

# Comparative study of optically activated nanocomposites with photocatalytic TiO<sub>2</sub> and ZnO nanoparticles for massive environmental decontamination

Sumeyra Tek,<sup>a,c</sup> Evren Mutlugun,<sup>a,c</sup> Ibrahim Murat Soganci,<sup>b,c</sup>  
Nihan Kosku Perkgoz,<sup>c</sup> Dilek Yucel,<sup>d</sup> Gulsen Celiker,<sup>d</sup> and  
Hilmi Volkan Demir<sup>a,b,c</sup>

<sup>a</sup>Department of Physics, <sup>b</sup>Department of Electrical and Electronics Engineering,

<sup>c</sup>Nanotechnology Research Center, Bilkent University, Ankara, 06800, Turkey

<sup>d</sup>DYO, Yasar Group, A. O. S. B., 10003 Sk. No.: 2, Cigli, Izmir 35620 Turkey

[volkan@bilkent.edu.tr](mailto:volkan@bilkent.edu.tr)

**Abstract.** Nanocomposites that incorporate TiO<sub>2</sub> and ZnO nanoparticles separately in three-dimensional solgel matrices through full chemical integration are prepared to perform highly efficient photocatalytic activities for applications of environmental decontamination. Spectral responses of photocatalytic TiO<sub>2</sub> and ZnO nanoparticles exposed to UV activation for self-cleaning process were obtained as also their optical relative spectral efficiency curves from 270 to 370 nm in the UV regime. Our investigations of the optimal conditions to increase their spectral photocatalytic efficiencies resulted in remarkably high levels of optical recovery and efficiency.

**Keywords:** nanoparticles, nanocomposites, photocatalysis, TiO<sub>2</sub>, ZnO, optical spectral response.

## 1 INTRODUCTION

The importance of photocatalytic materials has recently been better understood especially for their potential use as a solution to the problems of environmental and biological pollution. Since the increasing amount of carbon dioxide emission is considered as one of the major environmental problems around the globe due to the greenhouse effect, the use of photocatalysts is critically important to reduce CO<sub>2</sub> amount in the atmosphere [1]. Another serious issue related to both the atmosphere and aqueous environments is the existence of pollutants, such as nitrogen oxides, NO<sub>x</sub>; photocatalysts also help remove nitrogen oxides with the oxidation of those materials [1]. Furthermore, photocatalysts accelerate the degradation of organic compounds after oxidation processes. This helps decontaminate aqueous solutions that include dyes and other organic species dispersed or dissolved inside [2, 3]. Additionally, the degradation of organic compounds makes it possible to decompose some hazardous biological species to protect human health, such as bacteria, viruses, and fungi by converting them to harmless inorganic anions, H<sub>2</sub>O, and CO<sub>2</sub> [4].

The efficiency of such photocatalysts becomes critical especially for the applications that target the decontamination of massive media such as the atmosphere and large aqueous environments. The energy band structure, particle size, and surface properties of the photocatalytic material, incident light intensity, and pH of the solution are effective to determine the efficiency of the photocatalytic semiconductors when used as photocatalysts [5]. In photocatalytic processes, semiconductors such as TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, CdS, and ZnS are optically activated to act as sensitizers for light-induced redox-processes.

Among these various semiconductors,  $\text{TiO}_2$  and  $\text{ZnO}$  are the most commonly used photocatalysts especially employed for the degradation of several environmental contaminants because of their high photosensitivity, stability, and large band gaps [4]. To date most of the applications reported in the literature are conducted in aqueous media. This, however, gives rise to technical difficulties associated with the removal of photocatalyst from the medium and their use in wide-scale industrial applications.

To circumvent these issues, one remedy is to immobilize the photocatalyst in thin films on a suitable substrate. But the immobilization then leads to the reduction in the active surface area (and thus in the photocatalytic activity) [1]. To compensate for this reduction in the photocatalytic efficiency, though, nanoparticle can be utilized to effectively increase the active surface area provided that these nanoparticles are integrated into the thin film properly and well dispersed. In our previous work, we focused on mostly using  $\text{TiO}_2$  nanoparticles [5, 6] and recently started investigating  $\text{ZnO}$  nanoparticles [7]. In this work for the first time, we performed a comparative study of photocatalytic nanocomposites that incorporate immobilized  $\text{TiO}_2$  and  $\text{ZnO}$  nanoparticles well dispersed in three-dimensional solgel matrices through full chemical integration for highly efficient environmental decontamination. Here we experimentally investigated their spectral photocatalytic efficiencies from 270 to 370 nm in the UV and demonstrated very high photocatalytic recovery levels up to 93% for massive environmental decontamination.

