

# Titania-based Nanocomposite Materials as Highly Active Photocatalysts

(Paper #186c, Fundamentals of Environmental Catalysis I)

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## Introduction

Semiconductor photocatalysis has led to many novel applications beyond environmental remediation, such as chemical and fuel synthesis.<sup>(1-3)</sup> TiO<sub>2</sub>-based nanocomposites are promising materials that can potentially achieve the three major goals for modern photocatalysis: tailored reactivity, improved efficiency and enhanced visible-light response.<sup>(4-6)</sup> For example, photogenerated electrons can transfer from the conduction band of TiO<sub>2</sub> to doped metal, resulting in effective charge separation, hindered recombination and photocatalytic efficiency.<sup>(7, 8)</sup> Coupled semiconductors, such as CdS/TiO<sub>2</sub>, possess improved efficiency and visible-light response.<sup>(9, 10)</sup> Nitrogen-doped TiO<sub>2</sub> has been shown to be able to operate under visible-light illumination.<sup>(11-14)</sup>

The objective of this work is to prepare mixed-phase TiO<sub>2</sub> nanocomposites with highly active solid-solid interfaces and enhanced reactivity. Our previous studies reveal that electron transfer from the rutile conduction band to the trapping sites in anatase is responsible for the high photocatalytic activity of mixed-phase TiO<sub>2</sub>.<sup>(15-18)</sup> The preparation of nitrogen-doped TiO<sub>2</sub> nanocomposites with visible-light response is discussed as well.

## Results and Discussion

### 1. Mixed-phase TiO<sub>2</sub> prepared by hydration-dehydration

Mixed-phase TiO<sub>2</sub> nanocomposite (Nano A/R) was prepared by a simple hydration-dehydration process.<sup>(19)</sup> First, 2.0 g of anatase nanopowders (Sigma-Aldrich, 5 nm) and 0.5 g rutile nanopowders (Sigma-Aldrich, 10 nm × 40 nm) were thoroughly mixed in 100 ml deionized water, sonicated for 30 min before drying under ambient environment. For comparison, physical mixture A/R was prepared by simply mixing 2.0 g of anatase nanopowders with 0.5 g rutile nanopowders without adding water. The photocatalytic activities and EPR spectra of different TiO<sub>2</sub> samples are shown in Figures 1 and 2, respectively.

As can be seen from Figure 1, Nano A/R shows significantly high photoactivity than pure anatase nanopowder, while the physical mixture A/R does not show any improvement in activity than pure anatase. The relative intensity of trapped electrons in anatase ( $g = 1.995$ ) to that in rutile ( $g = 1.976$ ) in Nano A/R is much greater than in physical mixture A/R, indicating a better electron transfer between anatase and rutile in Nano A/R than physical mixture A/R (Figure 2).

In a recent work by Elser and co-workers, nanocrystalline anatase particles formed a three-dimensional, mesoporous network by a hydration-dehydration process.<sup>(19)</sup> The

dehydration process was carried out at 473 K under vacuum. It was found that the energy required for defects formation at particle interfaces was substantially reduced by the treatment. In addition, EPR studies revealed the presence of polarizable conduction band electrons. The authors further suggested possible chemical bonding between the nanoparticles.(19) In our present study, Nano A/R with improved photoactivity was prepared by hydration-dehydration at room temperature. Similar treatment of anatase nanopowders did not enhanced the photocatalytic acitivity.

