3P090

Regarding the nanostructure of silver metal produced photocatalytically in TiO_2 films and the mechanism of the resulting photochromic behavior.

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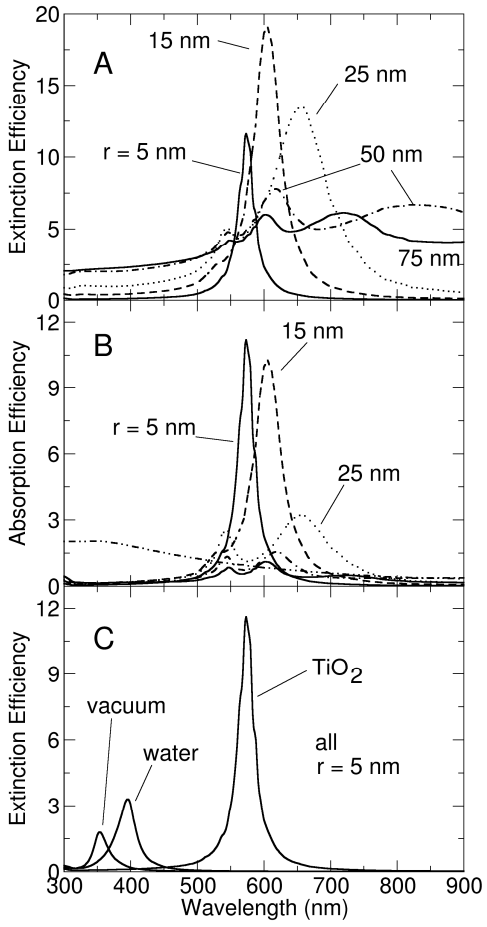
A topic of recent interest in experimental nanoparticle sysnthesis has been the shape change of silver metal nanoparticles from spherical shapes to pill or triangular prism shapes. [For example, Jin, *et. al.* Nature **426**, 487 (2003)] Concurrently, unrelated experimental research involving the photosensitization of TiO2 nanocrystalline films has demonstrated multicolor photochromic based on the optical response of silver. [Naoi, Ohko, Tatsuma, JACS **126**, 3664 (2004)] We find similarities between these two studies, and we propose that shape change mediated by typical room light, *i.e.* low power, is occurring in the TiO_2/Ag system.



The optical activity of composite films created by the photocatalytic reduction of silver or gold ions in TiO_2 upon irradiation by UV light has up to now been discussed in terms of the formation and light-induced destruction of distinct nanoparticles molded inside the porous nanocrystalline film. We present results from light scattering calculations and analysis of experimental observations which adds detail to the mechanism. As opposed to regularly shaped particles, random extended structures and coatings in heterogeneous external dielectric environments account for observations such as the broad optical spectrum. In addition, for some steps of the photochromic process, we propose a visible light-induced equilibrium that induces the growth and destruction of small metal features or suspended particles. We conclude by discussing the consequence of the interaction of the plasmon with the electronically active TiO_2 surrounding matrix, leading to mass transfer and shape change of the metal.