



# Spherical superstructures of oxide nanoparticles for catalytic reactions in microchemical reactors



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## ABSTRACT

We report the fabrication of spherical superstructures composed of SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles and their applications in catalyzing organic reactions. Assembling of the nanoparticles into superstructures is done by heating a water-in-oil micro-emulsion, which contains chemically activated oxide nanoparticles in the aqueous microdroplet phase. Water vapour-induced convective flow leads to microdroplet fusion and subsequent concentric arrangement of all nanoparticles of the emulsion into a larger superstructure, mimicking a pearl-like, layer-over-layer, growth mechanism. These superstructures are subsequently employed for catalyzing the anti-Markovnikov addition reaction of thiol to olefin, and in an aromatic azo-compound synthesis in microchemical reactors under static and dynamic flow conditions. The superstructure format presents the advantage of an easier recovery of the catalysts from the reactor, compared to the use of the native individual nanoparticles.

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## 1. Introduction

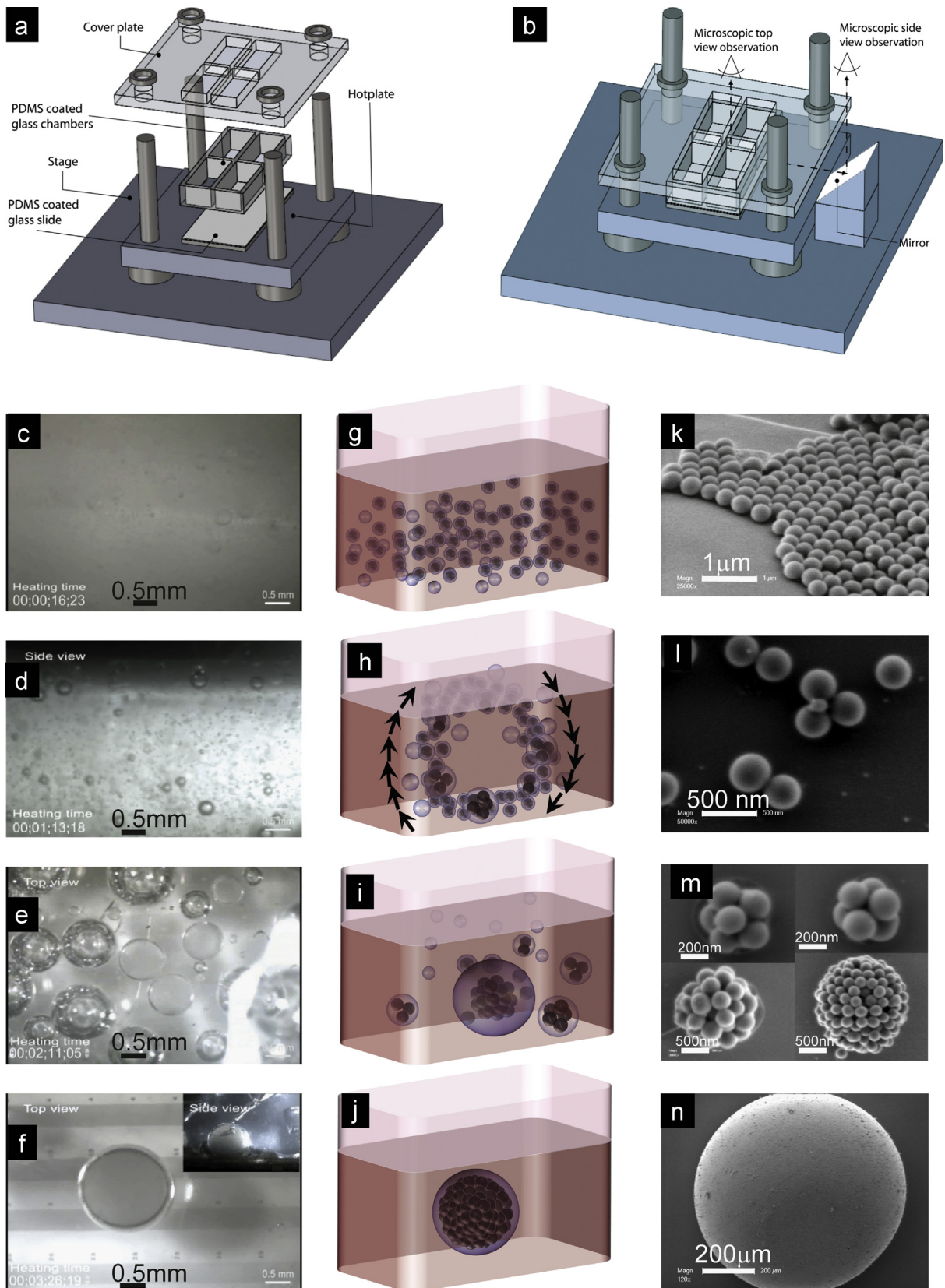
Currently, microchemical reactors are increasingly used in fine chemical synthesis, but catalysis by individual nanoparticles in these systems can cause problems, like blocking of the reactor channels due to the tendency of agglomeration of the nanoparticles and their difficult recoverability and reusability after the reaction [1–3]. These problems can be mostly avoided by employing a catalytic substrate that is large enough to be easily manipulable, but still provides the distinctive catalytic properties of the nanoparticles. Such solution would be enabled by employing nanoparticle superstructures [4–6], if they can be large enough so that they can be easily separated from the solution after catalytic use and still have the inherent properties of the individual nanoparticles. In particular, such nanoparticle superstructures should have a high number of interfaces and be characterized by a high specific catalytic area. Previous superstructure formation approaches employed the assembly of nanoparticles already present in a single colloidal droplet [5,7]. This method gave either smaller clusters with a few nanoparticles or hollow assemblies. In our present study, we form much bigger assemblies by merging the numerous aqueous microdroplets of a