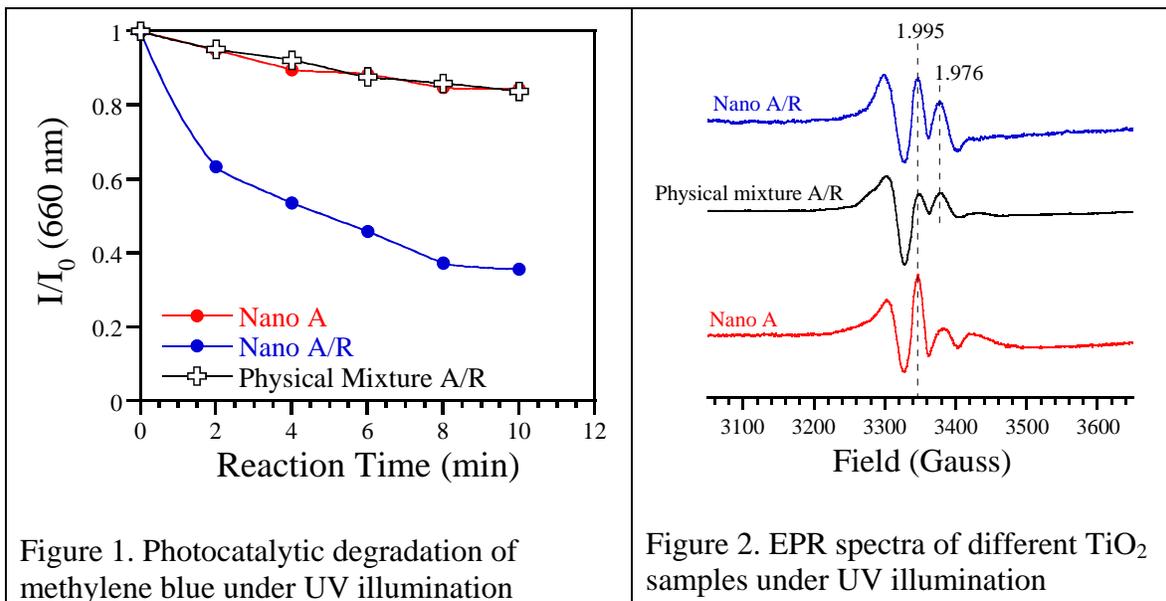


Figure 1. Photocatalytic degradation of methylene blue under UV illumination

Figure 2. EPR spectra of different TiO<sub>2</sub> samples under UV illumination

## 2. Mixed-phase TiO<sub>2</sub> prepared by hydrothermal processing

Mixed-phase TiO<sub>2</sub> nanocomposite was prepared by hydrothermal processing, a more robust solvent treatment. It has been reported that hydrothermal treatment can enhanced the photocatalytic activity.(20, 21) Amorphous TiO<sub>2</sub> gel was obtained by hydrolysis of TiCl<sub>4</sub> at room temperature. Then 0.5 ml 5% Triton-X 100 in ethanol and a certain amount of commercially available anatase (Sigma-Aldrich, average particle size 100 nm, BET surface area 8.6 m<sup>2</sup>/g) were added to the gel and the resulting mixture was reflux at 373 K for 24 h. The prepared mixed-phase nanocomposite (A + Sol-gel) was washed, centrifuged and naturally dried. Some of the materials were further calcined at 773 K (A + Sol-gel 773 K, BET surface area 11.5 m<sup>2</sup>/g) for a better crystallinity. It can be seen from the XRD diffraction patterns that the prepared mixed-phase TiO<sub>2</sub> has a formulation similar to Degussa P25 (Figure 3). Microscopic studies show that rod-like rutile nanoparticles were generated in the hydrothermal process and were in close contact with round anatase particles.(Figure 4)

Figure 5 demonstrates that the sample A + Sol-gel 773 K has a much better photocatalytic activity than pure anatase and Degussa P25. Again, EPR studies indicate that the close contact between the rod-like rutile and round anatase particles facilitates the interfacial charge transfer in A + Sol-gel 773 K. It should be point out that the EPR spectrum of A + Sol-gel is similar to that of Degussa P25. There might be other factors

that contribute to the enhanced photocatalytic activity of A + Sol-gel 773 K than pure anatase, such as improved porosity and surface area.

