Electronic Supplementary Information for

Coordination reaction between tetraphenylporphyrin and nickel on a TiO_2(110) surface†

Cici Wang,[a] Qitang Fan,[a] Shanwei Hu,[a] Huanxin Ju,[a] Xuefei Feng,[a] Yong Han,[a] Haibin Pan,[a] Junfa Zhu,[*a] and J. Michael Gottfried[*b]

[a]*National Synchrotron Radiation Laboratory and Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei, 230029, P. R. China, jfzhu@ustc.edu.cn.*
[b]*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-St., 35032 Marburg, Germany, michael.gottfried@chemie.uni-marburg.de.*

Experimental conditions

The experiments were performed in two separate ultrahigh vacuum systems, which have been described in detail previously.[1] The XP spectra were acquired in the photoemission endstation at beamline U20 in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The photoelectrons were detected at an angle of 70° with respect to the surface normal. Mg Kα (1253.6 eV) was used to probe C 1s and N 1s core levels. Ni $2p_{3/2}$ spectra were taken by Al Kα (1486.6 eV) to avoid the overlap with the signal from Ti KLL. All binding energies (BEs) were calibrated with respect to Au $4f_{7/2}$ (BE = 84 eV) which was measured from the Au foil under the sample after each spectrum. To obtain better agreement, the fits of N 1s XP spectra include an additional satellite peak (at 399.9 eV) to account for shakeup processes.[2] In the fit, the peak intensity of pyrrolic nitrogen (–NH–) is equal to the sum of iminic nitrogen (=N–) and satellite peak. The STM experiments were carried out in a SPECS STM 150 Aarhus with SPECS 260 electronics. All given voltages were applied to the sample and the images were taken in constant-current mode using a tungsten tip. The STM images were processed with WSxM software.[3]

A one-side polished rutile TiO_2(110) sample (10 × 10 × 0.5 mm^3, Princeton Scientific) was cleaned by several cycles of Ar^+ sputtering and annealing at 900-1000 K for 30 minutes in UHV. 2HTPP and NiTPP (purity > 98%, Porphyrin Systems GbR) were degassed in vacuo at 450 K for 24 h. Their monolayers were prepared by vapor deposition of multilayers onto TiO_2(110) held at room temperature and subsequently heating to 550 K. Ni (purity > 99.999%) was evaporated from a Knudsen cell evaporator with a boron nitride crucible. The evaporation rates (2HTPP, NiTPP: 0.35 ± 0.01 Å/min; Ni: 0.04 ± 0.01 Å/min.) were estimated from the attenuation of the Au 4f XPS peak intensity when molecules or Ni atoms were directly deposited onto an Au foil sample.

In this work, the term "monolayer" is used to characterize a closed layer of molecules in direct contact to the substrate surface. The coverage θ is defined as the number of adsorbed molecules divided by the number of TiO_2(110)-(1x1) surface unit cells (2.96 Å × 6.49 Å). According to monolayers of 2HTPP and metallotetraphenylporphyrins on Ag (111) (θ = 0.037)[4] and the surface density of TiO_2(110) surface unit cells (5.2×10^{14} unit cells per cm^2)[5], the coverage corresponding to one monolayer of 2HTPP or NiTPP on TiO_2(110) is θ =0.0985.

Table S1. Degree of metalation between 2HTPP and Ni obtained from XPS and STM experiment.

Post-deposited Ni	XPS (%)	STM (%)
Ni/2HTPP =1:1	35 ± 5	32 ± 8
Ni/2HTPP =2:1	53 ± 5	40 ± 8
Ni/2HTPP =3:1	60 ± 5	44 ± 8
After heating to 550 K	60 ± 5	44 ± 8
Pre-deposited Ni	XPS (%)	STM (%)
Ni/2HTPP =1:1, after heating to 550 K	60 ± 5	53 ± 8

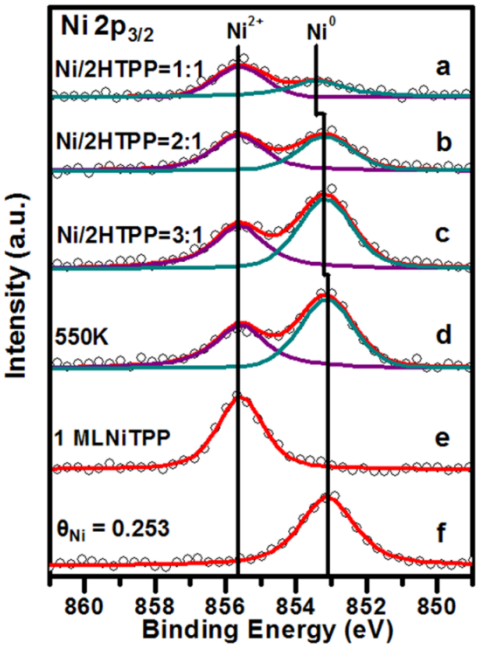

Figure S1. Ni $2p_{3/2}$ XP spectra of (a-c) deposition of increasing amounts of Ni on a monolayer of 2HTPP on TiO_2(110)-1×1, the ratio of Ni/2HTPP is 1:1, 2:1, 3:1 at 300 K; (d) after heating sample (c) to 550 K; (e) a monolayer of NiTPP on TiO_2(110)-1×1 and (f) θ_{Ni} = 0.253 on TiO_2(110)-1×1 for comparison. All Ni deposition was performed at 300 K.

References

1 (a) Y. Pan, Y. Gao, D. Kong, G. Wang, J. Hou, S. Hu, H. Pan and J. Zhu, *Langmuir*, 2012, **28**, 6045; (b) Q. Fan, C. Wang, Y. Han, J. Zhu, W. Hieringer, J. Kuttner, G. Hilt and J. M. Gottfried, *Angew. Chem., Int. Ed.*, 2013, **52**, 4668.

2 Y. Li, J. Xiao, T. E. Shubina, M. Chen, Z. Shi, M. Schmid, H.-P. Steinrück, J. M. Gottfried and N. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 6401.

3 I. Horcas, R. Fernández, J. M. Gómez-Rodriguez, J. Colchero, J. Gómez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705.

4 (a) T. Lukasczyk, K. Flechtner, L. R. Merte, N. Jux, F. Maier, J. M. Gottfried and H.-P. Steinrück, *J. Phys. Chem. C*, 2007, **111**, 3090; (b) F. Buchner, V. Schwald, K. Comanici, H.-P. Steinrück and H. Marbach, *ChemPhysChem*, 2007, **8**, 241; (c) F. Buchner, K. Flechtner, Y. Bai, E. Zillner, I. Kellner, H.-P. Steinrück, H. Marbach and J. M. Gottfried, *J. Phys. Chem. C*, 2008, **112**, 15458.

5 A. W. Grant and C. T. Campbell, *Phys. Rev. B*, 1997, **55**, 1844.