Freezing-Induced Loading of TiO₂ into Porous Vaterite Microparticles: Preparation of CaCO₃/TiO₂ Composites as Templates To Assemble UV-Responsive Microcapsules for Wastewater Treatment

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ABSTRACT: The photocatalytic degradation of organic molecules is one of the effective ways for water purification. At this point, photocatalytic microreactor systems seem to be promising to enhance the versatility of the photoassisted degradation approach. Herein, we propose photoresponsive microcapsules prepared via layer-by-layer assembly of polyelectrolytes on the novel CaCO₃/TiO₂ composite template cores. The preparation of CaCO₃/TiO₂ composite particles is challenging because of the poor compatibility of TiO₂ and CaCO₃ in an aqueous medium. To prepare stable CaCO₃/TiO₂ composites, TiO₂ nanoparticles were loaded into mesoporous CaCO₃ micro-particles with a freezing-induced loading technique. The inclusion of TiO₂ nanoparticles into CaCO₃ templates was evaluated with scanning electron microscopy and elemental analysis with respect to their type, concentration, and number of loading iterations. Upon polyelectrolyte shell assembly, the CaCO₃ matrix was dissolved, resulting in microreactor capsules loaded with TiO₂ nanoparticles. The photoresponsive properties of the resulted capsules were tested by photoinduced degradation of the low-molecule dye rhodamine B in aqueous solution and fluorescently labeled polymer molecules absorbed on the capsule surface under UV light. The exposure of the capsules to UV light resulted in a pronounced degradation of rhodamine B in capsule microvolume and fluorescent molecules on the capsule surface. Finally, the versatility of preparation of multifunctional photocatalytic and magnetically responsive capsules was demonstrated by iterative freezing-induced loading of TiO₂ and magnetite Fe₃O₄ nanoparticles into CaCO₃ templates.

INTRODUCTION

The development of novel effective systems to degrade water pollutants and bacterial contamination is an essential task of modern chemistry. Photoassisted catalytic degradation of organic compounds in the presence of titanium dioxide appears to be a promising approach to wastewater treatment, disinfection, antifouling, and elimination of various pollutants. TiO₂ nanoparticles possess unique photocatalytic properties for the decomposition of organic and inorganic waste, deactivation of viruses, bacteria, microfungi and microalgae, and destruction of cancer cells. On the other hand, the employment of bare TiO₂ particles remains unfavorable with respect to practical applications. One way to enhance the safety and selectivity of photoinduced decomposition with TiO₂ particles is to encapsulate them into photoactive microcontainers. From this point, the hybrid microcapsules were prepared via layer-by-layer (LbL) self-assembly on the template cores appear the most promising as they suggest several ways to improve photocatalytic efficiency. The first one is the composite containers locally increase the concentration of the TiO₂ particles and the pollutant in the given microvolume. The pollutant may absorb on the container surface or diffuse into the cavity. Second, the controllable stepwise assembly allows to adjust the structure, chemical, and functional properties of the capsules, opening a broad avenue for their modification. For instance, the capsules may be modified with self-assembled layers of organic molecules with various molecular recognition sites to improve the selectivity to the desired pollutant. Additionally, the noble metal particles acting as an electron sink can be enclosed to improve the efficiency of photocatalysis because of the reduction of charge carrier recombination and by shifting the spectral maximum of absorption to the visible band, utilizing more energy to trigger the photocatalytic reaction from the visible light. Finally, the composite microcontainers can be more easily removed from the purified water compared to the bare...
TiO₂ particles. The inclusion of magnetic particles into containers allows for magnetic separation to remove the containers upon purification, with the possibility of further recovery and regeneration of the catalyst.