$\text{TiO}_2$  is a large band gap semiconductor, with its conduction and valence bands composed of pure 3d orbital of titanium and 2p orbitals of oxygen hybridized with Ti 3d states, respectively. Electrons in the  $\text{TiO}_2$  valence band are conveniently excited to its conduction band when exposed to UV light. The dissimilar parity of the respective bands desirably reduces the electron-hole recombination rate to allow the  $e^-h^+$  pair to diffuse to the surface and initiate a chain of reactions to produce reactive oxygen species and hydroxyl radicals ( $\cdot\text{OH}$ ) that are powerful indiscriminate oxidizing agents.

Similarly,  $\text{ZnO}$  is a member of the 3d metal-oxide series. As in  $\text{TiO}_2$ , the photoexcited  $e^-h^+$  pair of  $\text{ZnO}$  has also dissimilar parity, making  $\text{ZnO}$  a good candidate for photocatalyst.  $\text{ZnO}$  and  $\text{TiO}_2$  are the only two among the 3d transition metal-oxide semiconductors that remain stable upon photoexcitation. Comparing  $\text{ZnO}$  and  $\text{TiO}_2$ , it is reported that  $\text{ZnO}$  powder has significantly larger quantum efficiency than that of  $\text{TiO}_2$  powder [2]. Also for comparative work, many research studies in water have been conducted, but there is little research available in the literature for immobilized nanoparticles, although immobilized form is by far more versatile for applications. This motivates us to focus on the photocatalytic efficiency characteristics of both  $\text{ZnO}$  and  $\text{TiO}_2$  in thin films.

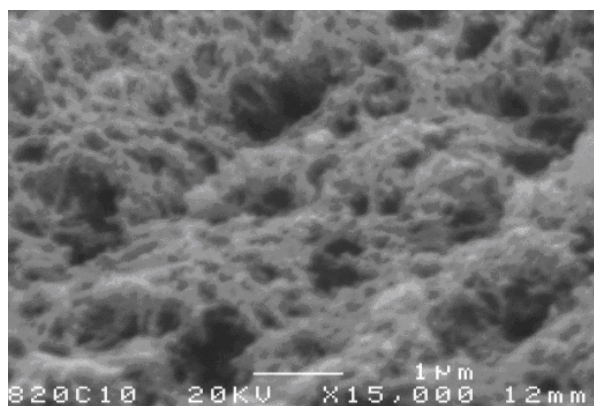


Fig. 1. SEM image of our photocatalytic nanocomposites that integrate nanoparticles in three-dimensional solgel matrices.

## 2 EXPERIMENTAL

In this work, we chemically embedded our metal oxide nanoparticles into the three dimensional matrix of the solgel resin via covalent bonding (Figs. 1 and 2) [5-8]. During the solgel synthesis two types of silicon alkoxides were used to obtain the hybrid organic-inorganic material that leads to the formation of a 3D silica network. The solvent plays an important role to control the formation and properties of silica gels. Thus, to achieve an appropriate host resin, we used ethyl alcohol and iso-propyl alcohol. Hydrolysis and condensation rates of silicon alkoxides were further enhanced by HCl (0.1 N) catalysis. Reaction initiation temperature was 50 °C. Nanoparticle dispersion integrated into the resulting solgel was applied on acetate film through spray coating method. As a result of the chemical integration, we obtained nanocomposite materials with their nanoparticles dispersed more uniformly than mere blending. Here we used TiO<sub>2</sub> nanoparticles of 6 nm in size and ZnO nanoparticles of 150 nm in size, with the mass ratio of the incorporated nanoparticles to the host solgel of 6.0% for TiO<sub>2</sub> and of 9.5% for ZnO in thin films of about 10 μm in thickness.

