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XPS analysis of Fe$_2$O$_3$-TiO$_2$-Au nanocomposites prepared by a plasma-assisted route

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Fe$_2$O$_3$ nanodeposits have been grown on fluorine-doped tin oxide (FTO) substrates by plasma enhanced-chemical vapor deposition (PE-CVD). Subsequently, the obtained systems have been functionalized through the sequential introduction of TiO$_2$ and Au nanoparticles (NPs) by means of radio frequency (RF)-sputtering. The target nanocomposites have been specifically optimized in view of their ultimate functional application in solar-driven H$_2$ generation. In the present study, our attention is focused on a detailed X-ray photoelectron spectroscopy (XPS) characterization of the surface composition for a representative Fe$_2$O$_3$-TiO$_2$-Au specimen. In particular, this report provides a detailed discussion of the analyzed C 1s, O 1s, Fe 2p, Ti 2p, and Au 4f regions. The obtained results point to the formation of pure Fe$_2$O$_3$-TiO$_2$-Au composites, with gold present only in its metallic state and each of the constituents maintaining its chemical identity. © 2016 American Vacuum Society. [http://dx.doi.org/10.1116/1.4954387]

Keywords: PE-CVD; RF-Sputtering; Fe$_2$O$_3$; TiO$_2$; Au; nanocomposites

INTRODUCTION

Fe$_2$O$_3$ has been widely used in sunlight-assisted H$_2$ generation, mainly via photoelectrochemical (PEC) water splitting, thanks to its advantageous chemico-physical characteristics, such as ample abundance, good photochemical stability in aqueous media, and favorable band gap (2.2 eV), allowing the absorption of visible light (Refs. 1–3). Nevertheless, to date some drawbacks are still limiting the efficient exploitation of Fe$_2$O$_3$ for PEC applications, such as the poor charge transport and fast recombination of photogenerated carriers (Refs. 4–7). A strategic solution to overcome the above limitations is offered by the functionalization of iron oxide with suitable agents. In this context, in spite of its wide band gap (3.3 eV) enabling the harvesting of the sole UV light, TiO$_2$ is an amenable candidate (Refs. 8 and 9). Indeed, the deposition of TiO$_2$ overlayers on Fe$_2$O$_3$ has recently drawn a great deal of attention as an appealing route to improve charge carrier separation and transport (Refs. 3 and 9–15). In addition, the introduction of metal nanoparticles, such as Au ones, can further promote radiation harvesting thanks to the surface plasmon resonance (SPR) phenomenon (Refs. 8 and 16–20), resulting thus in an additional improvement of the composite functional properties.

In the framework of our ongoing research activities, we have recently developed and implemented a plasma-assisted route to Fe$_2$O$_3$-TiO$_2$-Au nanocomposites. In this strategy, iron(III) oxide systems have been synthesized by PE-CVD on FTO substrates under optimized processing conditions, and subsequently functionalized by sequential RF-sputtering of TiO$_2$ and Au. In particular, in the present contribution a detailed XPS investigation of a representative Fe$_2$O$_3$-TiO$_2$-Au nanocomposite specimen is reported, providing a detailed insight into the surface chemical states of the main elements by the analysis of the principal core level spectra (C 1s, O 1s, Fe 2p, Ti 2p, Au 4f).

SPECIMEN DESCRIPTION (ACCESSION #01373)

Host Material: Fe$_2$O$_3$-TiO$_2$-Au

CAS Registry #: unknown

Host Material Characteristics: homogeneous; solid; polycrystalline; semiconductor; composite; thin film

Chemical Name: iron (III) oxide - titanium (IV) oxide - gold

Host Composition: Fe, Ti, Au, O

Form: supported nanocomposite

Structure: X-ray diffraction (XRD) analyses revealed the presence of peaks at 24.1, 35.6, 40.9, 49.5°, corresponding to the (012), (110), (113), and (024) reflections of rhombohedral α-Fe$_2$O$_3$ (hematite) (Ref. 21), the most thermodynamically stable iron(III) oxide polymorph. No XRD signals related to titania or gold could be detected, likely due to the relatively low amount and high dispersion of the deposited TiO$_2$ and Au (Ref. 22). High resolution-transmission electron microscopy (HR-TEM) investigation revealed the occurrence of rod-shaped denticritic Fe$_2$O$_3$, conformally covered by a TiO$_2$ overlayer (thickness <5 nm). The fuctionalization with gold resulted in the dispersion of Au nanoparticles (diameter ~50 nm) uniformly decorating the system outermost region.

