X-ray photoelectron spectroscopy of transition metal ions attached to the surface of rod-shape anatase TiO₂ nanocrystals

Ajay Sathe,[|] Matthea A. Peck,^{||} Choumini Balasanthiran,[‡] Marjorie A. Langell,^{||} Robert M. Rioux,^{*†} James D. Hoefelmeyer^{*‡}

[‡] *Department of Chemistry, University of South Dakota, 414 E. Clark St., Vermillion, SD 57069*

^{||} *Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304*

[†] *Department of Chemical Engineering, The Pennsylvania State University, 165 Fenske Laboratory, University Park, PA 16802-4400*

[|] *Department of Chemistry, The Pennsylvania State University, 102 Fenske Laboratory, University Park, PA 16802-4400*

* Authors to whom correspondence should be addressed: rioux@engr.psu.edu; james.hoefelmeyer@usd.edu

Abstract

X-ray photoelectron spectra were obtained for a series of M-TiO₂ samples in which transition metal ions are directly attached to the surface of anatase TiO₂ nanocrystals. The samples were prepared using CrCl₃.nH₂O, MnCl₂.nH₂O, FeCl₂.nH₂O, CoCl₂.nH₂O, NiCl₂.nH₂O, and CuCl₂.nH₂O as metal sources. We observed spontaneous air oxidation of the metal for the Mn-TiO₂ and Fe-TiO₂ samples as indicated by rapid color changes. X-ray photoelectron spectroscopy (XPS) data confirms the oxidation states of the metals Cr, Co, and Ni are unchanged from the precursor, Mn and Fe are oxidized, and Cu is in a more reduced state. The reduction of Cu likely arises during the XPS experiment – a phenomenon well-documented in the literature; whereas UV-visible data of the Cu-TiO₂ dispersions are consistent with Cu²⁺.

Introduction

There is much interest in the development of solar fuels catalysts that utilize earth-abundant materials.¹⁻⁴ Recently it has been demonstrated that first-row transition metal redox couples paired with a polyprotic acid give rise to self-healing films that are highly active water oxidation catalysts.^{5,6} The systems developed so far are cobalt/phosphate and nickel/borate, and are particularly inspiring due to the abundant feedstocks, ease of fabrication of the catalyst, robust nature of the catalyst, and high activity. Such films have been incorporated into wireless photoelectrochemical cells (PECs) that consist of a triple-junction Si-based solar cell on a steel backing modified with a thin film of Ni-Mo-Zn alloy.^{7,8} The alloy was yet another innovation in that this material catalyzes proton reduction at neutral pH with low-overpotential and utilizes earth-abundant metals. The opposing side of the cell has the layer of metal/polyprotic acid thin film. The device is capable of complete stoichiometric water splitting under solar irradiation with a yield of 4.7%. Further improvements to the surface catalysts can contribute substantially to better device performance, and development of earth-abundant, low-overpotential water oxidation catalysts has been a major bottleneck in photoelectrochemical cells.⁹ Reduction of film thickness from the micron to <5 nm range has advantages that there is no porosity to inhibit mass transport reactants and products, the electrocatalyst conductivity does not influence the

catalyst overpotential, and the interfacial interactions of the catalyst with solution or semiconductor do not contribute significantly to the overpotential.¹⁰ To this end, the water oxidation activity of NiO_x, CoO_x, Ni_yCo_{1-y}O_x, Ni_{0.9}Fe_{0.1}O_x, IrO_x, MnO_x, and FeO_x ~2-3 nm film catalysts has been quantified and compared. The Ni_{0.9}Fe_{0.1}O_x catalyst was especially active with turnover frequency two orders of magnitude higher than IrO_x. In addition to thin film electrocatalysts, single site molecular catalysts have been explored. A homogeneous inorganic catalyst, [Co₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ exhibited a turnover frequency for water oxidation that is comparable in activity to a ~2-3 nm film CoO_x catalyst.^{10,11} Single site Co²⁺ was recently shown to exhibit substantially higher activity than Co₃O₄ clusters.¹² Based on these findings, the investigation of single site first-row transition metal ions could be promising for development of earth-abundant solar fuels catalysts.

