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

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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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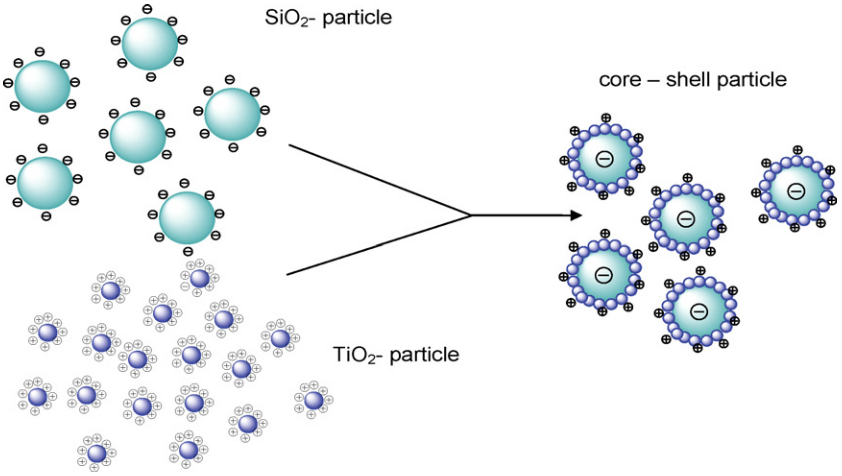


Scheme 1. Heterocoagulation method based on electrostatic attraction forces.

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

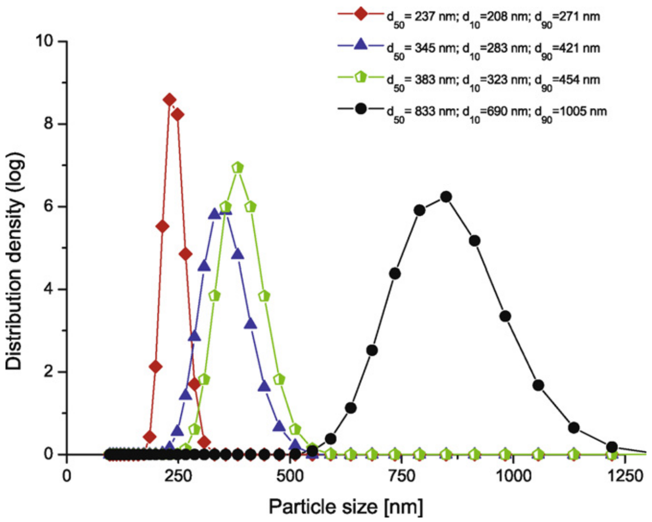


Fig. 1. Particle size distribution of silica cores measured via PCCS.

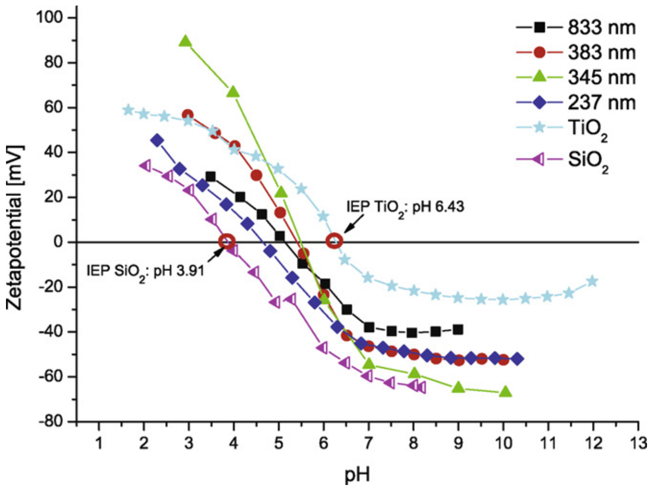
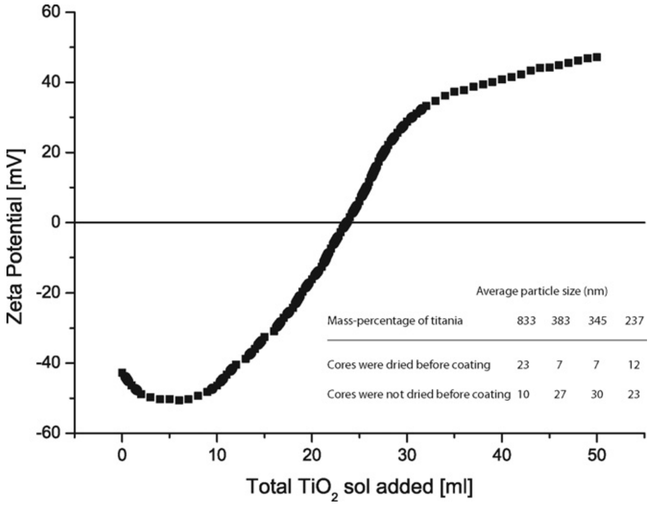