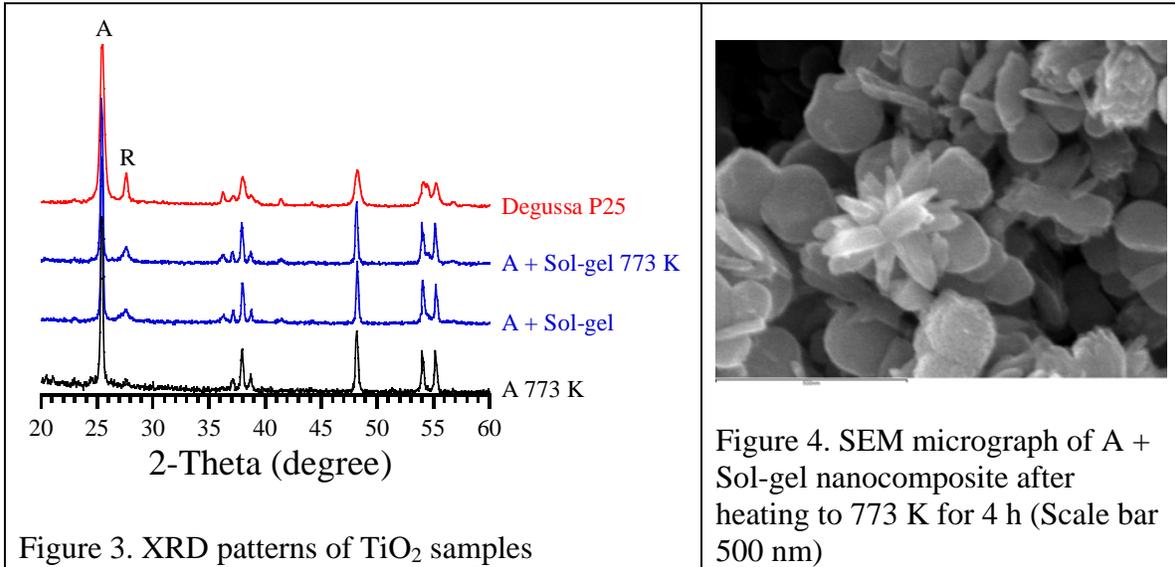


Figure 3. XRD patterns of TiO<sub>2</sub> samples

Figure 4. SEM micrograph of A + Sol-gel nanocomposite after heating to 773 K for 4 h (Scale bar 500 nm)