We have taken an interest in the development of new materials that feature transition metal ions attached to high surface area, solution processable nanocrystals for applications in photocatalysis. To this end, we have recently reported a facile method to attach transition metal ions to the surface of oleic acid stabilized rod-shape anatase TiO₂ nanocrystals.¹³ That report followed our initial discovery that Co(II) ions could attach directly to the surface of oleylamine stabilized rod-shape brookite TiO₂ nanocrystals, and that the material exhibited an increase in turnover frequency for the degradation of 5,8-dihydroxy-1,4-naphthoquinone under visible light irradiation in comparison to nanocrystals without Co(II) ions.¹⁴ Our experimental investigations have a parallel theoretical project to understand the electronic structure and dynamics of photogenerated charge-carriers in anatase TiO₂ nanomaterials^{15,16} doped with metal ions on the surface.¹⁷⁻²¹ In these systems, the frontier electronic orbitals are localized on the transition metal dopant ions. Photodynamics simulations show that photogenerated charge carriers become localized on the transition metal ion dopant upon relaxation. Interestingly, the electron and hole localize on the dopant ion at different times. Absolute knowledge of the oxidation state of the dopant ion is critical input to the computational models. The energies of the d atomic orbitals associated with the dopant metal are dependent on the identity of the transition metal and its oxidation state. Furthermore, the rate of energy dissipation is influenced by surface charge.

Our preparation of M-TiO₂ samples involves the addition of metal chloride hydrates to TiO₂ nanocrystals in high temperature non-polar media in which oleylamine assists in the transport of the metal ions in solution and adsorption on the nanocrystal surface. While the oxidation states of the metals in the starting materials are known (Cr³⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺), it should not be assumed they remain unchanged in the isolated solid product. Moreover, we have observed spontaneous color changes in air when the Mn or Fe metalated samples are taken from N₂ atmosphere to air. So far, information regarding the oxidation states of the metal ions attached to the surface of the TiO₂ nanocrystals is limited. Herein, we report X-ray photoelectron spectroscopy (XPS) data for M-TiO₂ samples. In prior studies of metal ions grafted onto the surface of TiO₂, XPS proved to be an important characterization tool. For example rutile or anatase TiO₂ powders were grafted with Cr(III),²² Fe(III),^{23,24} or Cu(II)²⁵ and evaluated as photocatalysts. Visible light irradiation of the grafted samples induces interfacial charge transfer from the metal to the conduction band of the TiO₂, and the materials were highly active for the decomposition of 2-propanol in visible light. In these studies, XPS data allowed assignment of the metal oxidation states that supported the catalyst description as metal ions grafted to the support.

Experimental

TiO₂ nanocrystals (rod shape, anatase, [001] growth direction, oleic acid stabilized) were prepared according to the literature.²⁶ Metalation of TiO₂ nanocrystals was described elsewhere.¹³ Briefly, metal chloride hydrate, oleylamine, and oleic acid stabilized rod-shape anatase TiO₂ nanocrystals were combined in 1-octadecene under N₂ atmosphere and heated at a specific metal-dependent time-temperature combination in order to adsorb metal ions on the TiO₂ surface. All samples were prepared with 5% metal content. UV-Visible absorption spectra were recorded with Cary 50-Bio UV- Visible spectrophotometer.

XPS@PSU: The XPS data were collected using a Kratos Axis Ultra XPS with a monochromatic Al K α X-ray source operated at 14 kV, 20 mA in hybrid slot mode. The samples were allowed to dry in air and were ground into a powder with a mortar and pestle. The powder samples were pressed onto double-side Scotch tape secured to a 100 mm² Si wafer, and loose powder was blown off with a jet of dry N₂ before being loaded into the instrument. The survey scans were done using a pass energy of 80 eV, with a 0.5 eV step size and 150 ms dwell time. The high resolution scans were done using a pass energy of 20 eV and a step size of 0.1 eV.

XPS@UNL: The XPS data were collected with an Omicron Nanotechnology EA 125 Hemispherical Energy Analyzer in the pulse-count mode and photoemission was initiated with an Mg K α (1253.6 eV) radiation using a Physical Electronics 04-548 dual Mg/Al anode. The samples were dispersed in hexane, dropcast onto Al foil, and allowed to dry before being mounted on the manipulator and loaded into the vacuum chamber. Two specimens of each sample were scanned to ensure sample uniformity. Sample data were collected in the 2-3 $\times 10^{-9}$ Torr range. The survey scans were done using a pass energy of 50 eV. The high resolution scans were done using a pass energy of 25 or 50 eV, step size of 0.1 eV, and dwell time of 250 ms.