History & Significance: Fe$_2$O$_3$ was deposited using a two-electrode custom-built PE-CVD apparatus equipped with a RF (frequency = 13.56 MHz) generator (Refs. 23 and 24). Experiments were performed using Ar/0$_2$ plasmas under previously optimized operating conditions (RF-power = 10 W, total pressure = 1.0 mbar, duration = 1 h). The iron precursor, Fe(dpm)$_3$ (Hdpm = 2,2,6,6-tetramethyl-3,5-heptanedione), synthesized according to a previously

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reported procedure (Ref. 25), was vaporized in an external glass vessel maintained at 130 °C by means of an oil bath, and transported into the reaction chamber by an electronic grade Ar flow (purity = 5.0; flow rate = 60 sccm). Two additional gas lines were used to introduce Ar (flow rate = 15 sccm) and electronic grade O₂ (flow rate = 20 sccm) directly into the reactor chamber. Growth experiments were carried out at a temperature of 100 °C on FTO-coated glass substrates (Aldrich ⁵; lateral dimensions = 2.0 cm × 1.0 cm; FTO thickness = 600 nm), fixed on the grounded electrode by means of metallic clips. Prior to each deposition, FTO substrates were cleaned by means of an established procedure (Ref. 24), aimed at minimizing the presence of surface contamination.

Subsequently, TiO₂ dispersion was carried out by RF-sputtering from Ar plasma in the same reactor used for PE-CVD experiments. A Ti target (Alfa Aesar ⁵; thickness = 0.3 mm; purity = 99.99%) was fixed on the RF-electrode, whereas FTO-supported Fe₂O₃ deposits were mounted on the grounded electrode. After preliminary experiments, depositions were performed under the following conditions: substrate temperature = 60 °C; Ar flow rate = 10 sccm; total pressure = 0.3 mbar; RF-power = 20 W; sputtering time = 3 h. Subsequently, Au NPs were sputtered starting from an Au target (BALTEC AG; thickness = 0.1 mm; purity = 99.99%), adopting the following experimental parameters: substrate temperature = 60 °C; Ar flow rate = 10 sccm; total pressure = 0.3 mbar; RF-power = 5 W; sputtering time = 20 min.

Finally, the obtained specimen was annealed ex-situ in air using a Carbolite HST 12/200 tubular oven for 1 h at 650 °C.

As Received Condition: as-grown

Ex Situ Preparation/Mounting: Specimen mounted as received with a metallic clip on a grounded sample holder and introduced into the analysis chamber through a fast entry lock system.

In Situ Preparation: none

Pre-Analysis Beam Exposure: The analyzed region was exposed to X-ray irradiation for alignment for a period no longer than 5 min.

Charge Control: No flood gun was used. For further details, see Data Analysis Method, Energy Scale Correction.

Temp. During Analysis: 298 K

Pressure During Analysis: < 10⁻⁸ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Perkin-Elmer Physical Electronics, Inc. 5600ci

Analyzer Type: spherical sector

Detector: multi-channel detector, part number 619103

Number of Detector Elements: 16

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

- **Spectrometer**
  - Analyzer Mode: constant pass energy
  - Throughput (T = E-split): N = 0

Excitation Source Window: 1.5 μm Al window

Excitation Source: Al Kα

Source Energy: 1486.6 eV

Source Strength: 200 W

Source Beam Size: >25000 μm × >25000 μm

Signal Mode: multichannel direct

- **Geometry**
  - Incident Angle: 9°F
  - Source to Analyzer Angle: 53.8°F
  - Emission Angle: 45°F
  - Specimen Azimuthal Angle: 0°F
  - Acceptance Angle from Analyzer Axis: 0°F
  - Analyzer Angular Acceptance Width: 14°F × 14°F

- **Ion Gun**
  - Manufacturer and Model: PHI 04-303A
  - Energy: 3000 eV
  - Current: 0.4 mA/cm²
  - Current Measurement Method: Faraday Cup
  - Sputtering Species: Ar⁺
  - Spot Size (un rastered): 250 μm
  - Raster Size: 2000 μm × 2000 μm
  - Incident Angle: 40°F
  - Polar Angle: 45°F
  - Azimuthal Angle: 111°F
  - Comment: differentially pumped ion gun

DATA ANALYSIS METHOD

Energy Scale Correction: The reported BEs were corrected for charging phenomena by assigning a BE of 284.8 eV to the adventitious C 1s photopeak (Ref. 36).