Fig. 3. Variation of zeta potential with pH values of silica–titania (833–237 nm) and pure silica and titania particles (silica cores were dried before coating).

mean diameter size in this case is mainly that of such agglomerates. Particle size of titania prepared using TPOT as the precursor was measured by dispersing the titania powder in water ultrasonically. The particle size distribution was $d_{50} = 17.6$ nm, $d_{10} = 14.0$ nm, $d_{90} = 22.0$ nm. The BET specific surface area was 107 m^2/g. Before any heat treatment the mineralogical composition of these titania particles was as follows, 50 wt% brookite, 44 wt% anatase and 6 wt% rutile. Titania prepared from $TiCl_4$ was amorphous for XRD and not further characterized as the sol was directly used for the coating process.

For the coating process the dispersion stabilities of the initial silica and titania sols are of high relevance to prevent homocoagulation. To achieve heterocoagulation by electrostatic attraction forces opposing surface charges are important. These aspects were investigated via zeta-potential measurements as functions of pH values. As the dispersion stability was highest at pH 1–2 for titania and pH 8–9 for silica and opposing surface charges were also guaranteed for theses pH values, they were taken as the starting pH values. The coating process was monitored via zeta-potential measurements while titrating with the titania sol obtained from TPOT. Fig. 2 demonstrates exemplarily the change in zeta potential in dependency to the total amount of titania added to silica spheres with an average particle size of 833 nm. The zeta potential becomes more and more positive while adding titania as a result of change in pH and adsorption of titania particles on silica spheres. However, after a certain amount of titania was added a plateau was reached, which indicated the end of the coating process. Further rise of zeta potential was due to change of pH. The decrease of zeta potential at very low amounts of added titania can be due to overlapping effects, which result of the change of pH and conductivity. The exact cause is not yet clear.



	Average particle size (nm)			
Mass-percentage of titania	833	383	345	237
Cores were dried before coating	23	7	7	12
Cores were not dried before coating	10	27	30	23

Fig. 2. Left: Coating process of silica (833 nm) with titania (TPOT) visualized by zeta-potential measurement. Right: Mass percentages of titania deposited on the silica cores during the coating processes.

The resulting core–shell particles as well as the single core and shell materials were characterized via zeta-potential measurements, electron micrographs and gas adsorption analysis.

The zeta potentials were measured to characterize surface properties of the core–shell particles. Upon increasing the pH of the solutions containing either the core–shell particles or pure titania or silica, the zeta potential gradually decreased (Fig. 3). When the pH is higher than the isoelectric point (IEP), the surface and therefore the zeta potential becomes negative because of deprotonation. It was observed that the IEP of the core–shell particles ranged between those of pure silica (IEP at pH 3.91) and titania (IEP at pH 6.43). This indicates that titania particles have adsorbed on the surface of silica particles. Transmission electron micrographs show the uncoated silica spheres in contrast to the coated particles, where the surface morphology is rough, due to adsorbed titania particles (Fig. 4).

