Final report

In accordance with the original workplan the major objectives of the proposal were implemented. Results with various hollow semiconductor photocatalysts and related materials were presented at the many international and domestic (incl. TDK) conferences (not all listed in the table). At least fifteen students from all educational levels (BSc, MSc, PhD) were involved in the research. Our results related to this project were published in international journals (21+3 papers with summa impact factor 90.749+ 17.239).

1st year

Carbon spheres were applied as templates to synthesize titanium dioxide-carbon sphere (TiO_2-CS) composites and TiO_2 hollow structures (HS) by the removal of template. CS templates were prepared by the hydrothermal treatment of ordinary table sugar (sucrose). CSs were characterized by scanning electron microscopy (SEM), infrared spectroscopy (IR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). TiO_2-CS composites were fabricated by coating CSs with homemade sensitized TiO_2. TiO_2-HSs were obtained by removing CSs by calcination at 400 °C for 4 h. The as-prepared TiO_2-CS composites and TiO_2-HSs were compared and characterized by diffuse reflectance spectroscopy (DRS), SEM, XRD, XPS. The photocatalytic activity was investigated by phenol model pollutant under visible light (and in some cases UV) irradiation. As reference photocatalysts the following photocatalysts were used: commercial Evonik Aeroxide P25 TiO_2, homemade non-hollow 'Rutile-H2', and 'Rutile-H2_calc from which the latter was synthesized similarly to the hollow titanium dioxides (including the calcination step), just without the application of carbon sphere templates, thus providing appropriate reference to measure the activity gain by the morphology.

First, CS templates were characterized, which were prepared by the utilization of various purification methods including vacuum filtration, centrifugation, and membrane filtration, to remove organic residues formed during the hydrothermal synthesis. Based on the SEM and XRD analysis, no differences were observed between the variously purified CSs. The SEM micrographs showed well-defined sphere morphology with a mean diameter of 458 nm ± 75 nm. Based on the XRD analysis, one broad peak was observed, which was attributed to amorphous carbon. CSs purified with membrane filtration using different amounts of acetone were characterized further by IR measurements to investigate the correlation between carbon sphere purity and the quality of the resulting hollow structures. The IR spectra indicated no significant difference between the quality of the carbon spheres' surface and purity, from which it was presumed, that by the utilization of these CSs no considerable difference would occur in the properties of the resulting HSs. (10.3390/ma12162537)

Second, a TiO_2-CS composite and TiO_2-HS sample were compared, and it was found that the addition of CS templates decreased the crystallinity of the TiO_2 in the composite sample (compared to TiO_2-HS). IR measurements exhibited the same characteristics which were observed in case of the CS templates, with the addition of a peak corresponding to the transverse optical vibration of Ti–O bonds, proving the presence of TiO_2 coating layer. During the evaluation of photocatalytic activity, it was found, that TiO_2-CS composite possessed less than half of the photocatalytic efficiency of the TiO_2-HS sample; therefore, more emphasis was put on the characterization of hollow structures. (10.3390/ma12162537)

Third, a series of TiO_2 HSs (denoted as 'H2_HS_1–6') was synthesized by applying different synthesis conditions (various purification methods of carbon spheres, different precursor quantity and furnace). Membrane filtration was found to be the most feasible CS purification method (resulting in the highest CS yield in a unit of time); however, purification via centrifugation resulted in the most efficient TiO_2 HSs. Applying muffle furnace (without additional air supply) resulted in the best photocatalyst (H2_HS_5) with excellent hollow structural morphology and high rutile content when acetone was used as a solvent to purify CSs. H2_HS_5 possessed both the best absolute and surface normalized photocatalytic activity among the investigated TiO_2-s. On one hand, this was attributed to its increased light-harvesting capabilities (due to its unique morphology), and on the other, to the lowest carbon content on its surface and the higher ratio of polar O–C=O functional groups, which presumably facilitated the direct contact between water (the matrix of the photocatalytic process) and the surface of the photocatalyst. The stability of this TiO_2 proved to be remarkable as it retained its photocatalytic activity, crystal phase composition and morphology after three consecutive phenol degradation measurements. (10.3390/ma12162537)

Graphene oxide (GO) was prepared by the improved Hummers' method. The preparation steps were thoroughly analyzed to understand the formation of functional groups on GO [JTAC].