All XPS spectra were calibrated by setting the C 1s peak equal to 284.6 eV. A Shirley background²⁷ was removed prior to curve fitting with the freeware program XPSpeak 4.1.²⁸ XPS Spectra were fit with the minimum number of peaks required to reproduce the spectral features with a 60% Gaussian/40% Lorentzian peak shape using a Gaussian-Lorentzian product function.

Results and Discussion

The M-TiO₂ samples contain the elements H, C, N, O, Cl, Ti, and M. Survey scans show the presence of all elements (H typically not detected with XPS). The surface of the M-TiO₂ nanocrystals are passivated with a mixed layer of oleic acid and oleylamine that accounts for the C, N, and some of the O content. Metal chloride hydrate salts were used as precursors to adsorb metal ions to the surface of the TiO₂ nanocrystals. Observed Cl originated from the reaction precursors; however, it is unknown whether its role is as an inner-sphere ligand, outer-sphere ligand, or associated with surface RNH₃⁺ cations. The elements Ti and O are present in the *anatase* TiO₂ nanocrystals that have diameter = 3.3 $\pm$ 0.4 nm and length = 43.3 $\pm$ 7.6 nm.¹³ Based on geometry, we estimate the surface area to be approximately 320 m²/g. The inelastic mean free path (IMFP) of the photoelectron should be considered to assess the observable Ti and O atoms in the nanocrystals. Most photoelectrons originate from a depth of 1*IMFP; however

3*IMFP is typically taken as the limit for the maximum depth from which photoelectrons can escape the sample. The kinetic energies of the Ti 2p and O 1s photoelectrons are ~1028 eV and ~957 eV, respectively. The IMFP of ~ 1 keV electrons in TiO₂ have been calculated as ~1.5 nm.²⁹ Thus it is possible to observe all of the Ti and O environments in the nanocrystal. The transition metal ion dopants, M, are found on the surface of the M-TiO₂ nanocrystals samples, as has been previously shown via type I adsorption isotherms,¹³ therefore all of the M environments are observable. Our presentation and analysis will focus on the elements Ti and M.

In figure 1, the photoelectron spectra of the M-TiO₂ samples in the Ti 2p region are shown. In all samples a Ti 2p_{3/2} and Ti 2p_{1/2} doublet was observed. The binding energies (BE) of the Ti 2p_{3/2} and Ti 2p_{1/2} peaks were 458.0-458.3 eV and 463.7-464.1 eV, respectively. The Δ BE values were quite similar within this series, falling within the range of 5.73-5.77 eV. The Ti 2p_{3/2} peak of a clean, stoichiometric TiO₂ surface with a carefully calibrated sample is located at 459.3 eV, attributed to Ti⁴⁺;³⁰ however, surface defects can cause band bending and shift of the spectrum that likely accounts for variation in experimental data.³¹ Similarly, the Ti 2p_{3/2} and Ti 2p_{1/2} binding energies of a clean, stoichiometric anatase (001) surface were 459.2 eV and 464.7 eV, respectively.³² Among a sample of 16 literature data, a mean value of 458.7 eV with standard deviation of 1.3 eV was found.³³ XPS data of the Ti 2p region of a rutile TiO₂ (110) single crystal surface show Ti 2p_{3/2} and Ti 2p_{1/2} binding energies of 459.3 eV and 465.1 eV, respectively with no changes upon adsorption of DL-proline (bound via its carboxylate group).³⁴ Adsorption of amines to TiO₂ had no effect on the Ti 2p_{3/2} and Ti 2p_{1/2} binding energies.³⁵ Given the literature data, it appears that adsorption of surfactants on the TiO₂ surface should not have a significant effect on the Ti 2p binding energies. We note that the Ti 2p binding energies of all M-TiO₂ materials show slightly lower binding energies compared to those reported for TiO₂ in the literature.

Figure 1. XPS spectra of Ti 2p region of M-TiO₂ nanocrystals.