It was also observed that the IEP of the core–shell particles were higher when the silica cores were not dried and then redispersed in water again before the coating process (Fig. 5).

TEM images show that in this case discrete (non-agglomerated) particles with quite homogenous shells were derived (Fig. 4.4 and 4.5). When the cores were dried before the coating process more agglomerates were observed as transmission electron micrograph shows in Fig. 4.3. Non-agglomerated particles consist of a higher surface area, therefore electrostatic attraction forces are higher and lead to more adsorption of titania particles, which again leads to higher IEP's.

The apparent surface coverage (ASC) [8,9] increased therefore, compared to the cases were the cores were dried before the coating process (Fig. 6). It has to be considered that titania particles which are not adsorbed on the surface were washed away during the washing step. Regardless of this, the amounts of titania adsorbed on the silica surfaces where concluded from the zeta-potential data derived during the coating process. The mass-percent of titania

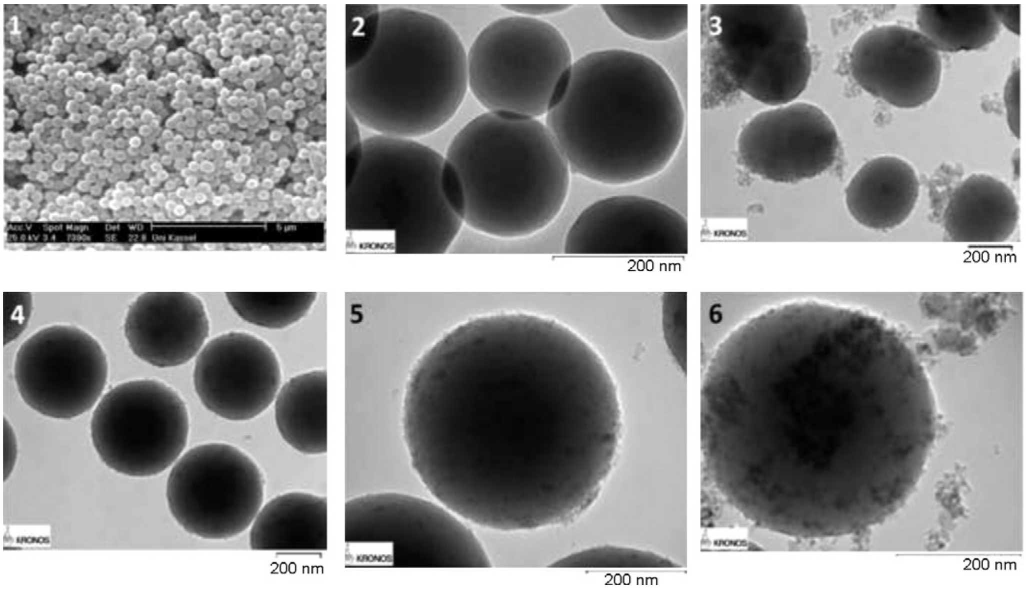


Fig. 4. Scanning electron (SEM) and transmission electron micrographs (TEM). (1) SEM image of uncoated Stöber silica spheres. (2) TEM image of uncoated Stöber silica spheres. (3) Titania coated silica spheres (silica cores were dried before the coating process—HK1). (4) Titania coated silica spheres (silica cores were *not* dried before the coating process—HK2). (5) Titania coated silica sphere (silica cores were *not* dried before the coating process—HK2). (6) Titania coated silica sphere. Titania was synthesized from $TiCl_4$ in this case.

deposited on the silica core in consideration of the concentrations of titania and silica sols are given in Fig. 2.

The aqueous titania dispersion obtained through hydrolysis of $TiCl_4$ was added dropwise to silica spheres with a mean diameter of 833 nm using a peristaltic pump. Zeta-potential analysis revealed that the IEP of the resulting core–shell particles is at pH 4.75, which indicates the adsorption of titania particles on the surface even in this case. Transmission electron micrographs confirm this finding (Fig. 4.6). It was observed that this procedure has produced more agglomerates of nano titania than in the process with the alternative titania sol.

