

Photo-induced Transformations at Semiconductor-Metal Interface: XAFS Investigation of UV-irradiated Au/TiO₂ Films

D. Dey,¹ V. Subramanian,² T. Shibata,¹ M. Boyanov,¹ P. Kamat,² B. Bunker¹

¹Department of Physics and ²Radiation Laboratory,
University of Notre Dame, Notre Dame, IN, U.S.A.

Introduction

The deposition of noble metals on oxide surfaces is a commonly adopted method in heterogeneous catalysis. Noble metal deposited on semiconductor nanoparticles is often found to be beneficial for maximizing the efficiency of photocatalytic reactions [1]. Semiconductor-metal composite nanoparticles facilitate charge rectification and promote interfacial charge transfer processes.

Recently, attention has been drawn to the modification of oxide surfaces with gold nanoparticles. Improved photoelectrochemical performance was observed in the case of gold-coated TiO₂ films [2]. The improved performance of the nanostructured composite film was attributed to the charging of metal nanoparticles followed by Fermi-level equilibration between the metal and semiconductor in the composite film [3]. However, when the ultraviolet (UV) irradiation was extended for a longer duration (30-60 min), these composite films exhibited a deterioration in photoelectrochemical performance [2]. The possibility of oxidation of metal by the photogenerated holes and/or surface hydroxyl radicals was proposed in this study as the reason for the deterioration (Fig. 1). Such a phenomenon obviously raises the question of what species (metal/metal ion) might have a direct influence on the photocatalytic activity of the semiconductor/metal nanocomposite.

The photocatalytic oxidation of noble metals such as Au on a TiO₂ surface will not only disrupt the TiO₂/metal

interface but will also create additional electron-hole recombination centers. The decreased photocurrent observed with UV-irradiated composite films supports such an argument. Whereas modification of the semiconductor surface with metal nanoparticles is advantageous to promote the charge transfer process at the interface, it is important to establish the chemical transformations at the semiconductor/metal interface and track down the metal ion species formed during such transformations.

Extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) measurements provide a convenient tool to identify the oxidation state of the metal ion as well as the neighboring atoms, co-ordination number, bond lengths, and Debye-Waller factors. We have now employed these techniques to elucidate the chemical transformation at the UV-irradiated TiO₂/metal interface.

Methods and Materials

All chemicals used to prepare the catalyst were used as obtained from Aldrich Chemical Company without further purification. The main constituent of the study, colloidal titanium dioxide, was prepared from titanium isopropoxide by using glacial acetic acid in water [4]. Metal colloids (Au) were prepared from their respective chloride salts in toluene [5]. The substrate — an optically transparent electrode (OTE), soda glass, having a thin layer of indium SnO₂ as conducting material — was obtained from Pilkington (Libbey Owens Ford) and cut to 1 × 5.5 cm. Thin c-TiO₂ films (area of 1 × 2.3 cm) were cast on OTE by syringing out colloidal TiO₂ and dried in air. They were later heated at 400°C for 1 h. This process produced a thin and stable transparent film about 1-μm thick [4]. Gold colloids diluted to 2.5 mM could be used to deposit on the TiO₂ film by the electrophoretic deposition (ED) technique. ED was carried out at 400 V dc in a cylindrical cell (6 mL in volume). This system was then illuminated with UV radiation. The artificial UV lamp source used was a 150-W Xe lamp from SLM Instruments, Inc. (IL). A high-intensity grating monochromator (Bausch and Lomb) was used to generate a columnated beam for selecting different wavelengths for excitation. The illumination time was 15 min. After illumination, the external Au was leached with KCN, leaving only the Au at the interface. Two sample systems

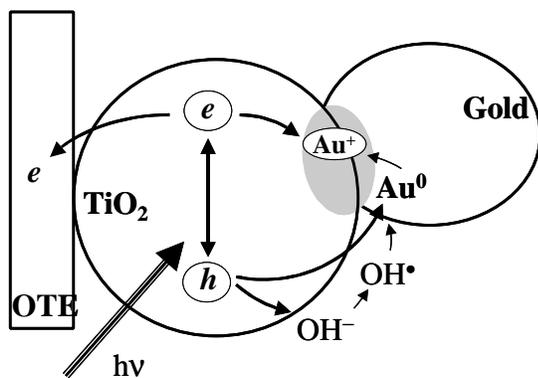


FIG. 1. Oxidation of gold by photogenerated holes and hydroxide radicals.

were measured: one UV-illuminated and the other unirradiated for comparison and to gain understanding.