GO was used as a substrate for depositing TiO_2, ZnO and Al_2O_3 thin films by atomic layer deposition (ALD). The functional groups and heteroatoms of GO provided appropriate nucleation sites for ALD grown oxides. The as-deposited Al_2O_3 and TiO_2 were amorphous, while ZnO was crystalline. The carbon nanostructure/semiconductor oxide composites were studied as photocatalysts. The best photocatalyst was the GO/ZnO composite. Unexpectedly, the GO/TiO_2 composite was almost as good in photocatalysis; in spite of the TiO_2 being amorphous, revealing that ALD grown amorphous TiO_2 has unique features. This corroborates the previous results of the BME group on the photocatalytic properties of amorphous TiO_2 ALD layers [APSUS].

By combining electrospinning and ALD, polymer/oxide core/shell nanofibers and oxide nanotubes were prepared. As pilot investigation, PVP and PVA nanofibers were synthesized by electrospinning, then coated with Al_2O_3 thin films by ALD to obtain the polymer/oxide composite nanofibers. The polymer core was removed by annealing and thus Al_2O_3 nanotubes were formed. The method is planned to be used to obtain TiO_2 nanotubes to be used in photocatalysis [RRC].

A review paper was published about the application of ALD in nanotechnology. The paper discussed the results achieved in the field by the BME group. Special emphasis was put to covering carbon nanostructures (e.g., carbon nanotubes, fullerene, graphene oxide, etc.) by oxide ALD layers, and preparing photocatalytic nanocomposites [MKF].

Beside photocatalysis, the application of ALD grown oxide films was also studied in gas sensing. TiO_2 nanofilms were deposited by ALD onto a QCM (quartz crystal microbalance) gas sensor, and it was shown that already ultrathin (10 nm) oxide films had gas sensitivity [JPCS].

2nd year

Titanium dioxide hollow spheres (TiO_2-HSs) were fabricated by applying carbon spheres (CSs) as templates. CSs were prepared from ordinary table sugar (sucrose) by hydrothermal treatment and were purified using either acetone or ethanol. Calcination (at 500 or 800 °C, under continuous air supply in a tube furnace) was applied to eliminate the CSs resulting in TiO_2-HSs with regular hollow spherical morphology. The effects of different synthesis parameters (solvent for purification, calcination temperature) on the properties of the TiO_2 samples were investigated. TiO_2-HSs were characterized by XRD, SEM, TEM, DRS, and IR. The most suitable TiO_2 was selected, and an attempt was made to increase its photocatalytic activity *via* noble metal (Au and Pt, at 0.25 wt%) deposition. The photocatalytic efficiency of the samples obtained was determined by the decomposition of phenol and oxalic acid under UV and visible light irradiation. As references our own hollow spherical TiO_2 containing no noble metals were used on one hand, and a non-hollow but spherical TiO_2 on the other that was prepared without using CS templates. The cause for the photocatalytic enhancement in the case of either the unique morphology or presence of noble metals was examined using these references.

First, TiO_2-HSs were prepared then characterized to determine which TiO_2-HS possesses the best characteristics to be used as the base material for the deposition of noble metals. In the case of samples calcined at 500 °C well-defined spheres were observed possessing near perfect morphology, which were not damaged during calcination. Based on the TEM images of the samples calcined at 500 °C it was ascertained that they had regular hollow cavities, as intended. The theoretical (70 nm) and calculated thickness (60±8 nm) of the TiO_2 shell were in reasonably good accordance with one another. Increasing the calcination temperature to 800 °C spheres with decreased orderliness were observed, resulting in raspberry-like surface in contrast with the smooth surfaces detected in the previous cases. The higher temperature also caused the hollow cavity to be smaller. Based on the XRD measurements samples calcined at lower temperature consisted of anatase, while samples calcined at the higher temperature contained predominantly rutile phase and larger crystallites. The crystalline phase ratio of the synthesized TiO_2-HSs was ~80% in every case. According to the DR measurements rutile phase TiO_2-s possessed lower band gaps compared to the anatase phase TiO_2-s. In summary, the sample denoted as TiO_2-HS^{Ac}_{500} possessed the best characteristics to be used as base material for the determination of photocatalytic activity gain caused by the unique morphology (highest circularity value, regular hollow cavity), and for the deposition of noble metals. (10.1016/j.apsusc.2020.147327)