From the variety of methods to combine the functional nanoparticles with self-assembled microcapsules, the one resulting in the highest particle containment is preferable as the efficiency of the photocatalytic reaction is directly related to the amount of the catalyst.20 Regarding the microcapsules’ recovery and regeneration of the catalyst, containers upon puri-

cation. In this paper, the FIL method was employed for the first time to prepare the stable CaCO₃/TiO₂ composite micro-

particles with high TiO₂ loading as template cores for the preparation of multilayered self-assembled microcapsules for photocatalytic degradation of organic pollutants. The photocatalytic activity of these capsules was tested in two ways, mimicking possible options for capsules to be involved in degradation activity. In particular, these are the decomposition of low-molecular dye under UV light in an aqueous medium in inner capsule microvolume and decomposition of preabsorbed dye under UV light onto the capsule surface. Additionally, we have demonstrated the possibility of preparation of multifunc-

tional microcapsules possessing photocatalytic and magnetic properties by iterative FIL loading of TiO₂ and Fe₃O₄ nanoparticles into CaCO₃ cores.

■ RESULTS AND DISCUSSION

Preparation of CaCO₃/TiO₂ Composite Microparticles. A comparison of the measured anatase and P25 anatase + rutile particle properties is shown in Table S1 (Supporting Information). On the one hand, the specific surface of the particles is almost the same and, therefore, should not affect their comparative photocatalytic activity. On the other hand, according to dynamic light scattering (DLS) measurements, anatase particles tend to form larger aggregates in the aqueous medium compared to P25 anatase + rutile particles (Figure 1a), which can be related to their lower ζ-potential (5.5 and 17.8 mV, respectively, under pH 5, Figure 1b).

Figure 1c demonstrates the time dependence of the sedimentation stability of nanoparticles in the aqueous medium estimated with respect to particle suspension transmittance. The inset shows the scheme of the experiment. The transmittance of the anatase particle solution climbs from 50% to almost 100% in 10 min, indicating that most of the particles passed the laser line and sedimented on the cuvette bottom. In contrast, the transmittance of P25 anatase + rutile particle suspension remains at the same level (about 3–5%) for 20 min and even further (the measurement was carried out for 3 h, the data are not shown). Accomplished with the DLS and ζ-potential data, this indicates that P25 anatase + rutile nanoparticles are more stable in the aqueous solution.

Mesoporous calcium carbonate microparticles with vaterite structure are widely used as templates for assembling of multifunctional carriers because of their high porosity (with an average pore size of 20–70 nm)25 and solubility under mild pH conditions (pH 7).24 Moreover, the porous nature and developed surface of CaCO₃ microparticles are preferable in some applications, for example, sensing.25

Currently, the most common methods for the preparation of vaterite particles loaded with active agents and inorganic nanoparticles are the coprecipitation method (encapsulation during particle preparation)26,27 and adsorption from solution.28 Additionally, the synthesis of inorganic nanoparticles in CaCO₃ pores in situ can be employed,29 yet it is more complicated and less common. However, as the aqueous dispersion of TiO₂ nanoparticles has a pH of 4.5–5,30 and the formation of vaterite particles occurs in alkaline medium, it is challenging to obtain CaCO₃/TiO₂ composites using these methods. Figure 2a,b shows the scanning electron microscopy (SEM) images of the resulted CaCO₃/TiO₂ particles prepared with the coprecipitation technique. The addition of TiO₂ suspension with acidic pH during the CaCO₃ nucleation leads to the formation of cubic calcite microparticles that are not suitable for further capsule preparation.

The attempt to adsorb the TiO₂ nanoparticles on vaterite templates (the SEM image of the initial vaterite template is shown in Figure S3, Supporting Information) from aqueous solution resulted in a clear separation of micro- and nanoparticles (Figure 2c,d). This can be explained by the fact that both CaCO₃ and TiO₂ particles in an aqueous medium under pH 7 are charged slightly negatively,30,31 and, therefore, their adsorption is hardly possible because of electrostatic repulsion.

In turn, FIL implies the pushing off of TiO₂ and CaCO₃ particles in aqueous solution by the moving of the water crystalization front during controllable freezing. The particles are concentrated ahead of the crystalization front, reducing the water freezing point. Finally, upon nano- and microparticles being concentrated in a given microvolume, the nanoparticles are embedded into the CaCO₃ pores, substituting the residual water under the growing pressure of the ice front.