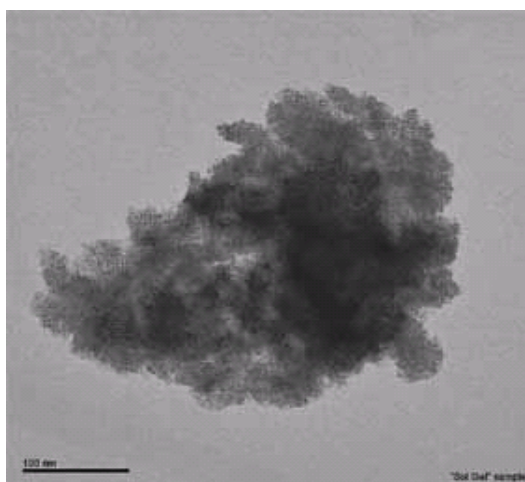


Fig. 2. TEM image of our prepared solgel.

Optical characterization was conducted through optical transmission spectroscopy of our samples in the visible range before contamination, after contamination and after activation at selected wavelengths in the UV regime. In our experiments, methylene blue was used as the standard chemical contaminant. The intentional chemical contamination of our samples with methylene blue significantly decreased their optical transmission in the visible, and subsequently, upon optical activating them at a particular wavelength in the UV regime, the photocatalytic degradation increased their optical transmission in the visible back toward the original level. Thus, the ratio of the spectral area integrated between the transmittance curves before and after photocatalytic degradation to the area between transmission spectrum of the initial and contaminated sample indicates the level of relative photocatalytic efficiency at the particular activation wavelength. Repeating this experiment at different activation wavelengths and varying the level of optical activation energy per unit area, we obtain the relative spectral photocatalytic efficiency.

### 3 RESULTS AND DISCUSSIONS

Figure 3 shows the comparative spectral photocatalytic efficiencies of the resulting TiO<sub>2</sub> and ZnO nanocomposite films parameterized with respect to the excitation wavelengths (from 270 to 370 nm) as a function of the incident total optical energy per unit area (i.e., incident optical intensity  $\times$  time) (increased from 18000 Joules/m<sup>2</sup> to 73000 Joules/m<sup>2</sup>). These photocatalytic efficiency curves were experimentally measured using transmission spectroscopy in the visible spectral range with intervals of UV exposure at the selected wavelengths for the decontamination of the nanocomposite films. In the control group (only resin with no metal oxide nanoparticles), no optical recovery is observed in the case of methylene blue after optically illuminated in the UV regime under identical conditions.

In Fig. 3, we observe a general trend of higher photocatalytic activity for the smaller-size TiO<sub>2</sub> nanoparticles (despite their lower concentration in this work) than the larger-size ZnO nanoparticles, although ZnO has higher quantum efficiency. Thus, for immobilized metal oxides, we show that the size effect (surface-to-volume ratio) and the total active surface area (morphology of the thin film) are evidently very effective in photocatalytic process, in addition to the metal oxide type. We also find out that there is an optimal activation wavelength to spectrally maximize the photocatalytic activity due to the optical absorption properties of the nanoparticles and the host. Here we achieve the highest optical recovery level of 93% with TiO<sub>2</sub> at 310 nm and of 55% with ZnO at 290 nm. This indicates that it could be possible to tune the optimal activation wavelength using combinations of TiO<sub>2</sub> and ZnO nanoparticles integration in one resin [8].

Using the slopes of the linear fits to these efficiency curves in Fig. 3, we obtain the differential efficiencies at different activation wavelengths as a figure-of-merit to represent the incremental photocatalytic activity per unit optical energy/area (optical intensity  $\times$  time). Table 1 shows the relative differential efficiencies both for TiO<sub>2</sub> and ZnO films, with TiO<sub>2</sub> exhibiting better differential behavior. Here we observe good correlation between the relative photocatalytic efficiency and the relative differential efficiency in general since the photocatalytic efficiency curves require larger slopes to reach high levels within a finite period of optical activation at a certain optical intensity. We expectedly achieve the highest differential efficiencies for both nanoparticles at the same activation wavelengths where the highest photocatalytic efficiencies are obtained.

