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Composition analysis of Ta$_3$N$_5$/W$_{18}$O$_{49}$ nanocomposite through XPS

Daniel R. Jones, Michael E. A. Warwick, James D. McGettrick, and Charles W. Dunnill

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A characterization of a nanocomposite material consisting of Ta$_3$N$_5$ nanoparticles and W$_{18}$O$_{49}$ nanowires is presented. The material is of interest for photocatalytic applications, with a focus on pollution reduction through the photodegradation of dye waste; under white light illumination, the combination of Ta$_3$N$_5$ and W$_{18}$O$_{49}$ yielded an enhanced rate of dye degradation relative to Ta$_3$N$_5$ particles alone. The facile method of synthesis is thought to be a promising route for both upscale and commercial utilization of the material. X-ray photoelectron spectroscopy revealed a core–shell composite structure with W$_{18}$O$_{49}$ present as an overlayer on Ta$_3$N$_5$; the analyzed spectra for the C 1s, O 1s, Ta 4f, N 1s, W 4f, and Na 1s regions are reported. It should be noted that due to differential charging of the underlying Ta$_3$N$_5$ component relative to the W$_{18}$O$_{49}$ shell, an additional uncompensated voltage shift may exist in the Ta 4f and N 1s spectra. Published by the AVS.

https://doi.org/10.1116/1.5047860

Keywords: Ta$_3$N$_5$, W$_{18}$O$_{49}$, photocatalysis, dye degradation, composite, nanowires, x-ray photoelectron spectroscopy, XPS

INTRODUCTION

Many synthetic dyes are toxic to both human (Ref. 1) and marine life (Ref. 2) and inhibit aquatic photosynthesis through light absorption (Ref. 3), leading to concerns for global oxygen production. Many synthetic dyes are, by design, chemically stable and are therefore difficult to degrade via common biological treatment (Refs. 4 and 5), while alternative techniques can lead to the production of unwanted by-products which are also harmful (Refs. 6–9). One promising, low-energy solution for the remediation of dye-polluted water is the use of photocatalysts for oxidation of the dyes. Much work has focused on the use of TiO$_2$ nanopowders for this purpose (Refs. 10–17); however, TiO$_2$ has a wide bandgap (3.2 eV) and can therefore utilize only the ultraviolet portion of the solar spectrum, which accounts for a small percentage of solar radiation that reaches the earth. With this in mind, it is preferable to employ a material with a narrower bandgap so that dye oxidation may be instigated by visible light. With its low bandgap of 2.1 eV (Ref. 18), Ta$_3$N$_5$ has been shown to work well as a visible light photocatalyst for the degradation of organic dyes (Refs. 19–21), although our recent study demonstrated how the catalytic performance of this material may be enhanced through a strategic combination with tungsten(IV) suboxide nanowires in the form of a composite (Ref. 22). Within this investigation, a solvothermal approach was employed to grow W$_{18}$O$_{49}$ nanofibers on Ta$_3$N$_5$ nanoparticles inside a polytetrafluoroethylene-lined stainless steel acid digestion bomb, and it was found that the combination of these materials resulted in improved charge carrier separation due to electron–hole transfer at the interface of the two components; the increase in charge separation afforded longer charge carrier lifetimes, resulting in a marked increase in the photocatalytic activity of the material. To the best of the authors’ knowledge, this system has not before been synthesized for the purpose of water remediation.

