

# Exploitations of Novel Spectroscopic Methods for Material and Surface Science

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### Keywords

X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism

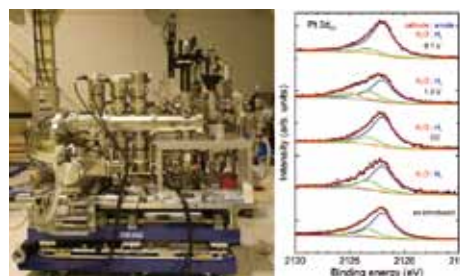
For the developments of novel functional materials, it is quite important to exploit new characterization methods based on advanced technology simultaneously. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using synchrotron radiation and lasers.

The first topic is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism photoelectron emission microscopy, which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed in situ x-ray magnetic circular dichroism (XMCD) system using a ultrahigh vacuum superconducting magnet and a liq. He cryostat. The XMCD apparatus is widely open for public usage and many researchers even from abroad visit every year. We are currently interested in metal phthalocyanine monolayers on nonmagnetic and ferromagnetic surfaces, whose electronic and magnetic properties are tunable by changing the central metal atom and/or modifying the ligand. Our recent achievement concerning vanadyl phthalocyanine will be presented in the next page.

The second topic is the exploitation of ambient pressure

hard x-ray photoelectron spectroscopy (XPS) for polymer electrolyte fuel cells (PEFC) under working conditions. We have successfully installed ambient pressure (up to 3000 Pa) hard x-ray photoelectron spectrometer (Figure 1). We have designed in situ fuel cells under working conditions and have successfully recorded Pt 3d XPS (Figure 1) of Pt/C and PtCo/C cathode catalysts in PEFC.

Furthermore, we have just started the third topic of the picosecond time resolved x-ray absorption fine structure (XAFS) spectroscopy. The installation of a picosecond laser system was completed and the performance test using a short-lived photoexcited metal complex was successful.



**Figure 1.** Ambient pressure hard x-ray photoelectron spectrometer (left) and typical Pt3d spectra from the Pt/C cathode catalyst in PEFC (right).

### Selected Publications

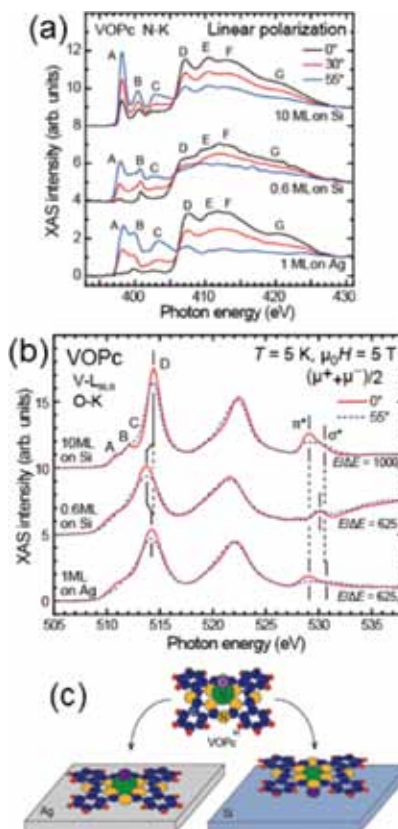
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## 1. Structural and Magnetic Properties of Submonolayer Vanadyl Phthalocyanine<sup>1,2)</sup>

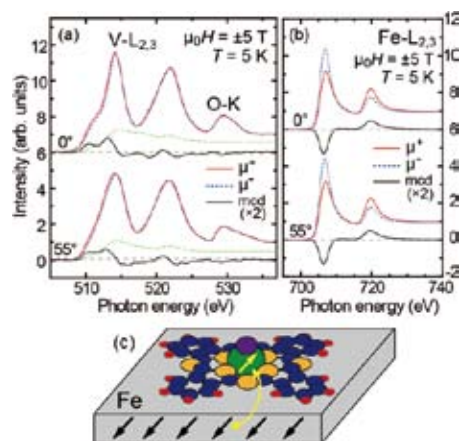
Controlling a wide range of functionalities of metal complexes on substrate surfaces for the applications such as molecular spintronics, molecular devices, and molecular catalysis is of special importance. Metal phthalocyanine (MPc) is one of the most promising materials. Although extensive studies on late 3d transition metal Pc monolayers on metal surfaces have been reported, much less investigations have been conducted on early 3d transition metal Pcs. We have studied structural and magnetic properties of vanadyl phthalocyanine (VOPc) on Si(111) and Ag(111) single crystal surfaces and also ferromagnetic ultrathin Fe, Co and Ni films grown epitaxially on Cu(001), by means of soft x-ray absorption spectroscopy and x-ray magnetic circular dichroism using our synchrotron radiation facility UVSOR-III and other surface scientific methods.

Figures 2(a) and 2(b) show the N and O K-edge x-ray absorption spectra of 10 monolayer (ML) VOPc on Si(111), 0.6 ML VOPc on Si(111) and 1 ML VOPc on Ag(111). From these spectra, it is concluded that the adsorbed submonolayer VOPc is lying flat on both the surfaces and that on Si(111) the VOPc molecule adsorbs with the oxygen downward configuration due to the formation of the Si–O–V bond, while on Ag(111) the oxygen-up configuration is preferred because of a stronger interaction between Ag and the Pc  $\pi/\pi^*$  orbitals. This is the first experimental proof for the oxygen-down configuration of MOPc on semiconductor surfaces, consistent with the theoretical prediction on the VOPc/GaAs system.

Figure 3 shows the V and Fe L-edge XMCD spectra of monolayer VOPc on 3 ML Fe films grown epitaxially on Cu(001). The Fe film exhibits perpendicular magnetic easy axis. The V  $L_{III}$ -edge signals are found to be reversed compared to the Fe ones; namely the V magnetic moment is antiparallel to the magnetic field. This indicates that the magnetic interaction between VOPc and Fe is antiferromagnetic even under  $\pm 5$  T. The V L-edge spectra of VOPc on the Co film (not shown) reveal that the interaction between VOPc and Co is again antiferromagnetic, though the coupling seems to be considerably weaker. On the contrary, VOPc on the Ni films exhibits inherent paramagnetism without noticeable magnetic interaction between VOPc and Ni. This is consistent with a previous theoretical study that concluded much longer spacing between MPc and Ni than Fe and Co. The present observation of antiferromagnetic coupling between MPc and the ferromagnetic films is quite rare and VOPc should be a possible candidate for molecular magnetic devices to preserve or enhance the ferromagnetism of the substrate metals. Since VOPc itself seems to show the perpendicular easy axis with respect to the molecular plane, this molecule could be also suitable for perpendicular magnetic anisotropy.



**Figure 2.** (a,b) N K-edge (a) and V L- and O K-edge x-ray absorption spectra of multilayer VOPc on Si(111), 0.6 ML VOPc on Si(111) and 1 ML VOPc on Ag(111). (c) Schematic structural views of adsorbed VOPc on Ag(111) and Si(111) surfaces.



**Figure 3.** (a,b) V and Fe L-edge x-ray magnetic circular dichroism spectra of monolayer VOPc on 3 ML Fe films grown on Cu(001) recorded at  $T = 5$  K and  $H = \pm 5$  T. (c) Schematic views of antiferromagnetic interaction between VOPc and the Fe film.

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