

## Size effect in optical activation of TiO<sub>2</sub> nanoparticles in photocatalytic process

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At nano scale, the size of particles becomes an important parameter that significantly affects the associated quantum processes due to tighter quantum confinement and some of the classical processes due to increasing ratio of surface atoms to bulk atoms as the volume of the particle shrinks. The size effect is evident in the characteristics of commonly known nano structures such as quantum dots and carbon nanotubes. Another class of relatively less known nanostructures where we observe significant influence of the size is titaniumdioxide (TiO<sub>2</sub>) nanoparticles in photocatalytic activity due to their optical activation process [1]. Such photocatalytic nanoparticles are attractive for different self-cleaning applications such as environmental bio-decontamination for a large variety of organics, viruses, bacteria, fungi and cancer cells, and chemical and biological purification of water [2-3]; and in such applications, the efficiency of the optical activation is critical, for which the nanoparticle size matters. In this work, we optically investigate and characterize the photocatalytic recovery of contaminated TiO<sub>2</sub> nanoparticles of different sizes that are incorporated in solgel films to study the size effect. We demonstrate significant improvement in the optical efficiency of the photocatalytic nanoparticles as we reduce the particle size.

Figures 1a and 1b show pictures of our samples that include 21 nm and 6 nm, anatase-type TiO<sub>2</sub> nanoparticles, respectively, both of which are embedded in 10 μm thick acrylic solgel films and contaminated with the same methylene blue solution. Figures 1a and 1b exhibit the self-cleaning effect within the spot size of the activating UV illumination at the centers of the 21 nm and 6 nm samples, respectively, in contrast to the non-activated region around these spots on the samples. Comparing these pictures, we observe that the contaminated region is optically recovered back further towards its original with the use of the size effect. This is due to the increased TiO<sub>2</sub> surface with reducing nanoparticle size, which gives rise to enhancement of the photoefficiency and hence the photocatalytic process.



Figure 1: Pictures of 10 μm thick acrylic solgel film embedded with (a) 21 nm and (b) 6 nm TiO<sub>2</sub> nanoparticles that are contaminated with the same methylene blue solution and activated under the same conditions.

Figure 2a shows the optical transmission spectra of 21 nm TiO<sub>2</sub> samples before and after the methylene blue contamination in the visible range from 400 nm to 700 nm, along with the time evolution of the transmission spectra under UV activation with the optical power of 200 μW at 330 nm after 6 and 16 hours. The methylene blue contamination shifts the optical transmission curve significantly in the visible range. We observe that the optical transmission of the contaminated sample shifts significantly back after the first 6 hours of photoexcitation, but shifts only slightly after the 16 hours of photoexcitation. On the other hand, Fig. 2b plots the optical transmission spectra of 6 nm TiO<sub>2</sub> samples in the same spectral range at the same time intervals under the same UV radiation conditions. In this experiment, we observe that the decontamination process of the 6 nm nanoparticles does not saturate after 6 hours of activation, unlike the 21 nm sample, but continues further to higher recovery levels. This is clearly evident in the optical transmission spectrum measured after 16 hours of photoexcitation in Fig. 2b.

