Chinese Chemical Letters Vol. 15, No. 10, pp 1233-1236, 2004
http://www.imm.ac.cn/journal/ccl.html

Covalently Attached Monolayer of Phthalocyanine on Chemically Modified Silicon Oxide Surface

Quan ZHOU[1], Hong Zheng CHEN[1,2]*, Jing Zhi SUN[2], Mang WANG[1,2]*, Duan Lin QUE[1]

[1]State Key Lab of Silicon Materials, Hangzhou 310027
[2]Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027

Abstract: Highly stable monolayers of 2,9,16,23-tetracarboxyl phthalocyanine on 3-aminopropyl-triethoxysilane (ATS) modified silicon and quartz substrates were prepared by reaction of carboxyl and amine. The monolayers were characterized by UV-Vis spectra and AFM measurements. The results indicated that the ultra-thin films on silicon or quartz were smooth, and the ordered structures were observed in these films.

Keywords: Monolayer, phthalocyanine, silicon, quartz, covalence.

In the past 26 years, probably there is no other single element, whose application has change the world more than that of silicon. Silicon-based organic-inorganic hybrid is one of the most important points of study right now, such as the modification of the silicon surface[1], building controllable ordered organic functional units on silicon[2], *etc*.. On the other hand, there have been great interests in self–assembled monolayers (SAMs) or multilayers in the past 15 years, because of their tremendous promise in applications in electronics, photonics, and optoelectronics[2-10]. Many articles reported on the self-assembled mono- and multilayers of organic semiconductors, and phthalocyanine (Pc) was one of them[2,9-10]. Most of such Pc films were anchored by attraction of opposite charges. In this paper, we report a kind of monolayer of Pc on silicon and quartz by covalence, which, as known is more stable than ionic bond, aiming at searching a way to fabricate silicon-based organic-inorganic hybrids.

P-Silicon (100) wafer and quartz substrates were sonicated with acetone, toluene, acetone, alcohol in turn first, then were put into 100℃ piranha solution (30% H_2O_2:H_2SO_4=30:70, V/V) for 2 hours, followed by rinsing them with deionized water (resistivity = 18MΩ) for three times. After drying, the substrates were put into a homemade reactor, submerged in the vapor of solution of 2 mL 3-aminopropyl-triethoxysilane (ATS) in 25 mL toluene for 5 h[11], then were sonicated with toluene and acetone, respectively. The pretreated substrates were finally put into saturated solution of 2,9,16,23-tertracarboxyl copper phthalocyanine (TCPc, synthesized according to the

---

* E-mail: hzchen@zju.edu.cn, mwang@zju.edu.cn

reference 13) in DMF at 150°C. After that, the substrates were sonicated with DMF and acetone in turn once more. The process is depicting in **Scheme 1**.

Si and quartz substrates with hydroxy groups on the surface were chemically modified by the reaction between the hydroxy and ATS *via* alkoxysilanes on silicon oxide, leading to form a monolayer of ATS on the surface of substrate. Since ATS bears a reactive terminal amine group, it can react with one carboxyl group locating on the outer side of phthalocyanine, resulting in another closely packed monolayer of TCPc on the modified surface of the substrate. It has been demonstrated that the resulting TCPc monolayer film is very stable as shown in UV/Vis spectra. The optical absorption keeps almost the same upon sonication.

Figure 1 shows the UV-Vis spectra of TCPc monolayer on quartz and TCPc diluted solution in DMF obtained on the Beckman-DU50 UV-Vis spectrophotometer. The spectrum of TCPc on quartz is almost identical to that of TCPc in solution with the three characteristic absorption bands of phthalocyanine at 340.64 (Soret band) as well as 631.13 and 685.52 nm (Q-band), indicating TCPc has indeed bonded to the surface of substrate. The Q-band of TCPc monolayer is red-shifted 15 and 3 nm, respectively, relative to those in the diluted solution, which can be attributed to the interactions between neighboring phthalocyanine molecules, a crystalline behavior of TCPc monolayer[12]. It is noticed that the absorbance at 631.13 nm is about 0.007, very close to the reported one (0.008) from the