Recommended Energy Scale Shift: −0.5 eV

Peak Shape and Background Method: After having performed a Shirley-type background subtraction (Ref. 37), peak position and widths were obtained by means of a least-square fitting procedure, using Gaussian/Lorentzian functions.

Quantitation Method: Atomic concentrations were determined using sensitivity factors from standard PHI V5.4A software (Ref. 38). The peak areas were measured above an integrated background.

ACKNOWLEDGMENTS

The authors acknowledge the financial support under the FP7 project “SOLAROGENIX” (NMP4-SL-2012-310333), as well as from Padova University ex-60% 2012-2015 projects, Padova University SOLLEONE (CPDR132937/13) and ACTION grants, and Regione Lombardia-INSTM ATLANTE project.

Fe₂O₃-TiO₂-Au nanocomposites by XPS
REFERENCES

21. JCPDS, Pattern No. 00-033-0664 (2000).
### SPECTRAL FEATURES TABLE

<table>
<thead>
<tr>
<th>Spectrum ID #</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV × cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>01373-02</td>
<td>C 1s</td>
<td>284.8</td>
<td>2.2</td>
<td>9531</td>
<td>0.296</td>
<td>20.7</td>
<td>Adventitious surface contamination</td>
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<tr>
<td>01373-03a</td>
<td>O 1s</td>
<td>530.2</td>
<td>1.7</td>
<td>37391</td>
<td>0.711</td>
<td>33.8</td>
<td>Lattice oxygen in Fe$_2$O$_3$ and TiO$_2$</td>
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<tr>
<td>01373-03a</td>
<td>O 1s</td>
<td>531.5</td>
<td>2.7</td>
<td>8483</td>
<td>0.711</td>
<td>7.6</td>
<td>Adsorbed surface -OH and carbonate groups</td>
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<tr>
<td>01373-04</td>
<td>Fe 2p</td>
<td>711.3</td>
<td>4.0</td>
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<td>Fe(III) in Fe$_2$O$_3$</td>
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<tr>
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<td>Fe 2p$_{3/2}$</td>
<td>724.7</td>
<td>4.6</td>
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<td>...</td>
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<tr>
<td>01373-04</td>
<td>Fe 2p$_{1/2}$</td>
<td>724.7</td>
<td>4.6</td>
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<td>...</td>
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<td>01373-05</td>
<td>Ti 2p</td>
<td>458.5</td>
<td>2.0</td>
<td>8953</td>
<td>2.001</td>
<td>2.9</td>
<td>Ti(IV) in TiO$_2$</td>
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<tr>
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<td>Ti 2p$_{3/2}$</td>
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<td>2.7</td>
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<tr>
<td>01373-06</td>
<td>Au 4f$_{7/2}$</td>
<td>84.3</td>
<td>1.6</td>
<td>75582</td>
<td>5.240</td>
<td>7.8</td>
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<tr>
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<td>Au 4f$_{5/2}$</td>
<td>87.9</td>
<td>1.6</td>
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### ANALYZER CALIBRATION TABLE

<table>
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<tr>
<th>Spectrum ID #</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV × cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
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<tbody>
<tr>
<td>01374-01a</td>
<td>Au 4f$_{7/2}$</td>
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<td>1.4</td>
<td>186403</td>
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<td>Au(0)</td>
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<tr>
<td>01375-01a</td>
<td>Cu 2p$_{3/2}$</td>
<td>932.7</td>
<td>1.6</td>
<td>86973</td>
<td>...</td>
<td>...</td>
<td>Cu(0)</td>
</tr>
</tbody>
</table>

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*The sensitivity factor is referred to the whole O 1s signal.

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**Footnote to Spectrum 01373-02:** The C 1s peak can be traced back to the occurrence of adventitious carbon contamination. The slight tailing at higher binding energy can be traced back to the presence of carbonate species arising from atmospheric exposure (Refs. 26 and 27).