The Au/TiO₂ interface was probed with the x-ray absorption fine structure (XAFS) technique. XAFS is an oscillatory structure in the x-ray absorption spectrum above the absorption edge of the constituent atoms. XAFS is a result of photoelectron scattering by the surrounding atoms, and it provides local structural information around the x-ray-excited atom of interest [3]. The analysis of the XAFS breaks up into two parts: EXAFS and XANES. In the EXAFS regime, where x-ray energy E is higher than 15 eV from the absorption edge E_0 , the analysis is based on the Fourier transform, and quantitative information about the coordination number, bond lengths, and bond length distribution (Debye-Waller factor) is obtained. In the XANES regime, where the x-ray energy is within 10-15 eV above E_0 , the absorption spectrum is sensitive to the local electronic structure and thus useful for determining the oxidation state and site symmetry. Therefore, XAFS is particularly useful for the present system, where important reactions such as charge transfer and structural changes take place.

The XAFS measurements were performed at the Materials Research Collaborative Access Team (MR-CAT) undulator beamline at the APS. The undulator parameters were optimized to obtain a large photon flux with nearly constant intensity within the XAFS energy range. A liquid-nitrogen-cooled double-crystal Si(111) monochromator and a harmonic rejection mirror were used. The XAFS measurements were performed in fluorescence mode. The incident photon intensity was measured by an ion chamber filled with 80% He and 20% N₂ gas. The fluorescence photon intensity was measured by a conventional three-grid Lytle detector filled with Kr gas. Since the concentration of Au atoms in the sample was low, a thick Ga₂O₃ x-ray filter of nine absorption lengths was used in conjunction with Soller slits. Since the samples were prone to radiation damage or reduction by the x-rays, the incident photon flux was reduced under 30-40% of the intensity of the bare beam cutoff with an aluminum filter. In this case, the incident photon flux through a 1-mm² slit on a sample was on the order of 10⁸ photons/sec. The fluorescence x-rays were typically 10⁵ photons/s, which gives reasonable counting statistics. The data were collected over 20 scans to provide the required million-counts statistics for XAFS detection. The measurement time for each scan was 3-5 min. The XANES of the samples did not show any change in an hour, assuring us of no radiation damage.

The EXAFS oscillations are derived by using the standard method [6]. The oscillations are plotted as a function of the electron wave vector (k) by using the relation $k = \sqrt{2m(E - E_0)}/\hbar$, where m = the electron mass. The background-subtracted $\chi(k)$ is then Fourier-transformed into r-space $\chi(r)$, which is similar to a radial

distribution function. By using FEFFIT [7], the $\chi(r)$ has been fit to a model constructed by using the theoretical scattering amplitudes from FEFF8, with a fitting range of 1.00 to 6.05 Å. To ensure the possible systematic errors from the theoretical calculation, we measured Au foils by transmission mode as a known standard and ensured the parameters (bond lengths, coordination number, and Debye-Waller factor) were reasonable when compared with the bulk fcc gold crystal structure.

The oxidation states of the systems were determined by comparing their XANES with the XANES of the known standard materials. Fortunately, the edge energy is very sensitive to the oxidation state and can be used to interpolate and determine the oxidation state from those of Au foil (Au⁰), Au₂S (Au⁺), and Au₂O₃ (Au³⁺). For each measurement, Au foils are also measured as a photon energy calibration.