Second, either gold or platinum noble metals were deposited at 0.25 wt% on the TiO_2-HS^{Ac}_{500} sample, and the samples obtained were characterized by TEM, XRD, DRS and IR. Based on the TEM images after the deposition process the regular hollow spherical morphology remained intact, the noble metals were evenly distributed on the surface and no aggregation occurred. HRTEM images were used to measure the d-spacing of the TiO_2 shell and the noble metal nanoparticles to confirm the presence of the latter. Accordingly, the measured 0.34 nm value was attributed to the TiO_2 (101) crystallographic plane, 0.24 nm to the Au (111) plane and 0.20 nm to the Pt (200) plane. Then, based on the XRD measurements it was established that after the deposition recrystallization took place resulting in the appearance of rutile crystal phase in ~8–10 wt%. According to the DR spectra, after the deposition of noble metals the band gap increased slightly. The inflection point at ~542 nm in the derivative spectrum was attributed to the plasmon resonance of the gold nanoparticles for sample TiO_2-HS^{Ac}_{500}-Au. (10.1016/j.apsusc.2020.147327)

Third, the photocatalytic activity of the noble metal-containing samples and the references were measured and compared. Under visible light irradiation, the gold-deposited hollow spherical TiO_2 had the best photocatalytic activity, while in the case of UV irradiation the platinum containing hollow spherical TiO_2 proved to be the most efficient for the degradation of both oxalic acid and phenol. The results concerning the activity gain caused by the presence of noble metals could be correlated well with literature data and our previous findings. (10.1016/j.apsusc.2020.147327)

The application of the atomic layer deposition was extended for depositing TiO_2 on resorcinol-formaldehyde aerogel (RFA) and carbon aerogel (RFCA) substrates to obtain composites for photocatalytic purposes. Before the ALD depositions, the thermal properties of nitrogen doped carbon aerogels were studied and compared to non-doped ones.

The RFA had negligible photocatalytic activity, while the crystalline TiO_2 deposited on it increased it significantly, and even the amorphous TiO_2 had observable photocatalytic property. Our results clearly demonstrate that the RFCA substrate alone has photocatalytic activity, owing to its higher specific surface area and semiconductor nature. When RFCA was covered with amorphous or crystalline TiO_2 by ALD, unexpectedly the photocatalytic activity decreased. This was because due the oxide coating the average density and hence the specific surface area of the RSCA decreased, yielding a lower photocatalytic performance. In addition, the heat treatment of the RFACE substrate during the ALD reaction at 250 °C resulted in the loss of functional groups and photocatalytic reactive sites. When the decrease in specific surface area and the annealing effect were compensated, it was obvious that the ALD TiO_2 layers significantly improved the photocatalytic activity of RFCA. All carbonized samples showed better activity than the reference P25 TiO_2.

As a conclusion, when porous carbon nanostructures are coated with ALD oxide layers, several factors must be taken into account when studying the composites in various applications. The ALD layer might improve certain properties or provide new functionalities. However, the change in overall density and hence in specific surface area must be paid attention to. It is worth considering how much the heat treatment, which the substrate receives during the ALD reaction, might change the functional properties of the substrates.

Interestingly, photocatalytic property of amorphous TiO_2 grown by ALD was confirmed for the RFA/TiO_2, RFCA/TiO_2 composites, but also for SiO_2/TiO_2 core/shell nanoparticles prepared via sol-gel synthesis. It is obvious that amorphous TiO_2 prepared via low temperature-ALD of has a high potential, and can be used in e.g., coating highly structured heat sensitive substrates with self-cleaning films. Vertically aligned carbon nanotubes (VACNTs or “CNT forest”) – as a different form of carbon materials – were also decorated with semiconductor particles (TiO_2 and ZnO) by atomic layer deposition.

3rd year

Carbon spheres (CSs) were applied as templates to prepare titanium dioxide hollow spheres (TiO_2-HSs). (i) A series of TiO_2-HSs were synthesized applying CSs purified either by acetone (Ac) or ethanol (EtOH) to investigate the effects of these solvents on the properties of the TiO_2 samples. (ii) Another series of TiO_2-HSs were synthesized containing 0.25 wt% Au and Pt nanoparticles, and the presence of these noble metals on the hydrogen evolution efficiency was investigated under sunlight and UV light irradiation.