XPS spectra of the 2p region for the metals deposited onto the TiO₂ nanocrystals are shown in figure 2 and the peak maxima of the 2p_{3/2} component are listed in Table 1. Due to the low signal:noise ratio, we focus the analysis on the 2p_{3/2} features. For the Cr-TiO₂ sample, the Cr 2p region showed a Cr 2p_{3/2} and 2p_{1/2} doublet. The Cr 2p_{3/2} feature was fitted to a peak with a binding energy of 576.6 eV (FWHM = 2.9 eV). A shake-up peak was fitted to a peak with a binding energy of 579.4 eV (FWHM = 4.5 eV). For comparison, a sample of Cr₂O₃ exhibited Cr 2p_{3/2} energy of 577.0 eV, CrCl₃ of 577.6 eV, and Cr(OH)₃ of 577.3 eV.³⁶⁻³⁸ The data indicates the Cr³⁺ oxidation state for the Cr-TiO₂ sample. For the Mn-TiO₂ sample, the Mn 2p region showed a Mn 2p_{3/2} and 2p_{1/2} doublet. The Mn 2p_{3/2} feature was fitted to two peaks with binding energies of 640.3 eV (FWHM = 1.4 eV) and 641.4 eV (FWHM = 3.3 eV) with relative area of ~4:17. A shake-up feature was fitted to a peak with binding energy of 646.1 eV (FWHM = 4.7 eV); however, the peak is broad with low signal:noise and a second shake-up peak was difficult to fit. The Mn 2p_{3/2} binding energy for a MnO(100) single crystal was 640.8 eV, and upon introduction of 5×10⁻⁷ Torr O₂ with annealing at 625K for 150 min the surface oxidized to Mn₂O₃ that gave Mn 2p_{3/2} binding energy of 641.1 eV.³⁹ A shake-up peak was found at ~647 eV. A sample of MnO₂ calcined at 973K for 2 hours under flow of air yielded a sample of Mn₂O₃ that gave an XPS spectrum with Mn 2p_{3/2} binding energy of 641.6 eV.⁴⁰ A sample of LaMnO₃ exhibited a Mn 2p_{3/2} feature centered at 641.6 eV that was fitted to two components at 640.8 eV and 642.3 eV