**Footnote to Spectrum 01373-03:** The O 1s region could be fitted by two contributing bands. The dominant one located at BE = 530.2 eV (82% of the total oxygen), is attributed to lattice oxygen in TiO$_2$ and Fe$_2$O$_3$ (Refs. 26–28). The second component, centered at BE = 531.5 eV (18% of the total oxygen), is attributed to surface adsorbed -OH groups and carbonate species due to air exposure (Refs. 26 and 27).

**Footnote to Spectrum 01373-04:** The Fe 2p spectral shape, along with the positions of the two spin-orbit components [BE (Fe 2p$_{3/2}$) = 711.3 eV; Spin Orbit Separation (SOS) = 13.4 eV], were in good agreement with literature values for Fe(III) in Fe$_2$O$_3$ (Refs. 26, 27, 29, and 30).

**Footnote to Spectrum 01373-05:** The main Ti 2p spin-orbit component, Ti 2p$_{3/2}$, was centered at BE = 458.5 eV (SOS = 5.7 eV). These values were in line with the presence of Ti(IV) in an oxide environment (Refs. 8, 26, 28, 31, and 32).

**Footnote to Spectrum 01373-06:** The spectral data for the Au 4f region [BE (Au 4f$_{7/2}$) = 84.3 eV; SOS = 3.6 eV] indicated the presence of the sole Au(0) (Refs. 17, 19, 26, and 32–34). The shift in BE value of +0.2 eV compared to that of bulk materials could suggest the occurrence of core level shifts (Refs. 34 and 35).
<table>
<thead>
<tr>
<th>Spectrum (Accession) #</th>
<th>Spectral Region</th>
<th>Voltage Shift</th>
<th>Multiplier</th>
<th>Baseline</th>
<th>Comment #</th>
</tr>
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<td>0</td>
<td>1</td>
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<tr>
<td>1373-02</td>
<td>C 1s</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1373-03</td>
<td>O 1s</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1373-04</td>
<td>Fe 2p</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1373-05</td>
<td>Ti 2p</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1373-06</td>
<td>Au 4f</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>1</td>
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<tr>
<td>1374-01 [NP]**</td>
<td>Au 4f7/2</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>1375-01 [NP]</td>
<td>Cu 2p3/2</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

* Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.

** [NP] signifies not published; digital spectra are archived in SSS database but not reproduced in the printed journal.

1. Fe$_2$O$_3$-TiO$_2$-Au
2. Au calibration
3. Cu calibration
Accession #: 01373–04
Host Material: Fe$_2$O$_3$-TiO$_2$-Au
Technique: XPS
Spectral Region: Fe 2p

Instrument: Perkin-Elmer Physical Electronics, Inc. 5600ci
Excitation Source: Al K$_\alpha$
Source Energy: 1486.6 eV
Source Strength: 200 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 9°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 200.5 s
Total Elapsed Time: 220.6 s
Number of Scans: 10
Effective Detector Width: 0.6 eV
Comment: See footnote below the Spectral Features Table.

Accession #: 01373–05
Host Material: Fe$_2$O$_3$-TiO$_2$-Au
Technique: XPS
Spectral Region: Ti 2p

Instrument: Perkin-Elmer Physical Electronics, Inc. 5600ci
Excitation Source: Al K$_\alpha$
Source Energy: 1486.6 eV
Source Strength: 200 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 9°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 210.0 s
Total Elapsed Time: 231.0 s
Number of Scans: 20
Effective Detector Width: 0.6 eV
Comment: See footnote below the Spectral Features Table.
Accession #: 01373–06
Host Material: Fe₂O₃-TiO₂-Au
Technique: XPS
Spectral Region: Au 4f

Instrument: Perkin-Elmer Physical Electronics, Inc. 5600ci
Excitation Source: Al Kα
Source Energy: 1486.6 eV
Source Strength: 200 W
Source Size: >25 mm × >25 mm
Analyzer Type: spherical sector
Incident Angle: 9°
Emission Angle: 45°
Analyzer Pass Energy: 58.7 eV
Analyzer Resolution: 0.6 eV
Total Signal Accumulation Time: 80.5 s
Total Elapsed Time: 88.5 s
Number of Scans: 10
Effective Detector Width: 0.6 eV
Comment: See footnote below the Spectral Features Table.

Fe₂O₃-TiO₂-Au nanocomposites by XPS