SPECIMEN DESCRIPTION (ACCESSION #01477)

Host Material: Ta$_3$N$_5$/W$_{18}$O$_{49}$ nanocomposite

CAS Registry #: Unknown

Host Material Characteristics: Inhomogeneous; powder; polycrystalline; semiconductor; composite

Chemical Name: Tantalum(V) nitride/tungsten(IV) suboxide

Source: Solvothermally grown W$_{18}$O$_{49}$ on Ta$_3$N$_5$ from ammonolyzed TaCl$_5$

Host Composition: Ta$_3$N$_5$/W$_{18}$O$_{49}$

Form: Polycrystalline composite

Structure: Orthorhombic Ta$_3$N$_5$/monoclinic W$_{18}$O$_{49}$

History and Significance: Ta$_3$N$_5$ nanoparticles were prepared through ammonolysis of TaCl$_5$ powder in a 7:3 molar ratio of KCl and NaCl at 800 °C for 10 h. Nanowires of W$_{18}$O$_{49}$ were subsequently grown solvothermally on the surface of the Ta$_3$N$_5$ nanoparticles by annealing a suspension of the nanoparticles in a solution of WCl$_6$ in a 4:1 volumetric mixture of ethanol and ethylene glycol at 180 °C for 24 h, followed by centrifugation of the product in ethanol and deionized water.

As Received Condition: The as-synthesized composite had the form of a brown powder.

Analyzed Region: Same as the host material

Ex Situ Preparation/Mounting: The composite powder was loaded into a 5 mm pellet press and pelletized using a force of 2 tons. The pellet was retrieved from the press and mounted on an adhesive carbon tab for analysis.

In Situ Preparation: None
**Charge Control:** Electronic charge neutralization using magnetic immersion lens. Filament current = 0.4 A, charge balance = 3.3 V, filament bias = 1.0 V.

**Temp. During Analysis:** 300 K  
**Pressure During Analysis:** 4 \times 10^{-6} \text{Pa}  
**Preanalysis Beam Exposure:** 0 s

**INSTRUMENT DESCRIPTION**

**Manufacturer and Model:** Kratos Axis Supra  
**Analyzer Type:** Spherical sector  
**Detector:** Multichannel resistive plate  
**Number of Detector Elements:** 3 MCP, 128 channel DLD

**SPECTRA**

**Spectrometer**

**Analyzer Mode:** Constant pass energy  
**Throughput \( (T = E^0) \):** \( N = 0 \)

**Excitation Source Window:** Not specified  
**Excitation Source:** Al K \( \alpha \), monochromatic  
**Source Energy:** 1486.6 eV  
**Source Strength:** 225 W  
**Source Beam Size:** \( \mu \text{m} \times 2000 \mu \text{m} \)  
**Signal Mode:** Multichannel direct

**Geometry**

**Incident Angle:** 54.7°  
**Source-to-Analyzer Angle:** 54.7°  
**Emission Angle:** 0°  
**Specimen Azimuthal Angle:** N/A  
**Acceptance Angle from Analyzer Axis:** 0°  
**Analyzer Angular Acceptance Width:** 30° × 30°

**Ion Gun**

**Manufacturer and Model:** Kratos GCIS Minibeam 6  
**Energy:** 10 keV  
**Current:** 23 nA  
**Current Measurement Method:** Biased stage  
**Sputtering Species:** Argon 1000+ ion clusters  
**Spot Size (unrastered):** 200 \( \mu \text{m} \)  
**Raster Size:** \( \mu \text{m} \times 2000 \mu \text{m} \)  
**Incident Angle:** 40°  
**Polar Angle:** 0°  
**Azimuthal Angle:** 0°  
**Comment:** Sputtering was carried out on the reference samples only.

---

**DATA ANALYSIS METHOD**

**Energy Scale Correction:** The binding energy scale was referenced to C 1s = 284.8 eV.

**Recommended Energy Scale Shift:** 3.213 eV

**Peak Shape and Background Method:** Peak shape: Gaussian–Lorentzian product formula GL(30). Background: The Shirley background was used.

**Quantitation Method:** Quantitation was achieved through peak deconvolution using CASAXPS version 2.3.15. Relative sensitivity factors were supplied by Kratos Analytical.

**REFERENCES**

### SPECTRAL FEATURES 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 x counts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
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### ANALYZER CALIBRATION TABLE

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<th>Spectrum ID #</th>
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<th>Peak Energy (eV)</th>
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<th>Concentration (at. %)</th>
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<sup>a</sup>Voltage shift of the published figure relative to the as-measured spectrum; the energy correction accounts for the effects of sample charging.