that were assigned to Mn^{3+} and Mn^{4+} oxidation states;⁴¹ however, they appear to be more consistent with Mn^{2+} and Mn^{3+} . Similarly, a LaMnO_3 powder catalyst exhibited Mn $2p_{3/2}$ feature at 641.9 eV.⁴² The Mn $2p_{3/2}$ binding energy in LuMnO_3 was found at 642.3 eV with a shake-up peak at ~646.4 eV.⁴³ The Mn^{3+} cations in $\alpha\text{-Mn}_2\text{O}_3$ shows Mn $2p_{3/2}$ peak at 641.9 eV.⁴⁴ Based on comparison with literature data, we assign the curve-fitted peak at 640.7 eV to Mn^{2+} and the curve-fitted peak at 641.8 eV to Mn^{3+} . Based on the relative areas, there appears to be substantially more Mn^{3+} than Mn^{2+} in the sample. For the Fe- TiO_2 sample, the Fe 2p region showed a Fe $2p_{3/2}$ and $2p_{1/2}$ doublet. The Fe $2p_{3/2}$ feature was fitted to two peaks with binding energies of 709.4 eV (FWHM = 2.9 eV) and 711.6 eV (FWHM = 3.2 eV) with relative area of ~19:9. Two shake-up peaks were found at binding energies of 714.8 eV (FWHM = 4.5 eV) and 718.9 eV (FWHM = 2.1 eV). A sample of Fe_2SiO_4 was found to have a Fe $2p_{3/2}$ binding energy of 709.0 eV with a shake-up peak at 714.7 eV, whilst a sample of freshly cleaved Fe_2O_3 was found to have a Fe $2p_{3/2}$ binding energy of 711.0 eV with a shake-up peak at 718.8 eV.⁴⁵ Samples of FeO and Fe_2O_3 were found to have Fe $2p_{3/2}$ binding energies of 709.5 eV and 711.0 eV, respectively.⁴⁶ Comparison of our data with the literature suggests the presence of Fe^{2+} and Fe^{3+} in the Fe- TiO_2 sample, and the relative areas suggest greater proportion of Fe^{2+} . For the Co- TiO_2 sample, a Co $2p_{3/2}$ and Co $2p_{1/2}$ doublet was observed. The Co $2p_{3/2}$ and $2p_{1/2}$ binding energies were 780.9 eV and 796.5 eV, which indicate the presence of Co^{2+} .⁴⁷ For example, CoAl_2O_4 has a Co $2p_{3/2}$ binding energy of 780.6 eV. The XPS spectrum also exhibits shake-up peaks in the Co 2p region ($2p_{3/2}$ shake-up at 786.6 eV and $2p_{1/2}$ shake-up at 802.8 eV). The energy separation between the main peak and the shake-up peak matches well with those observed for Co(OH)_2 in the literature.⁴⁸ The Ni- TiO_2 sample gave rise to a Ni $2p_{3/2}$ and Ni $2p_{1/2}$ doublet. The Ni $2p_{3/2}$ and $2p_{1/2}$ binding energies were 855.3 eV and 872.9 eV. Shake-up peaks are also seen for both the $2p_{3/2}$ (861.3 eV) and the $2p_{1/2}$ main peaks. The shape and position of the peaks greatly resemble Ni(OH)_2 ,⁴⁷ which gives rise to Ni $2p_{3/2}$ binding energy of 856.2 eV with shake-up peak at 860.7 eV.⁴⁹ The Ni 2p XPS spectra are less consistent with NiO in both binding energies and peak structure.⁵⁰⁻⁵² While in the solid state, nickel is most commonly found as Ni^{2+} , oxygen defects and surface hydroxylation are common. The satellite to main peak intensity ratio has been found to be a good measure of surface stoichiometry, with $I_{\text{satellite}}/I_{\text{main}} \sim 0.6$ found for well-ordered, stoichiometric single crystal NiO surfaces. This ratio is substantially lower in the Ni- TiO_2 sample. The Cu- TiO_2 sample gave rise to a Cu $2p_{3/2}$ and $2p_{1/2}$ doublet with binding energies of 932.1 eV and 952.0 eV. The binding energies are consistent with Cu^+ or Cu^0 .⁴⁷ We attempted Auger electron spectroscopy of the sample to determine the oxidation state, but the data was inconclusive. Given that formation of Cu^0 represents a two-electron reduction and that atomically dispersed metals tend to be highly reactive, we assign the XPS feature to Cu^+ . No shake-up feature was observed, which has been attributed to the filled d -shell in Cu^+ that prevents the LMCT shake-up transition from occurring.⁵³ It is well known^{54,55} that Cu^{2+} oxides can undergo reduction under the flux of the XPS source, and the phenomenon has been traced directly to sample heating. We also note examples in the literature in which Cu^{2+} ion was grafted or adsorbed onto TiO_2 , the ion was detected as Cu^+ with XPS but determined as Cu^{2+} by an alternate experiment. X-ray absorption spectroscopy of Cu^{2+} -grafted TiO_2 samples indicated presence of Cu^{2+} ion; however an XPS experiment with the same sample detected Cu^+ .^{Error!}

The observation of Cu^+ was attributed to reduction of Cu^{2+} in the UHV environment. Alternately, Cu^{2+} adsorbed onto TiO_2 nanocrystalline electrodes was found with EPR spectroscopy and electrochemical methods as Cu^{2+} ; however, an XPS experiment indicated presence of Cu^+ and Cu^{2+} .⁵⁶

Metal	Sample	M 2p _{3/2} (in eV)	Reference
Cr	Cr-TiO ₂	576.4	this work
	Cr ₂ O ₃	576.5-576.8	37
	CrCl ₃ ·6H ₂ O	577.5	37
	Cr(OH) ₃	577.0-577.3	37
Mn	Mn-TiO ₂	640.3, 641.4	this work
	MnO	640.8	39
	Mn ₂ O ₃	641.1	39
	Mn ₂ O ₃	641.6	40
	LaMnO ₃	641.6	41
	LaMnO ₃	641.9	42
	LuMnO ₃	642.3	43
	Mn ₂ O ₃	641.9	44
Fe	Fe-TiO ₂	709.4, 711.6	this work
	Fe ₂ SiO ₄	709.0	45
	Fe ₂ O ₃	711.0	45
	FeO	709.5	46
	Fe ₂ O ₃	711.0	46
Co	Co-TiO ₂	780.9	this work
	CoAl ₂ O ₄	780.6	47
Ni	Ni-TiO ₂	855.3	this work
	Ni(OH) ₂	856.2	47
Cu	Cu-TiO ₂	932.1	this work
	Cu ₂ O	932.5	47

Table 1. M 2p binding energies and comparison with literature values.

