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The preparation of silica–titania core–shell particles and their impact as an alternative material to pure nano-titania photocatalysts

S. Kamaruddin, D. Stephan*

Faculty of Civil Engineering, Building Materials and Construction Chemistry, University of Kassel, Mönchebergstraße 7, 34125 Kassel, Germany

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ABSTRACT

In this study spherical core–shell particles in the range 200–800 nm were prepared. Heterocoagulation method was applied to deposit nano-crystalline titania on monodisperse Stöber silica spheres. Silica and titania were synthesized separately via sol–gel processes. Titania was obtained from tetrapropyl orthotitanate and titanium tetrachloride as the precursors. Particle sizes were analysed by photon cross correlation spectroscopy. Deposition of titania on the surface was verified by transmission electron micrographs. The extent of coverage was analysed by zeta-potential measurements and varied between 40 and 90%. The degradation of an aqueous methylene blue solution confirmed photocatalytic activity of the particles.

1. Introduction

Titania is widely used as a photocatalyst and shows high potential in reducing environmental contamination by decomposing organic and inorganic pollutants [1,2]. Its photocatalytic activity is based on semiconductor bandgap effects that occur when it is irradiated with UV-light. Subsequently electron–hole pairs are generated and then diffuse to the surface, where they are responsible for oxidation and reduction [3,4]. Especially in nanoscaled dimensions TiO_2 performs effectively, due to its high surface area. However, nanoparticles easily tend to agglomeration. As they are not thermally stable they also undergo phase transformation and crystallite growth at higher temperatures. These effects lead to a reduction in the effective surface area [5]. In different studies [6,7] it was found that fine particles, such as nano-TiO_2 can have an effect on health. Moreover, recovery of particles in that size range is a problem [8]. One method to solve these problems is to adsorb such fine particles on larger particles of another material to form a thin layer with high porosity and also high surface area [5,8,9]. As a result also hazardous effects on health, due to the small particle size can be reduced. These kinds of composite materials are known as core–shell particles and are also of great economic interest. Costs for the expensive photocatalytic material are reduced, as it is used only for the shell. The core may consist of a cheaper material like silica, since it has no influence on the photoinduced processes on the surface. It has also been reported that silica–titania core–shell particles showed enhanced photocatalytic activity as compared to pure titania [5,10]. Variability of size and thickness of core and shell is possible, which leads to tailored materials for different applications [11]. Several methods are known to prepare titania coated silica particles. For example Hu et al. synthesized such core–shell particles by a flame aerosol process [12]. Kalele et al. describe a method, where titania coated silica particles were derived by controlled hydrolysis of titanium butoxide, which gets condensed on the cores afterwards [13].

In this work, discrete photocatalytically active core–shell particles composed of silicon dioxide and nano-crystalline titanium dioxide were prepared via heterogenic coagulation [8,14]. Based on electrostatic attraction forces the adsorption of titania particles on the silica cores was performed (Scheme 1). The aim was to find out whether these particles show photocatalytic activity and have potential to be used as an alternative material to pure nano titania. The particles were characterized by using transmission electron microscopy (TEM), zeta potential and specific surface analysis. Photocatalytic activity was studied via degradation of an aqueous methylene blue solution.

2. Experimental

2.1. Synthesis of the silica core material

Monodisperse silica spheres were synthesized in various sizes between 200 and 800 nm via a method, which was first described by Stöber et al. [15].

To obtain different particle sizes the proportions of the reactants tetraethyl orthosilicate (TEOS, Wacker silicones), ammonia, water and ethanol were varied according to the data given in Table 1. First ethanol, ammonia and water were mixed, whereupon the

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* Corresponding author. Tel.: +49 561 804 2603.
E-mail address: dietmar.stephan@uni-kassel.de (D. Stephan).