BET surface areas of the samples are given in Fig. 7. In all cases the surface areas were increased significantly compared to the uncoated silica particles. The high surface for $TiCl_4$-derived core–shell particles is due to agglomerates of titania in the nanoscale.

3.2. Photocatalytic activity

According to DIN 52980 [16] degradation of methylene blue in the presence of the silica–titania core–shell particles and pure nano titania and silica was studied to confirm photocatalytic activity. 30 mg of each sample was dispersed in 40 ml of aqueous methylene blue solution (10 µmol/L) and irradiated with a UV-light intensity of approximately 2 mW/cm^2. During irradiation the solution was bubbled with air in constant intervals. The relative concentrations as a function of irradiation time are given in Fig. 8 for the coated particles as well as for pure titania and silica. The concentration of methylene blue decreases with irradiation time only for the coated particles and pure titania. Photocatalytic efficiency is illustrated in Fig. 9. The results show the highest photocatalytic efficiency for core–shell particles with an average core size of 345 nm, derived by coating with nano titania from the TPOT pre-

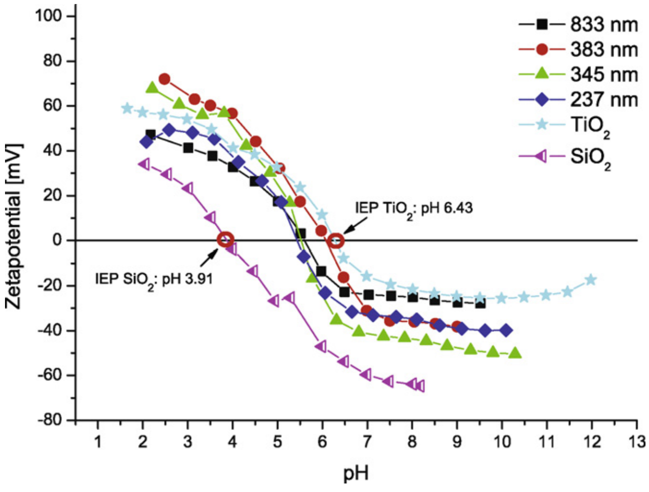


Fig. 5. Variation of zeta potential with pH values of silica–titania (833–237 nm) and pure silica and titania particles (silica cores were *not* dried before coating).

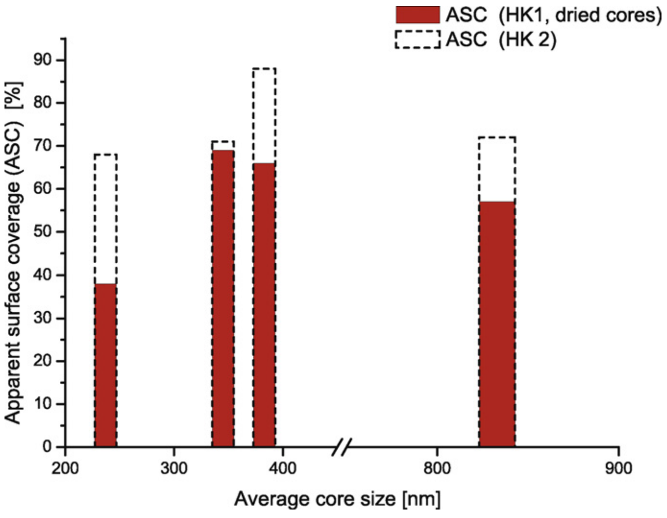


Fig. 6. Apparent surface coverages of silica–titania particles. HK1—silica cores were dried before coating. HK2—cores were not dried before coating.