Results

Figure 2 shows the XANES structure for Au/TiO₂ with and without UV samples compared with the standard samples. A sharp peak in the spectra just above the edge (called white line) is prominent for Au/TiO₂ both with and without UV samples. The white line is due to empty states appearing by a charge transfer, commonly observed in the oxide. The observation of these white line features in the Au/TiO₂ samples strongly indicates the charge transfer from Au to TiO₂. Although the edge position is significantly shifted from the pure Au by 1 eV, the samples with UV illumination show similar oscillatory structure in the XANES region. The XANES of the unirradiated sample does not follow any known standard

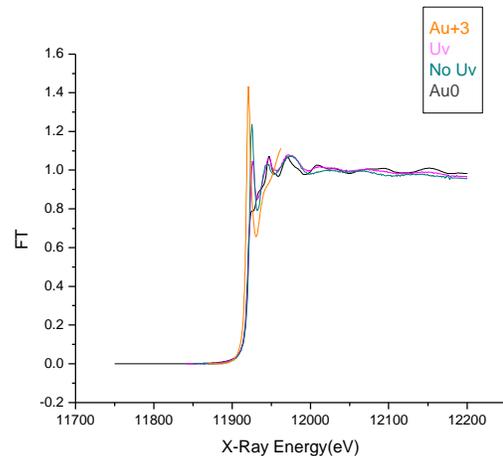


FIG. 2. XANES structure of Au/TiO₂ with and without UV illumination shown with Au and Au₂O₃ standards. A sharp peak just above the absorption edge indicates a charge transfer between Au and O, seen both with and without UV samples.

or even any linear combination of standards. The edge of the unirradiated sample is shifted 3 eV from that of pure Au. The EXAFS results are in accord with XANES. In the illuminated samples, there is a clear signature of gold nanoclustering; this is clearly absent in the unirradiated sample (Fig. 3). While the higher shell structure between 4 and 6 Å is present in the irradiated sample, it dies out in the unirradiated sample.

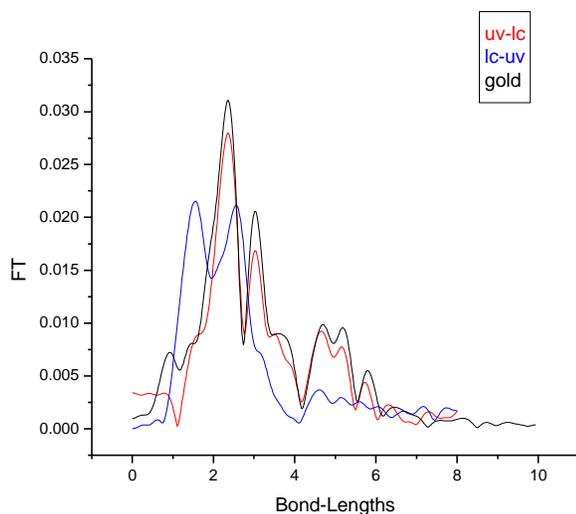


FIG. 3. Fourier transform of $c(k)$ for Au/TiO₂ samples with and without UV illumination, shown with Au foil. The sample without UV (blue) shows a low-distance peak from oxygen neighbors; however, the sample with UV (red) is similar to Au foil (black), indicating a clustering of Au atoms by UV light.

Discussion

Prior to UV illumination, gold nanoparticles are present on TiO₂. After irradiation, some of the gold still exists in a positive oxidation state, confirming the hypothesis that gold is oxidized by the holes from TiO₂ while some of the oxidized Au ions get reduced back to metallic Au by the electrons and tend to cluster. All these samples are leached before measurement so that only the Au diffused into the TiO₂ is measured.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. The MR-CAT is supported by DOE, DE-FG02-94-ER45525, and the member institutions.

References

- [1] H. Tada, T. K. Teranishi, I. Yo-ichi, S. Ito, *Langmuir* **16**, 3304-3309 (2000).
- [2] V. Subramanian, E. Wolf, and P. V. Kamat, *J. Phys. Chem.* **105**, 11439-11446 (2001).
- [3] A. Wood, M. Giersig, P. Mulvaney, *J. Phys. Chem. B* **105**, 8810-8815(2001).
- [4] K. Vinodgopal, S. Hotchandani, P. V. Kamat, *J. Phys. Chem.* **97**, 9040-9044(1993).
- [5] Y. M. Wang, P. V. Kamat, L.K. Patterson, *J. Phys. Chem.* **97**, 8793-8797 (1993).
- [6] *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, edited by D. C. Koningsberger and R. Prince (John Wiley & Sons, 1988).
- [7] M. Newville, B. Ravel, D. Haskel, J. J. Rehr, E. A. Stern, and Y. Yacoby, *Physica B* **208** and **209**, 154-155 (1995).