<sup>b</sup>1. Ta<sub>3</sub>N<sub>5</sub>/W<sub>18</sub>O<sub>49</sub> nanocomposite. 2. Ag calibration. 3. Au calibration. 4. Cu calibration.
Host Material: Ta₃N₅/W₁₈O₄₉ nanocomposite
Technique: XPS
Spectral Region: Survey
Instrument: Kratos Axis Supra
Excitation Source: Al K₂ monochromatic
Source Energy: 1486.6 eV
Source Strength: 225 W
Source Size: 0.7 mm × 0.3 mm
Analyzer Type: Spherical sector analyzer
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 160 eV
Analyzer Resolution: 1 eV
Total Signal Accumulation Time: 120 s
Total Elapsed Time: Not specified
Number of Scans: 1
Effective Detector Width: 16 eV
Composition analysis of Ta$_3$N$_5$/W$_{18}$O$_{49}$ nanocomposite

Instrument: Kratos Axis Supra
Excitation Source: Al K$_\alpha$, monochromatic
Source Energy: 1486.6 eV
Source Strength: 225 W
Source Size: 0.7 mm × 0.3 mm
Analyzer Type: Spherical sector
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 20 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 17.75 s
Total Elapsed Time: Not specified
Number of Scans: 1
Effective Detector Width: 2 eV
Accession #: 01477-04
Host Material: Ta$_3$N$_5$/W$_{18}$O$_{49}$ nanocomposite
Technique: XPS
Spectral Region: C 1s

Instrument: Kratos Axis Supra
Excitation Source: Al K$_\alpha$ monochromatic
Source Energy: 1486.6 eV
Source Strength: 225 W
Source Size: 0.7 mm $\times$ 0.3 mm
Analyzer Type: Spherical sector
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 20 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 29.5 s
Total Elapsed Time: Not specified
Number of Scans: 2
Effective Detector Width: 2 eV
**Host Material:** Ta$_3$N$_5$/W$_{18}$O$_{49}$ nanocomposite

**Technique:** XPS

**Spectral Region:**
- **Accession #: 01477-05**
- **Host Material:** Ta$_3$N$_5$/W$_{18}$O$_{49}$ nanocomposite

**Technique:** XPS

**Spectral Region:** Ta 4f

**Instrument:** Kratos Axis Supra

**Excitation Source:** Al K$_\alpha$ monochromatic

**Source Energy:** 1486.6 eV

**Source Strength:** 225 W

**Source Size:** 0.7 mm x 0.3 mm

**Analyzer Type:** Spherical sector

**Incident Angle:** 54.7°

**Emission Angle:** 0°

**Analyzer Pass Energy:** 20 eV

**Analyzer Resolution:** 0.1 eV

**Total Signal Accumulation Time:** 17.5 s

**Total Elapsed Time:** Not specified

**Number of Scans:** 1

**Effective Detector Width:** 2 eV

---

**Accession #: 01477-06**

**Host Material:** Ta$_3$N$_5$/W$_{18}$O$_{49}$ nanocomposite

**Technique:** XPS

**Spectral Region:** N 1s

**Instrument:** Kratos Axis Supra

**Excitation Source:** Al K$_\alpha$ monochromatic

**Source Energy:** 1486.6 eV

**Source Strength:** 225 W

**Source Size:** 0.7 mm x 0.3 mm

**Analyzer Type:** Spherical sector

**Incident Angle:** 54.7°

**Emission Angle:** 0°

**Analyzer Pass Energy:** 20 eV

**Analyzer Resolution:** 0.1 eV

**Total Signal Accumulation Time:** 62.5 s

**Total Elapsed Time:** Not specified

**Number of Scans:** 5

**Effective Detector Width:** 2 eV