(i) TiO_2-HSs were characterized by XRD, SEM, TEM, and IR. The photocatalytic efficiency of the titania was determined by the decomposition of phenol under visible light irradiation. As a function of CS template purification solvent, the crystal phase composition of the TiO_2-HSs was remarkably different: TiO_2-HS_Ac contained predominantly anatase phase, whereas TiO_2-HS_EtOH contained predominantly rutile phase. The morphology was also different, as the structure of TiO_2-HS_Ac was damaged, while for TiO_2-HS_EtOH mostly intact hollow spherical morphology was obtained. Similarly, in terms of photocatalytic activity huge differences were observed: the photocatalytic activity of TiO_2-HS_EtOH was more than three times higher than that of TiO_2-HS_Ac, surpassing the efficiency of every investigated reference, both commercial and homemade. The cause for these differences could be explained based on the results of the IR measurements: it was found, that due to the different surface properties of the CSs, TiO_2-HS_Ac contained carbonate species in its crystal lattice (additional band at 802 cm^{-1}). Carbonate ions facilitate the formation of anatase crystal phase, and they act as a scavenger for ·OH radicals, which are the most important reactive oxygen species for the degradation of phenol. (10.3390/catal11010112)

(ii) It was established that the hydrogen evolution efficiency was higher for UV light than for sunlight in every case. The Pt-containing samples were always more efficient compared to the Au-containing titania. The photocatalytic activity order observed under UV irradiation during the decomposition of phenol for the Pt-containing samples was attributed to the increased light harvesting capability of the catalysts as follows. The solid spherical counterparts of each hollow spherical sample were prepared. Then, the ratio of hollow spheres with enhanced light harvesting was calculated. The photocatalytic activity indeed increased with increasing proportions of titanium dioxide hollow sphere diameters close to the integer multiple of the excitation light source's wavelength, i.e., in which case the occurrence of constructive interference was more probable. The proposed explanation was in good agreement with the acquired results. (10.1016/j.apsusc.2020.14732)

Based on the successes achieved with CSs applied as sacrificial templates to prepare TiO_2 HSs, ZnO hollow spheres were also prepared. The CSs mentioned above were used as templates in various ZnO synthesis methods to prepare ZnO-coated CSs, which were then calcined to remove the template and obtain the same hollow sphere morphology as in the case of TiO_2.

Three well-known synthesis methods were investigated to coat the CS templates: chemical precipitation, chemical aging and solvothermal methods. Also, 3 different precursors (zinc-acetate, zinc-nitrate and zinc-acetylacetonate) were used as Zn sources. The synthesized ZnO-CS composites were calcined and investigated by XRD, SEM. The most efficient coating of the carbon template was achieved using the solvothermal method and zinc-acetylacetonate as the precursor. Thus, the ZnO HSs obtained via this synthesis procedure were investigated further by TEM and DRS, and their photocatalytic activity was also evaluated.

XRD measurements confirmed that ZnO with hexagonal wurtzite crystal structure was obtained. TEM results revealed that by calcinating the composites the carbon templates were removed leaving behind a cavity with a diameter corresponding to the average diameter of the CSs. Furthermore, the spherical morphology of the particles remained intact, and the average thickness of the shell was 220 nm. The photocatalytic activity of ZnO-HSs was investigated by phenol model pollutant under UV irradiation. Even though the ZnO-HSs were active in the photodegradation of phenol, the activity was found to be only a third of the TiO_2 mentioned above under the same conditions. This was most probably due to the thicker shell of ZnO compared to that of TiO_2.

The effect of CSs/Zn-precursor ratio on the properties of ZnO shells was investigated and based on SEM images it did not affect the morphology.

Au nanoparticles were deposited on ZnO-HSs via chemical reduction and Turkevich's method. TEM measurements confirmed the presence of Au nanoparticles in both cases. Their diameters were a few nanometers for chemical deposition and ~30 nm for the Turkevich method.

As-prepared carbon nanospheres were also used as templates to prepare titania inverse opal photonic crystal. From the spheres, opal colloid crystals were made by vertical deposition on microscope slides, and TiO_2 was grown on them using ALD. The samples possessed photocatalytic activity under UV and visible light in decomposing organic dyes, while bulk TiO_2 only worked under UV light. This behavior could be attributed to the presence of the photonic band gap due to the inverse opal structure. (10.1016/j.apsusc.2019.144443)

Other non-spherical carbonaceous materials were also tested in composite formation and photocatalytic activity. A nitrogen doped carbon aerogel was used as a substrate for the atomic layer deposition of TiO_2 and ZnO layers in various thicknesses. The bare and composite products were analyzed using Raman spectroscopy, XRD, N_2 adsorption, SEM-EDX, TEM, XPS, and ICP-OES and their photocatalytic activity was investigated in decomposing methyl orange dye under UV light irradiation. (10.1039/c9tc05953a)

TiO_2 and ZnO single and multilayers were also deposited on hydroxyl functionalized multi-walled carbon nanotubes using atomic layer deposition. The carbon nanotubes (CNTs) were uniformly covered with anatase TiO_2 and wurtzite ZnO layers and with their combinations. In the photocatalytic degradation of methyl orange, the most beneficial structures are those where ZnO is the external layer, both in the case of CNTs covered with single and double oxide layers (CNT-ZnO and CNT-TiO2-ZnO). (10.3390/nano10020252)

