

# Ultrasound Driven Design of Photocatalysts

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Ultrasonic irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure, and energy. The chemical and physical effects of ultrasound are driven by acoustic cavitation, the growth, oscillation and collapse of microbubbles in the medium. Short-lived, localized hot spots in a cold liquid produced by cavitation are characterized by temperature of ca. 5000 K, pressure of about 1000 atmospheres, lifetime considerably less than a microsecond, and heating and cooling rates above  $10^{10}$  K per second. When cavitation occurs in a liquid near a solid surface, the dynamics of cavity collapse changes dramatically. In pure liquids, the cavity remains spherical during collapse because its surroundings are uniform. However, near to a solid surface cavity collapse is very asymmetric and generates high speed jets of liquid which allows to use the ultrasound processes in a great variety of applications like formation of developed surfaces, finishing, catalysts formation, polymerization and surface polymer attachment, etc.<sup>[1-5]</sup> Here, we report on the ultrasound driven formation of photocatalysts such as zinc oxide and titania doped with fine metal particles.

For ultrasonic driven design of porous and unporous zinc oxide, 40 ml of 10 wt% suspension of metals in purified water were sonicated in a thermostated flow cell (at 65°C temperature) with a maximal output power of 1000 W ultrasonic horn. The maximum intensity was calculated to 57 W/cm<sup>2</sup> at a mechanical amplitude 81  $\mu$ m. For ultrasonic driven modification of mesoporous titania 40 ml of 10 wt% suspension of mesoporous titania<sup>[6]</sup> in purified water were sonicated in the presence of fine 4-8 nm silver, gold and palladium nanoparticles. The photocatalytic activity of sonochemically design photocatalysts were investigated using a photodegradation of arylmethane and azo dyes under UV illumination.

The ultrasound stimulated formation of zinc oxide on the surface of zinc particles occurs after short-term sonication yielding 2  $\mu$ m zinc oxide crystals of tubular morphology (Fig.). Probably due to their brittleness they are decomposed by further sonication. Long-term treatment (>30min) stimulates formation of stable nanorods with length  $\sim$  100 nm and diameter approximately 20 nm (Fig.). The maximum surface area for 15-min sonicated Zn sponges was 22 m<sup>2</sup>/g. The average pore diameter estimated by BET analysis is about 20 nm for the 15 min treated zinc particles, while 30- and 90- min-sonicated samples exhibit unporous structure. XRD

patterns reveal presence of zinc oxide after 90 min of sonication and, therefore, complete conversion of Zn in ZnO.

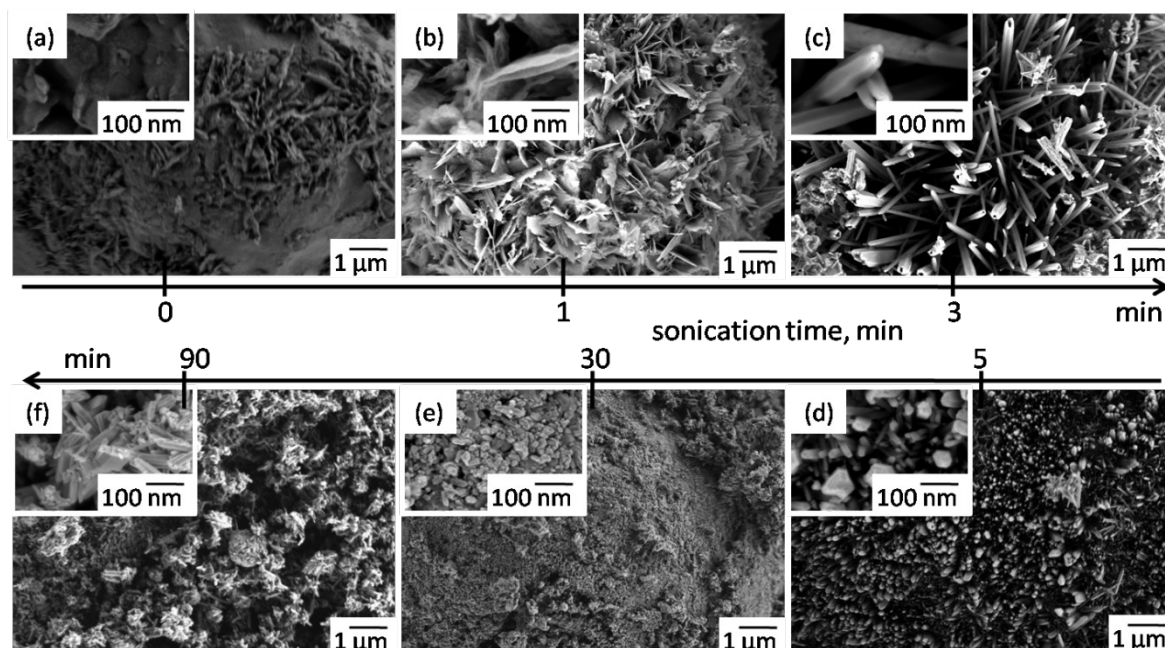


Fig. SEM images of initial Zn particles (a) and the particles sonicated at 57 W/cm<sup>2</sup> for 1 min (b), 3 min (c), 5 min (d), 30 min (e) and 90 min (f). The insets show the ZnO tubes and nanorods and the main pictures – overviews of the particle surface.

It has been shown that modification of TiO<sub>2</sub> with the nanoparticles of noble metals results in a drastic increase in the photoactivity. The observed changes in the photoactivity are discussed in terms of the effect of metal deposition on the recombination losses and the yield of superoxide generated in the system.<sup>[7]</sup> Simultaneously change of the intensity of ultrasonic irradiation provides the control of photocatalyst design.

- [1] Suslick, K. S.; Price, G. J. *Annu. Rev. Mater. Sci.* **1999**, 29, 295-326.
- [2] Lorimer, J. P.; Mason, T. J. *Chem. Soc. Rev.* **1987**, 16, 239-274.
- [3] Mdleleni, M. M.; Hyeon, T.; Suslick, K. S. *J. Am. Chem. Soc.* **1998**, 120, 6189-6190.
- [4] Suslick, K. S.; Choe, S.-B.; Cichowlas, A.; Grinstaff, M. W. *Nature* **1991**, 353, 414-416.
- [5] Chemistry with ultrasound. Ed. T J Mason. Elsevier Sci. Pub.: **1990**, Vol. 28, 195 p.
- [6] Skorb, E.V., Shchukin, D.G., Möhwald, H., Sviridov, D.V. *J. of Mater. Chem.* **2009**, 19, 931-4937.
- [7] Skorb, E.V., Antonouskaja, L.I., Belyasova, N.A., Shchukin, D.G., Sviridov, D.V. *Appl. Catal. B: Environ.* **2008**, 84, 94-99.