Bioinspired Au/TiO$_2$ photocatalyst derived from butterfly wing (Papilio Paris)
Overview

What?
The study of photocatalytic semiconductor materials based on a biological template.

Why?
Important materials research for high performance photocatalysis.

How?
Using X-rays for characterization and analysis. Methods of particular interest include XRD, XPS, SEM, and TEM.
Introduction

• Semiconductor Photocatalysis
• TiO$_2$
  o Cheap
  o Nontoxic
  o Readily available
  o Stable to photocorrosion
• Currently, two methods of development
  o Gaining porous hierarchical structure
  o Composition control
Why Butterflies?
Black areas of wings exhibit high light-harvesting

Great Template!
Synthesis

• Anhydrase ethanol wash: remove black areas
• Ti-precursor solution
• Butterfly wings immersed for 14h, rinsed, dried, calcined to remove organic template
  o Left TiO₂ w/ butterfly wing scales → Biomorphic TiO₂
• Control TiO₂ via hydrolyzing precursor solution
• Biomorphic Au/TiO₂: HAuCl₄+NaOH+Biomorphic TiO₂
Characterization Methods

Our focus will be on:
- X-ray Diffraction (XRD)
- X-ray Photoelectron Spectroscopy (XPS)
- Scanning electron microscopy (SEM)

Also discussed in paper:
- Transmission electron microscopy (TEM)
- Field-emission scanning electron microscopy (FESEM)
- High-resolution transmission electron microscopy (HRTEM)
- Selected area electron diffraction (SAED)
- UV-Vis Absorption
- Photoluminescence (PL)
Photocatalytic Methods

- 10mg of each sample dispersed in 10mL of $10^{-5}$ M methyl orange with distilled water in dark
- 1000W Xe lamp 120cm above solution
- Cut-off filters to remove wavelengths less than 400nm
- Monitored degradation every 20 minutes during irradiation by taking sample
  - Samples tested with UV-Vis spectrometer to get absorption spectra
Review I: Bragg’s Law

- Thompson (elastic) Scattering: only momentum transferred.
- Peaks of diffraction pattern directly related to atomic distances:

\[ n\lambda = 2d_{hkl}\sin\theta_{hkl} \]

- Peak position:

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

- Phase identification

Image from: http://e-education.psu.edu/matse201/
Review 2: Scherrer Equation

- Scherrer Equation: mean size of grains = \( \tau = \frac{K\lambda}{\beta \cos \theta} \)
- Peak width is inversely proportional to crystallite size
- \( \beta = \text{FWHM} \)
- \( K = \) constant of proportionality that depends on how width is determined, crystal shape, and size distribution. Most common value: FWHM spherical crystals with cubic symmetry 0.94
Review 3: XPS

• Based on the photoelectric effect:

\[ \varepsilon_{\text{kin}} = \frac{\hbar^2 q^2}{2m} = \hbar \omega - \phi - \varepsilon_B \]

• Soft X-rays (200-2000 eV)
• Determines surface chemistry

Image from: http://www.chem.qmul.ac.uk/surfaces/scc/images/scat5_3b.gif
Review 4: Microscopy

Scanning Microscope

Transmission Microscope
Results
X-ray Diffraction

Diffraction peak locations and corresponding planes:

$2\theta = 25.2^\circ \ (101), \ 37.8^\circ \ (004), \ 47.6^\circ \ (200)$
XPS

(a)

(b)
FESEM

Reticular hierarchical structure maintained
EDX Microanalysis
Photoabsorption

![Graph showing absorbance vs wavelength for Biomorphic Au/TiO₂, Biomorphic TiO₂, and Control TiO₂ (no template).]}
Photoluminescence
Photocatalytic Activity

Biomorphic Au/TiO2 shows the highest activity!
Conclusions

• Successfully made Au/TiO$_2$ nanocomposites using butterfly wings as a template
  o Au uniformly deposited
• The biomorphic Au/TiO$_2$ shows superior photocatalytic activity
  o Reticular hierarchical structures
    • Light harvesting and surface area
  o Au nanoparticles
    • Inhibit electron-hole recombination

• Effective way for synthesis of high-performance catalysts
References