Figure 2. XPS detail of M $2p_{3/2}$ and $2p_{1/2}$ features from the M-TiO₂ nanocrystals.

The preparation of M-TiO₂ materials utilize metal chloride hydrates as starting materials (CrCl₃.nH₂O, MnCl₂.nH₂O, FeCl₂.nH₂O, CoCl₂.nH₂O, NiCl₂.nH₂O, CuCl₂.nH₂O) with starting metal oxidation states of Cr³⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, and Cu²⁺. The XPS data of M-TiO₂ samples with M = Cr, Co, or Ni show metal ions in the same oxidation state as the starting precursor; however samples with M = Mn, Fe, or Cu show metals in different oxidation states than the starting precursors. We note that the M-TiO₂ samples (M = Mn, Fe) undergo a spontaneous color change when taken from N₂ atmosphere to air (figure 3). We believe this is a spontaneous air oxidation to M³⁺.⁵⁷ We note Mn²⁺ and Fe³⁺ ions are isoelectronic d⁵ ions and exhibit similar color. The aqueous ion Mn(H₂O)₆²⁺ is stable toward oxidation in air; however, under basic conditions Mn(OH)₂ is formed and rapidly darkens due to oxidation by atmospheric O₂. Based on our earlier work,¹³ we conclude the Mn ion is bound to the surface of TiO₂ in a bidentate geometry that gives (Ti-O)₂Mn fragments that resemble Mn(OH)₂. Therefore, we expect similar oxidation of Mn²⁺ to Mn³⁺ to occur in air. Aqueous Fe(H₂O)₆²⁺ oxidizes readily to Fe³⁺ species, and this process occurs more readily in basic conditions. Similar to the Mn-TiO₂ system, we expect that (Ti-O)₂Fe fragments on the surface of the nanocrystals are susceptible to rapid air oxidation. The XPS data of the Mn-TiO₂ and Fe-TiO₂ samples indicates the presence of

M^{2+} and M^{3+} oxidation states. We believe the presence of M^{3+} is consistent with the air-oxidation model; however, we expect that oxidation is complete in air. Under the UHV conditions of the XPS chamber, we believe there is partial reduction back to M^{2+} that accounts for the observation of both oxidation states. The dispersion of $Cu-TiO_2$ exhibits a turquoise color and the UV-visible absorbance spectrum shows a broad feature with $\lambda_{max} \sim 700$ nm (figure 4) that is quite similar to the spectroscopic properties of aqueous $Cu(H_2O)_6^{2+}$ and $Cu(H_2O)_6 \cdot x(NH_3)_x$.⁵⁷ Based on the model of a bidentate $(Ti-O)_2Cu$ fragment with oleylamine ligands bound to Cu, our observed spectroscopic features are consistent with Cu^{2+} . Furthermore, Cu^{2+} is a partially filled d^9 electronic configuration that allows for d-d transitions. The XPS data indicates Cu^+ . The filled d^{10} electronic configuration does not allow for d-d transitions, so in the absence of charge-transfer bands the ion should be colorless. Based on the UV-vis data, we do not believe the Cu^+ ion exists in the $Cu-TiO_2$ samples under N_2 atmosphere or air; however, as discussed previously reduction of Cu^{2+} to Cu^+ occurs.

Figure 3. Color changes associated with spontaneous air oxidation of $Mn-TiO_2$ and $Fe-TiO_2$ samples.

Figure 4. UV-visible absorbance spectrum of the Cu-TiO₂ dispersion in hexanes.

Conclusion

We report XPS data for the Ti 2p and M 2p regions of M-TiO₂ samples that feature transition metal ions attached to the surface of anatase TiO₂ nanocrystals. We observe very little change in the Ti 2p data among the samples. The XPS data shows that the oxidation state of the metal ion matches that of the metal precursor in the case of Cr³⁺, Co²⁺, and Ni²⁺. The XPS data shows Mn and Fe as M²⁺ and M³⁺ and Cu as Cu⁺. Under N₂ atmosphere, we believe the Mn-TiO₂, Fe-TiO₂, and Cu-TiO₂ samples have Mn²⁺, Fe²⁺, and Cu²⁺, and under air the metals are found as Mn³⁺, Fe³⁺, and Cu²⁺. The disparity in oxidation states appears to result from reduction of the metal ions under X-ray bombardment in UHV conditions.

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