SAMs by the molecule tether $(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{PS}_2\text{H}$.

Acknowledgement: This work was supported by the NNSF of China and the National Education Commission doctoral Foundation.

References

1. Hebard, A.F. et al. *Nature*, 350 (1991), 600.
2. Wang, X.K. et al. *J.B. Appl.Phys.Lett*, 60 (1992), 810.
3. Caldwell, W.B. et al. *Langmuir* 9 (1993), 1945.
4. Pierre C. and Jean C.M. *Compt.Rend.* 261(6) (group 8), 1965,1551-4.
5. Han Shiyin, Xu Zheng et al. *Acta.Chimica Sinica*, 4 (1988),302.
6. Andreas H. et al. *Angew.Chem.Int.Ed.Engl.* 30(1991) No.10 1309.
7. Dennis, L.L. et al. *Chem.Phys.Lett.* 176(2) (1991),203.

(Received 21 September 1996)