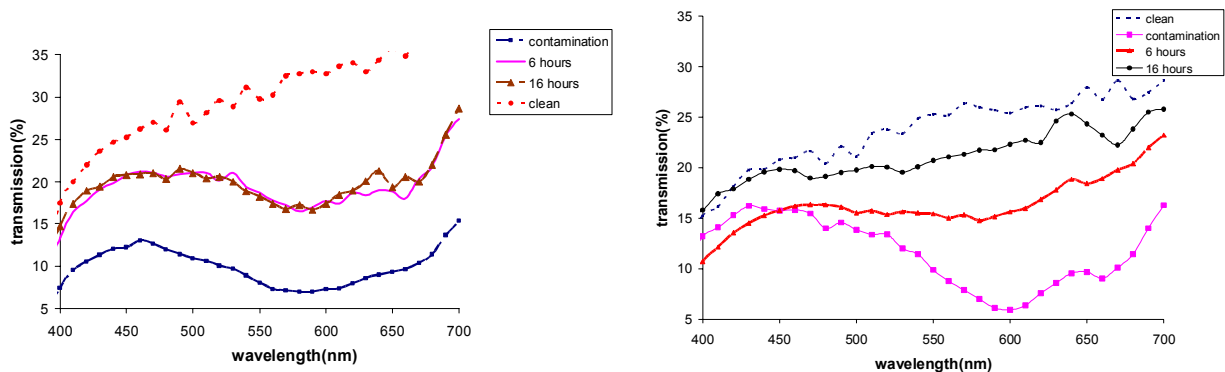


Figure 2: Optical transmission of the sol-gel films that incorporate (a) 21 nm and (b) 6 nm size TiO<sub>2</sub> nanoparticles before and after the contamination with UV activation after 0, 6, and 16 hours.

Figure 3a shows the optical efficiency in the initial recovery phase of 6 nm and 21 nm nanoparticles as a function of the number of incident activation photons per unit area. Here we calculate the optical efficiency by normalizing the area integrated between the optical transmission of the activated sample and that of the contaminated sample in the visible range from 400 nm to 700 nm with respect to the area between those of the original and contaminated samples. This characterization proves that the optical efficiency of the photocatalytic process for 6 nm nanoparticles is higher than that of the 21 nm nanoparticles. Figure 3b plots the extended optical recovery as a function of the number of activation photons per unit area for both 6 nm and 21 nm samples. We observe that, similar to the low recovery phase, the nanoparticles of 6 nm in size exhibit larger optical efficiency than those of 21 nm in size. As a result, while the optical recovery increases up to 80% for the 6 nm sample, it remains almost saturated around 50% for the 21 nm sample.

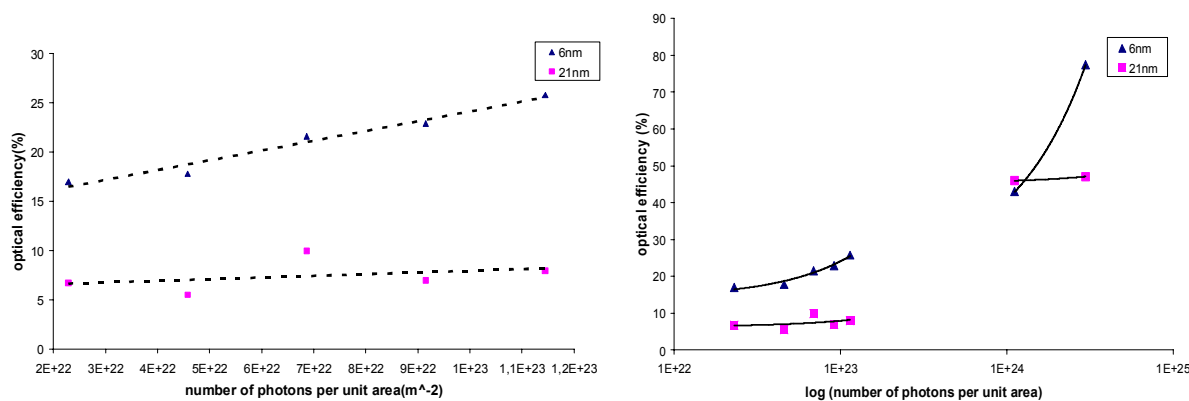


Figure 3: Optical efficiency of 21 nm and 6 nm nanoparticles (a) in the low recovery phase and (b) high recovery phase.

In conclusion, we demonstrate the size effect on the optical efficiency of 6 nm and 21 nm TiO<sub>2</sub> nanoparticles embedded in sol-gel during the photocatalytic decontamination process. We prove that smaller nanoparticles have significantly higher optical recovery efficiency than larger ones under the same activation conditions for both sizes.

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