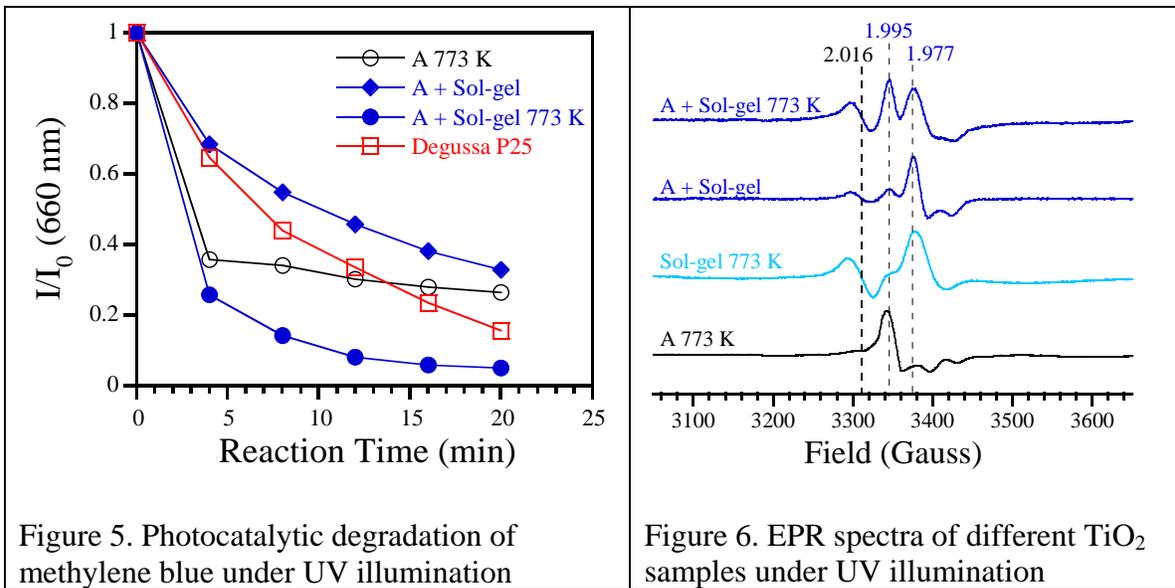


Figure 5. Photocatalytic degradation of methylene blue under UV illumination

Figure 6. EPR spectra of different TiO<sub>2</sub> samples under UV illumination

### 3. Mixed-phase TiO<sub>2</sub> thin films prepared by magnetron sputtering

Mixed-phase TiO<sub>2</sub> thin films were deposited by reactive DC magnetron sputtering, with RF bias, onto cleaned microscope glass slides.(22) Pure titanium (99.95%) was used as the sputtering target. High-purity argon and oxygen were used as sputtering and reactive gases respectively. The base pressure in the coating chamber was controlled below  $5.3 \times 10^{-4}$  Pa. Figure 7 shows the SEM micrographs of a mixed-phase TiO<sub>2</sub> film with 30% rutile and 70% anatase prepared by this method. The inset indicates that the prepared TiO<sub>2</sub> film has a scale-like morphology with TiO<sub>2</sub> particles tightly coupled to each other. It has been shown that the sputtered nanocomposite materials possess high photocatalytic activity for acetaldehyde degradation under UV illumination.(22)

It should be pointed out that the sputtered film has significant absorbance at visible-light region (Figure 8). Kikuchi and co-workers prepared visible-light response TiO<sub>2</sub> thin films by magnetron sputtering.(23) The prepared thin film with a mixed-phase structure showed high photoactivity for water splitting. The authors attributed the visible-light response to an oxygen-deficient, anisotropic structure of the thin films.(23) EPR studies of the charge transfer characteristics of our sputtered films are currently underway.

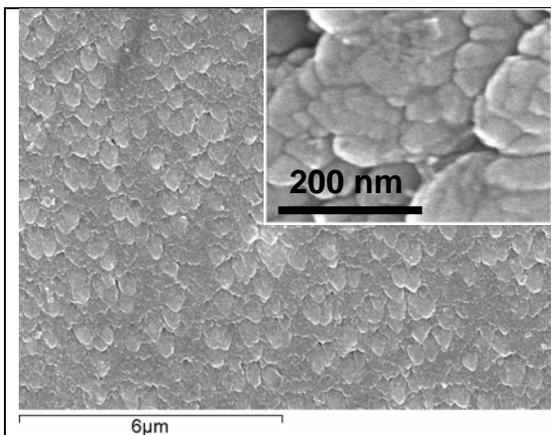


Figure 7. SEM micrograph of mixed-phase TiO<sub>2</sub> nanocomposite prepared by magnetron sputtering

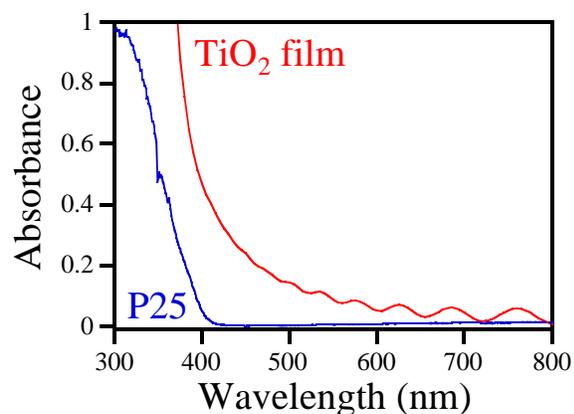


Figure 8. UV-Vis spectra of Degussa P25 and mixed-phase TiO<sub>2</sub> nanocomposite prepared by magnetron sputtering

## Conclusions

This study demonstrates that mixed-phase TiO<sub>2</sub> nanocomposites with high photocatalytic activity can be prepared by simple water-treatment and hydrothermal processing. The effective charge transfer between anatase and rutile contributes to the enhanced photoactivity of TiO<sub>2</sub> nanocomposites. Magnetron sputtering is shown to be a promising method for the preparation of TiO<sub>2</sub> nanocomposites with both visible-light response and high photocatalytic efficiency.

## Acknowledgements

The authors thank Prof. Michal Graham (Department of Materials Science and Engineering, Northwestern University), Prof. Richard Lueptow and Yuan Yao (Department of Mechanical Engineering, Northwestern University) for their help on preparing nanocomposite materials. The authors want to acknowledge Dr. Zoran Saponjic and Dr. Nada Dimitrijevic (Chemistry Division, Argonne National Laboratory) for their help with EPR spectroscopy, Degussa for their kind donation of Degussa P25 and funding from the US Department of Energy and National Science Foundation.

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