Figure 3a,b demonstrates the SEM images of the CaCO₃/TiO₂ particles prepared by FIL under various conditions as described in Table 1 in the Experimental Section. The images show that the visual appearance of the FIL-loaded CaCO₃ templates varies depending on the type and concentration of TiO₂ nanoparticles. This is the most prominent for the CaCO₃/TiO₂ composites with P25 anatase + rutile. The

Figure 1. TiO₂ nanoparticle size distribution measured by DLS (a), ζ-potential (b), and time dependence of the sedimentation stability of anatase and P25 anatase + rutile nanoparticle suspension (c).
surface becomes more developed and rougher with an increasing amount of loaded TiO$_2$ (Figure 3b) unlike the composites with anatase (Figure 3a).

The amount of Ti in the composite particles was estimated with energy-dispersive X-ray spectroscopy (EDX) analysis. Although EDX is a semiquantitative method and cannot provide direct information on the loading efficiency of TiO$_2$ nanoparticles, it is still useful for comparative sample analysis with respect to the percentage of Ti atoms relative to the total number of atoms in the region of interest. According to EDX data (SEM) (Figure 3c), the amount of Ti in the samples loaded with P25 anatase + rutile nanoparticles (B1−B4) is higher than that of the samples loaded with anatase nanoparticles (A1−A4). This can be attributed to the lower loading of anatase into CaCO$_3$ particles as the anatase is less stable in an aqueous medium. Noticeably, the amount of Ti in A2 and A3 samples is almost the same (within a margin of error) as in B2 and B3 samples. Therefore, it can be concluded that the loading efficiency of the TiO$_2$ nanoparticles with FIL is defined by the total amount of loaded particles and can be adjusted by the concentration and/or the number of loading cycles (within the particle concentration range used in this work).

Figure 3d shows the HR-STEM cross-sectional image of the CaCO$_3$/TiO$_2$ B4 composite microparticle merged with an energy-dispersive X-ray spectroscopy system (EDXS) map of the volume and near-surface area. The HR-STEM confirms a highly porous structure of CaCO$_3$ particles with the pore density decreasing from the center to the particle surface. The EDXS map reveals that the distribution of TiO$_2$ nanoparticles over the CaCO$_3$ microparticle surface is rather nonuniform. The nanoparticles are mainly located in the surface layer of 100 nm; however, in some areas, the depth of particle penetration reaches up to 400 nm (highlighted with a red dotted line), which is confirmed by the elemental analysis.

Preparation of UV-Responsive Microcontainers and Decomposition of the Low-Molecular Dye. The polyelectrolyte shells were assembled on the prepared composite CaCO$_3$/TiO$_2$ particles by the LbL method. The shells were assembled of poly(allylamine hydrochloride) (PAH) and poly(4-styrenesulfonate)sodium salt (PSS) polyelectrolytes because of the good stability and well-established properties of the resulted polyelectrolyte complex. As the shell is assembled and the CaCO$_3$ matrix is removed, the TiO$_2$ nanoparticles anchored onto the inner layer of the polyelectrolyte shell. The polyelectrolyte shell is permeable for low-molecular compounds, allowing for their photocatalytic degradation in the container microvolume directly on contact with preconcentrated TiO$_2$ particles.

Figure 4a,b demonstrates the SEM images of the capsules assembled on the CaCO$_3$/TiO$_2$ composite cores after the dissolution of the CaCO$_3$ matrix. Compared to the control PAH/PSS capsules (Figure 4c), the surface of TiO$_2$-loaded capsules becomes rougher and TiO$_2$ particle aggregates can be seen inside the capsule shells. This correlates with the data of EDX analysis, indicating the growth of Ti amount in the capsules with the surface roughness and the loading of TiO$_2$ in the initial composite microparticles (Figure 4d). However, the Ti amount in the resulted capsules is lower than in the corresponding CaCO$_3$/TiO$_2$ composites, which may be related to the desorption of some number of TiO$_2$ nanoparticles.
during the shell assembly. Nevertheless, the overall tendency in the distribution of Ti atoms depending on the loading and type of TiO$_2$ nanoparticles remains the same.