water-in-oil emulsion containing nanoparticles in the aqueous phase. Moreover, we explore, besides the superstructure formation, the demonstration of the superstructure's efficacy toward catalyzing organic reactions in microchemical reactors.

## 2. Materials and methods

Synthesis of silica, titania nanoparticles and gold linking of titania were done, as described earlier [8,9]. Chemical pre-activation of the silica nanoparticles was done in water at 120 °C at a nitrogen pressure of 6–8 bar. H<sub>2</sub>O<sub>2</sub>-induced pre-activation of the titania nanoparticles was done in a 1% H<sub>2</sub>O<sub>2</sub> (30 wt %) solution. Emulsions to use in the spherical assembly process were prepared using a 6 vol % oxide colloid (solid content 8 wt %) in di-octyl phthalate (DOP) oil medium containing 5 vol % TX-100 using a homogenizer or vortex at 40 Hz. This emulsion is poured into a preheated container at 120 °C. Water vapour-induced convective flow in this boiling-like process leads to microdroplet fusion and subsequent concentric assembling of the nanoparticles into superstructures. Spherical assemblies of silica and gold-linked titania nanoparticles were applied for nanoparticle-based catalytic reactions [10,11]. See electronic [supplementary materials \(ESM\)](#) for further details of processes and characterization techniques.

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**Fig. 1.** Setup for monitoring the superstructure formation process and characterization by optical microscopy and SEM of the superstructures. (a) Exploded and (b) assembled schematic view of the used setup. (c–f) Optical photographs and (g–j) corresponding pictorial views of the superstructure formation process. (c–f) are obtained from Movie 1 of the ESM, starting from an emulsion having 8 wt. % aqueous dispersed phase in DOP and 8 wt. % silica in water. The photographs are taken at different times after initiation of the process: (c) 16 s, (d) 73 s, (e) 131 s, while (f) presents the finally obtained spherical superstructure. (k–n): SEM photographs of (k) the native nanoparticles, samples collected from the process container at (l) 65 s, and (m) various times from 85 s to 125 s, and (n) the final superstructure after sintering.

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