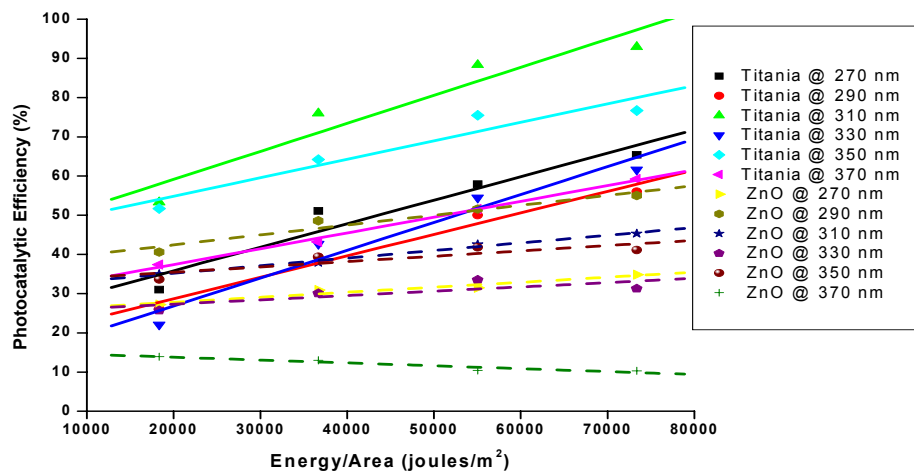


Fig. 3. Relative spectral photocatalytic efficiency of TiO<sub>2</sub> and ZnO nanocomposite films at activation wavelengths (270-370 nm) as a function of incident total optical energy per unit area (incident optical intensity  $\times$  time).

Table 1. Relative differential efficiencies of TiO<sub>2</sub> and ZnO nanocomposite films (1/Joules/m<sup>2</sup>).

| Wavelength       | 270 nm                  | 290 nm                  | 310 nm                  | 330 nm                  | 350 nm                  | 370 nm                   |
|------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| TiO <sub>2</sub> | 6.00 x 10 <sup>-4</sup> | 5.47 x 10 <sup>-4</sup> | 7.15 x 10 <sup>-4</sup> | 7.10 x 10 <sup>-4</sup> | 4.70 x 10 <sup>-4</sup> | 4.02 x 10 <sup>-4</sup>  |
| ZnO              | 1.28 x 10 <sup>-4</sup> | 2.52 x 10 <sup>-4</sup> | 1.94 x 10 <sup>-4</sup> | 1.10 x 10 <sup>-4</sup> | 1.36 x 10 <sup>-4</sup> | -0.73 x 10 <sup>-4</sup> |

#### 4 CONCLUSIONS

We developed and investigated highly efficient photocatalytic nanocomposites that incorporate TiO<sub>2</sub> and ZnO nanoparticles separately in three-dimensional sol-gel matrices through full chemical integration for applications of environmental decontamination. We presented optical characterization of the spectral response of photocatalytic TiO<sub>2</sub> and ZnO nanoparticles to UV activation for self-cleaning process and demonstrated their optical relative spectral efficiency curves from 270 to 370 nm in the UV. We also showed very high optical recovery levels up to 93% for the photocatalytic decontamination of these nanocomposites. In addition to their relative photocatalytic efficiency curves, we reported their relative differential efficiencies at excitation wavelengths from 270 nm to 370 nm for a comparative study of TiO<sub>2</sub> and ZnO nanoparticles immobilized in thin films. Investigating the optimal conditions to increase their spectral photocatalytic efficiencies, we concluded that these nanocomposites exhibit remarkably high levels of optical recovery and efficiency and hold great promise for future massive environmental decontamination.

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**Hilmi Volkan Demir** received a B.Sc. degree in electrical and electronics engineering from Bilkent University in 1998, and M.S. and Ph.D. degrees in electrical engineering from Stanford University in 2000 and 2004, respectively. In September 2004, he joined Bilkent University, where he is currently an Assistant Professor with joint appointments at the Department of Electrical and Electronics Engineering and the Department of Physics. He is the Associate Director of Nanotechnology Research Center and a faculty member of Advanced Research Laboratory at Bilkent University. Dr. Demir received the European Science Foundation (ESF) European Young Investigator Award (EURYI) in 2007, the Outstanding Young Persons Award (TOYP) of Junior Chamber International (JCI Worldwide Federation of Young Leaders and Entrepreneurs) in Scientific Leadership/Accomplishment in Turkey in 2006 and World First Prize in 2007, the Turkish National Academy of Sciences Distinguished Young Scientist Award (TUBA GEBIP) in 2006, and the European Union Marie Curie Fellowship (EU MC IRG) in 2005.