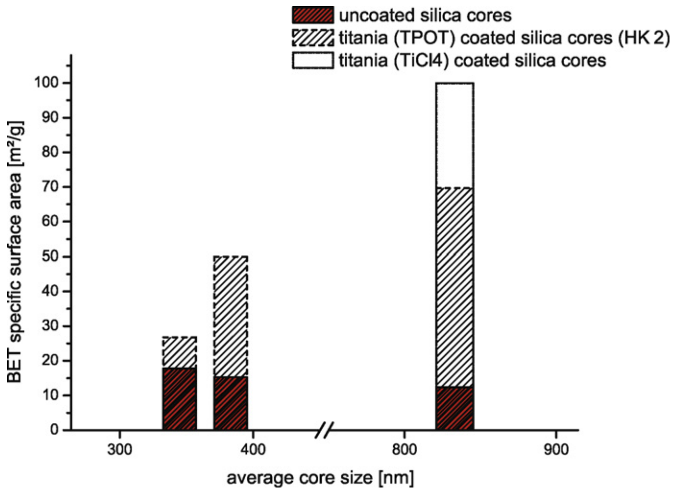


Fig. 7. BET specific surface areas of uncoated silica and titania coated silica.

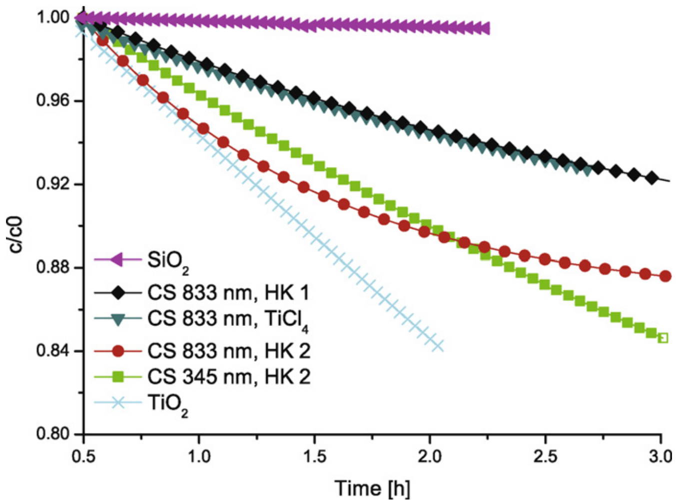


Fig. 8. Relative concentrations as a function of irradiation time for silica–titania particles, pure titania and pure silica. HK1—cores were dried before coating. HK2—cores were *not* dried before coating.

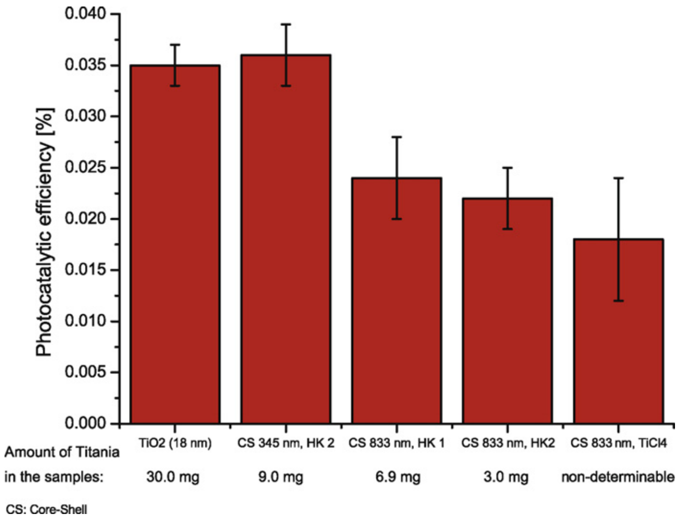


Fig. 9. Photocatalytic efficiency of pure titania and titania coated silica.

cursor. Considering the amount of titania in the sample from the data given in Fig. 2, this core–shell sample contained the highest amount of titania with 9 mg. It was observed that core–shell particles prepared using $TiCl_4$ showed photocatalytic efficiency only after calcination. It can therefore be concluded that the titania shells were amorphous before calcination. As the thickness of the shells ranged in nanometer scale, X-ray diffraction patterns did not show titania peaks. Although it can be concluded from Fig. 8, that pure nano titania shows the highest activity, one has to consider the particle sizes and the amount of titania in the different samples. The core–shell particles consist of just a thin layer in the nanoscale, therefore the amount of titania in these samples is much lower.