Scheme 1

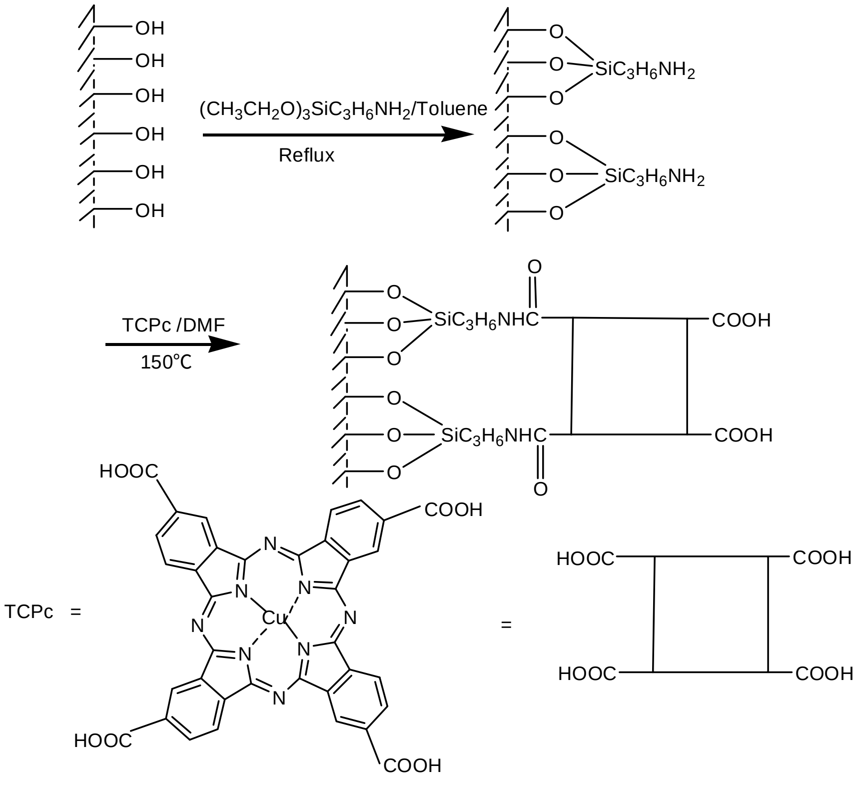


Figure 1 UV/Vis spectra of TCPc monolayer on quartz (a) and TCPc solution in DMF (b, the absorption intensity is reduced by 1/10)