Other types of semiconductors (beside the “traditional” titania and ZnO) were synthesized with various morphologies. Depending on the additives, sheet- and rod-like particles were obtained by a one-step hydrothermal method consisting of monoclinic WO_3 as potential photocatalysts. (doi: 10.1016/j.jssc.2019.121044) The morphology of Bi_2WO_6 produced by hydrothermal fabrication was controlled via the adjustment of the pH in the full range (0.3–13.5). Among others, the band gaps of the samples with fibers, sheets, irregular forms were calculated, and it was found that they varied between 2.66 and 2.59 eV which is rather promising for further applications. (10.3390/ma12111728) Bismuth oxybromide samples were also synthesized using solvothermal crystallization and different additives. Interestingly, using sodium dodecyl sulfate or polyvinylpyrrolidone during the hydrothermal treatment of BiOBr could form hollow microsphere structures without adding any template. (10.1016/j.apsusc.2020.146184)

4th year

Earlier the solvothermal synthesis of ZnO HSs was established as most successful method. The mass ratio of ZnO:CSs was further investigated to improve sphericity of the particles. The optimum value for this ratio is 9:1, as only miniscule amounts of debris is observable alongside the hollow spheres on the SEM micrographs and higher ratios result in thicker shell of the ZnO HSs.

ZnO solid spheres were synthesized with tunable average diameters between 0.15 and 2.20 μm with a similar solvothermal method used for the hollow spheres without the carbon templates (paper submitted). Using this method, a reference material was prepared as solid spheres with average particle diameter equal to that of the hollow spheres. The structural, morphological and optical of these solid spheres were investigated with the same methods as in case of hollow spheres (XRD, SEM, TEM, IR), to investigate the effect of the unique morphology. ZnO HSs, ZnO HSs composites with Pt and Au nanoparticles and the reference materials’ photocatalytic activity was investigated in the case of photocatalytic degradation of four different model pollutants (methyl orange, phenol, ibuprofen and diuron) under UV irradiation, in order to evaluate a wider range of applicability in photocatalysis. The ZnO HSs were more efficient than the solid spheres and the noble metal deposition further improved their catalytic performance. This enhancement of the photocatalytic efficiency is attributed to the unique hollow morphology. (paper submitted).

ZnO and TiO_2 mixed and layered hollow structures were attempted by two different methods:

- In situ method for layered structure: the established synthesis of hollow oxides were modified by adding the other hollow sphere oxide place of CSs, using as template.
- One pot method: the precursor of the oxide was added in corresponding amount into the other oxides’ synthesis method.

The samples were characterized by XRD, SEM, EDAX and DRS. Unfortunately, the EDAX measurements revealed that layered oxides were not resulted in any of the experiments and the ZnO and TiO_2 spheres were formed separately.

Titanium dioxide and zinc oxide hollow spheres were immobilized on ceramic paper support to investigate their practical applicability. A hydrolyzed titanium dioxide precursor was used as the adhesive, and the immobilization was carried out via spray coating. The photocatalytic activity was investigated in a fixed bed flow reactor under UV light irradiation. During the measurements, the water to be treated (containing phenol as model pollutant) was constantly recirculated. To evaluate the reusability of the photocatalysts, the photocatalytic oxidation of phenol was carried out three consecutive times. Based on XRD measurements, a calculation method was developed to determine the coverage of catalysts on the support. SEM micrographs confirmed the successfulness of the immobilization as the catalyst spheres were fixed to the fibers of the ceramic paper. IR results showed that, regarding the type of bonding, there was no chemical interaction between the support and catalyst. The catalysts showed higher photocatalytic activity in suspended form compared to that in immobilized form. However, they had remarkable stability, as they retained their efficiency even after three consecutive runs, and no catalyst leaching was observed. (paper submitted)

Additionally, background investigations were done regarding the possible effect of two noble metals (gold and platinum) and their ratio on photocatalytic activity (10.3390/met11040628). For comparison, the effect of various morphology on activity was studied *via* shape tailored Cu_2O regular cubic microparticles (10.3390/molecules26041149). As potential wider application, a comparative research on stability, viscosity, and thermal conductivity of carbon nanosphere (CNS) and carbon nanopowder (CNP) nanofluids was performed (10.3390/nano11030608; 10.1007/s10973-020-09365-9).