To evaluate the photocatalytic activity in the first set of experiments, microcapsules loaded with TiO$_2$ nanoparticles were incubated in the Rho B solution under UV light. Prior to this, the appropriate UV lamp wavelength was selected. It is known that TiO$_2$ is an n-type semiconductor. The measured values of the band gap for anatase and P25 anatase + rutile particles were 2.85 and 3.22 eV, respectively (the absorption spectra and Tauc plots are given in Figure S4 in the Supporting Information). The measured band gap for P25 anatase + rutile is in a good agreement with the reference one of the anatase phase, which is 3.2 eV. On the other hand, the measured band gap for anatase particles is different, which might be due to the fast sedimentation of the particles affecting the data acquisition. Nevertheless, the irradiation with a 367 nm UV lamp (corresponding to 3.38 eV photon energy) should result in the effective generation of electron−hole pairs in both types of nanoparticles.

Figure 5a,b,c,f shows the dependence of relative change of the concentration of Rho B dye incubated with photoactive microcontainers under UV light and the percentage of dye decomposition rate. The first point of every plot corresponds to the absorbance of an as-prepared mixture of capsules and Rho B, whereas the zero points were measured after 30 min of incubation without UV irradiation to reach an adsorption equilibrium in the mixture. The degradation rate curves (Figure 5b,f) demonstrate the decomposition of the dye incubated with TiO$_2$-loaded capsules (the standard plot for Rho B aqueous solution is given in Figure S6 in the Supporting Information). For both particle types, the degradation efficiency depends on the number of loaded particles. Noticeably, the capsules demonstrate almost the same photocatalytic activity, except those with minimal loading. Comparing the photocatalytic efficiency of capsules loaded with anatase and P25 anatase + rutile nanoparticles, the latter demonstrate more than 50% degradation of Rho B after 3 h of incubation under UV light, whereas incubation of the dye solution with anatase-loaded capsules resulted in only 30% degradation in the same time. This can be associated with...
better loading of P25 anatase + rutile particles. Additionally, some studies hypothesized that anatase with rutile inclusions appears to be more preferable for photocatalytic applications on comparing to pure anatase.\textsuperscript{35–37} Although the rutile phase is considered as low-active itself, the junction between anatase and rutile phases promotes the separation of charge carriers because of electron migration from rutile to anatase and hole migration to the surface. The rutile phase plays the role of a charge separator and provides additional sites for oxidation, which results in enhanced photocatalytic activity of P25 anatase + rutile particles.

The kinetics of dye decomposition in aqueous solution is generally described by the Langmuir–Hinshelwood equation, which also takes into account the adsorption of the degraded agent onto the catalyst’s surface.\textsuperscript{38} At low dye concentrations, the equation can be written as the first-order kinetics reaction

\begin{equation}
-\ln\left(\frac{C}{C_0}\right) = kt
\end{equation}

where \(C_0\) is an initial dye concentration, \(C\) is a measured dye concentration, \(k\) is a pseudo-first-order rate constant, and \(t\) is degradation time.\textsuperscript{39} Figure S5c,g shows the semi-log plots of \(C_0\) versus time for the capsules loaded with two types of TiO\(_2\) nanoparticles plotted based on the degradation rate measurements. The experimental data are well approximated with a linear fitting curve, which implies the pseudo-first-order of the degradation kinetics. The reaction constants can be figured from these plots as slopes of the fitting lines. Figure S5d,h shows the comparison in reaction constants of the capsules loaded with various numbers and types of TiO\(_2\) nanoparticles. This indicates that the capsules loaded with P25 anatase + rutile particles have higher photocatalytic performance compared with capsules loaded with anatase particles. It is also noticeable that the capsules loaded with the same number of TiO\(_2\) particles (A2/A3 and B2/B3 samples) have the same photocatalytic performance. Therefore, it can be concluded that the resulted photocatalytic efficiency of the photoactive containers depends on the type and the final number of the TiO\(_2\) particles loaded by FIL, which gives certain adjustability in the container preparation.