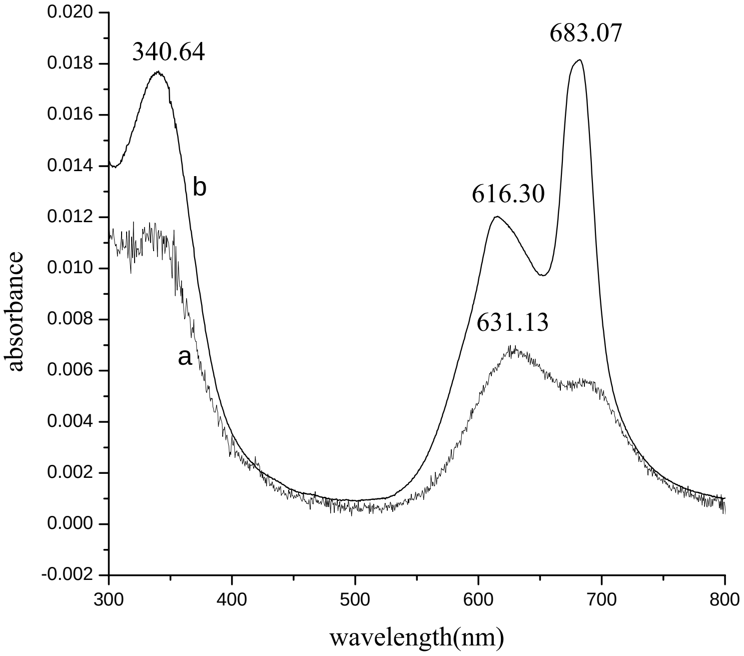
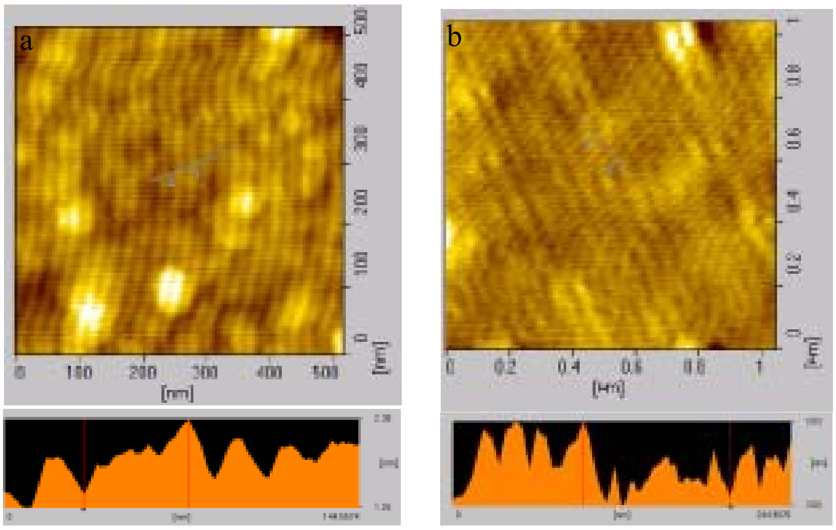


Figure 2 AFM images of (a) TCPc-silicon and (b) TCPc-quartz



macrocycle monolayer[2], demonstrating monolayer of TCPc to be on the modified surface of substrate indeed.

AFM images of TCPc monolayer on silicon and quartz substrates obtained on SFM (SEIKO, SPI3800N) are shown in **Figure 2**. The films look homogeneous, and TCPc monolayer surface on quartz appears more smooth than that on silicon wafer, with a roughness on the whole area of 7Å for TCPc-quartz and 9 Å for TCPc-silicon. The difference in surface roughness may come from different order degree of SiO_2 on the surface of quartz and silicon substrates. The ordered structures are also observed in these films.

In conclusion, highly stable and ordered TCPc monolayers on ATS modified silicon and quartz substrates were obtained *via* alkoxysilane on silicon oxide, providing an approach for silicon-based organic-inorganic hybrids fabrication.

Acknowledgments

This work was financed by the National Natural Science Foundation of China (Nos: 50225312, 90201009), and also partly supported by the fund for the doctoral program from the Education Department.

References

1. M. P. Stewart, J. M. Buriak, *Comments on Inorganic Chemistry*, **2002**, *23*, 179.
2. V. Huc, *et al*., *Langmuir*, **2001**, *17*, 1928.
3. G. Decher, *Science*, **1997**, 277, 1323
4. D. M. Kaschak, *J. Am. Chem. Soc.*, **1999**, *121*, 3435.
5. J. W. Ostrander, *J. Am. Chem. Soc.*, **2001**, *123*, 1101.
6. Y. J. Liu, *J. Phys. Chem.* B, **1997**, *101*, 1385.
7. D. Q. Li, *J. Am. Chem. Soc.*, **1998**, *120*, 8797.
8. Y. J. Liu, *J. Appl. Phys*., **1999**, *85*, 419.
9. J. Linlock, *Chem. Mater*., **2003**, *15*, 1404.
10. Y. Q. Fu, *Analytica Chimica Acta*, **2002**, *455*, 61.
11. J. Sagiv, *J. Am. Chem. Soc*., **1980**, *102*, 92.
12. K. Y. Law, *Chem. Rev.*, **1993**, 93, 449.
13. Y. F. Yu, *Science & Technology in Chemical Industry*, **1999**, *7*, 21.

Received 18 August, 2003