4. Conclusions

Titania coated silica particles in different sizes were successfully derived by coupling the oppositely charged components via electrostatic attraction forces. The spherical particles were monodisperse in size, non-agglomerated and showed photocatalytic activity. The BET specific surface area increased, due to adsorption of nano particles. In comparison to pure nano-crystalline titania one sample showed slightly higher photocatalytic efficiency. It has to be considered, that the amount of titania in the core–shell samples was lower, since the surface consists of just a thin nanoscaled layer. According to this, core–shell particles have potential to be used as an alternative material to pure nano titania. Cost for photocatalytically active material can be reduced and particle size can be tailored according to the application it is meant for. It was also found, that it is possible to obtain photocatalytically active core–shell particles by using $TiCl_4$ as the titania precursor. As $TiCl_4$ is a much cheaper titania precursor, this study shows that it is possible to prepare low cost photocatalytically active core–shell particles. As in this study the thickness of the titania shell was just a few nanometers, mineralogical analysis of the of the shell was not possible. Therefore thicker titania shell shall be deposited in further studies to allow analysis and comparison of the final titania shells on the silica support and also to enhance photocatalytic activity. Moreover a lot of agglomerates were observed in the sample, hence coating mechanism has to be optimized and studied further.

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References

[1] O.M. Alfano, D. Bahnemann, A.E. Cassano, R. Dillert, R. Goslich, Catal. Today 58 (2000) 199.
[2] D. Stephan, P. Wilhelm, Cement Int. 4 (2006) 76.
[3] D. Stephan, P. Wilhelm, in: J. Stark (Ed.), 16. ibausil, vol. 2, F.A. Finger-Institut für Baustoffkunde, Weimar, 2006, p. 0977.
[4] J. Winkler, Macromol. Symp. 187 (2002) 317.
[5] J.W. Lee, K. Hong, W.S. Kim, J. Kim, J. Ind. Eng. Chem. 11 (2005) 609.
[6] G. Oberdörster, Int. Arch. Occup. Environ. Health 74 (2000) 1.
[7] B. Trouiller, R. Reliene, A. Westbrook, P. Solaimani, R.H. Schiestl, Cancer Res. 69 (2009) 8784.
[8] S.T. Hwang, G.R. Jheong, Y.S. Lee, S.B. Ko, Y.S. Byoun, J. Ind. Eng. Chem. 10 (2004) 927.
[9] J.W. Lee, M.R. Othman, Y. Eom, T.G. Lee, W.S. Kim, J. Kim, Micropor. Mesopor. Mater. 116 (2008) 561.
[10] P. Cheng, M. Zheng, Y. Jin, O. Huang, M. Gu, Mater Lett. 57 (2003) 2989.
[11] P. Wilhelm, D. Stephan, J. Colloid Interface Sci. 293 (2006) 88.

[12] Y. Hu, C. Li, F. Gu, Y. Zhao, J. Alloys Compd. 432 (2007) L5.
[13] S. Kalele, R. Dey, N. Hebalkar, J. Urban, S.W. Gosavi, S.K. Kulkarni, Pramana-J. Phys. 65 (2005) 787.
[14] P. Wilhelm, D. Stephan, J. Photochem. Photobiol. A 185 (2007) 19.
[15] W. Stöber, A. Fink, E. Bohn, J. Colloid Interface Sci. 26 (1968) 62.
[16] DIN 52980 Photokatalytische Aktivität von Oberflächen - Bestimmung der photokatalytischen Aktivität im wässrigen Medium durch Abbau von Methylenblau, 2008.