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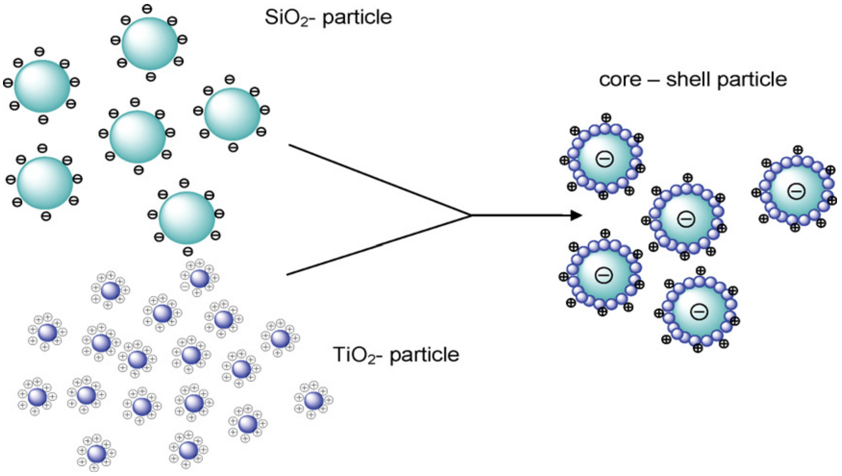

Scheme 1. Heterocoagulation method based on electrostatic attraction forces.

appendant amount of TEOS was added under continuous stirring. After 24 h the precipitates were repeatedly centrifuged and washed with water. The washed precipitates were then either dried at 40 °C and redispersed in water by ultrasonic treatment (samples HK1) or directly dispersed in water again (samples HK2) to obtain silica sols with pH 8–9.

2.2. Synthesis of the titania shell material

Two titania sols were prepared by using different titania precursors. The first titania sol was prepared by dissolving 30 g of tetrapropyl orthotitanate (TPOT, Merck KG) in 300 g ethanol and then adding 3 ml of hydrochloric acid to this solution. After 5 min 30 ml of distilled water was introduced under continuous stirring, whereupon hydrolysis took place. The resulting sol had transformed into a viscous gel after about 1 h. The precipitate was collected after 24 h by removing the solvent under reduced pressure. The residue was dispersed in water to obtain a transparent titania sol with pH 1–2. The concentration of the titania sol was adjusted to be double that of the silica sol.

For the second titania sol, 2 g $TiCl_4$ (Kronos International) were hydrolysed in 75 g of cold water (1 °C) under continuous stirring for 30 min. The resulting titania sol with pH 1 was used for the second coating process.

2.3. Coating process

Silica–titania core–shell particles were prepared via heterogenic coagulation method.

For the coating process the first titania sol was added with a feed rate of 0.5 ml/min to 270 ml silica sol under continuous stirring. The coating process was monitored via zeta-potential measurements as it was first done by Wilhelm and Stephan [11]. The zeta potential turned from negative to positive until a plateau was reached, which indicated the end of the coating process. The second titania sol ($TiCl_4$ precursor) was added with a feed rate of 0.5 ml/min to 640 ml sol of silica spheres with an average particle size of 833 nm using a peristaltic pump.

All coated spheres were stirred further for 16 h to complete the coating process. The particles were then purified by repeated sedimentation and redispersion in water and dried at 40 °C. Following, the core–shell particles obtained with titania sol from $TiCl_4$ were also calcined at 750 °C for 1 h. The core–shell particles prepared with titania particles from TPOT were not treated thermally.

2.4. Characterization

The particle size analysis of silica and titania particles was performed via photon cross correlation spectroscopy (PCCS) (Nanophox, Sympatec, Germany). The mineralogical composition of titania was determined by X-ray diffraction (Bruker AXS, Germany) and Rietveld analysis. Data of specific surface area where collected through BET physisorption method (Autosorb-1 Quantachrome, USA). Zeta potentials were derived from electrokinetic sonic amplitude signals of electroacoustic measurements (Zeta Probe Analyzer^{TM}, Colloidal Dynamics, USA). Morphology of the particles was examined using SEM (Philips XL 30, Netherland) and TEM (Tecnai 20, Fei, USA).

3. Results and discussion

3.1. Characterization

Silica particles in different sizes were synthesized via the well known Stöber process. The average particle sizes of the silica spheres were 237, 345, 383 and 833 nm as illustrated in Fig. 1. The particle size distribution of small particles was very narrow, that of bigger particles was broader. Particle sizes were measured via PCCS using aqueous dispersions of the samples. The sample with the mean diameter size of 833 nm contained agglomerates, so the

Table 1
Amounts of reactants for preparation of Stöber silica in different sizes.

Particle size [nm]	TEOS amount [ml]	$NH_{3(aq)}$ amount [ml]		EtOH amount [ml]
172	10	12	(NH_3 25%)	250
237	33	61	(NH_3 32%)	750
345	22	54	(NH_3 25%)	500
383	22	65	(NH_3 25%)	500
833	50	61	(NH_3 32%)	320