**Decomposition of the Fluorescent Label on the Surface of UV-Responsive Microcontainers.** The prepared photoactive containers are effective in the decomposition of the small-molecule dye that is able to penetrate into the capsule microvolume. However, some water treatment applications require decomposition of large molecules or microorganisms that will contact mainly the capsule surface. In this regard, it is of interest to figure out the degradation efficiency of the capsules with respect to the substances attached to the external layer that are unable to go inside the capsule volume. For this purpose, TRITC–PAH was absorbed instead of PAH during the assembly of the finishing capsule bilayer. The TRITC label was selected as it is known as a fairly photostable fluorophore under UV light.\textsuperscript{40}

Figure 6 shows the fluorescent confocal laser scanning microscopy (CLSM) images of the microcapsules assembled on the regular CaCO\(_3\) particles and on the CaCO\(_3\)/TiO\(_2\) composites. The difference in size and shape of the resulted fluorescent microcontainers assembled on various templates is clearly seen. The capsules assembled on the control CaCO\(_3\) cores (Figure 6a) demonstrate an almost round shape with prominent fluorescent properties. In turn, the capsules assembled on the composite CaCO\(_3\)/TiO\(_2\) cores are less spherical because of the roughness of the initial templates. The difference in size and shape of the capsules assembled on the initial CaCO\(_3\) cores and CaCO\(_3\)/TiO\(_2\) composite cores can be related to the various surface roughnesses of the templates, which were confirmed by SEM analysis. In turn, the capsules loaded with anatase and P25 anatase + rutile nanoparticles have a difference in size and shape as well, which can be associated with various loading efficiencies of the nanoparticles. The P25 particles demonstrate better loading and, therefore, the resulted composite cores have a more developed surface, which can be seen also by nonuniform adsorption of fluorescently labeled molecules and inhomogeneous capsule shell thickness. Additionally, the initial CaCO\(_3\) particles are not monodisperse intrinsically, which results in capsule size variation. Moreover, the fluorescent images captured with the same settings demonstrate a decrease in the fluorescent signal of the capsules that may be associated with the initiation of fluorophore photodegradation.

The collected data on the dye photodegradation after 3 h under UV light are shown in Figure 7. Photodegradation curves for all fluorescent capsules loaded with TiO\(_2\) nanoparticles lie below the control curve with statistical confidence. This indicates that TiO\(_2\) nanoparticles significantly affect the photodecomposition process. Noticeably, the absolute values of the relative change of the concentration of the degradable fluorescent agent \(\Delta c/c\) for all capsules loaded with P25 anatase + rutile nanoparticles (Figure 7b) are greater than that for capsules loaded with anatase (Figure 7a). The \(\Delta c/c\) values are in the range of 10–30% for A1–A4 samples, and in the range of 25–50% for B1–B4 samples for 1 to 3 h of exposure with UV light. This is comparable with the degradation rates of small-molecule dye in the capsule volume for the highest loading of TiO\(_2\) particles. However, in the case of degradation on the surface, the dependence of degradation on the particle loading is more pronounced.

**Preparation of UV-Responsive Magnetic Microcontainers.** Finally, the FIL method was employed for iterative loading of CaCO\(_3\) templates with TiO\(_2\) and Fe\(_3\)O\(_4\) nanoparticles for the preparation of multifunctional capsules possessing photocatalytic activity and magnetic responsiveness. To do this, P25 anatase + rutile nanoparticles were used as previous experiments demonstrated their better stability in an aqueous medium, better loading ability, and, what is more important, better photocatalytic activity. Figure 8a shows the SEM image of CaCO\(_3\)/TiO\(_2\)/Fe\(_3\)O\(_4\) composite particle loaded by 1 FIL cycle with P25 anatase + rutile nanoparticles (1 mg/mL) and by 1 FIL cycle with Fe\(_3\)O\(_4\) nanoparticles. The morphology and surface roughness of these composites look similar to those of B4 core samples loaded by 2 FIL cycles with
P25 anatase + rutile particles (see Figure 3b). The EDX analysis (Figure 8c) shows a relatively high amount of Ti (about 5 at. %) and Fe (about 4 at. %) atoms in the composite cores. Analogous to TiO2 loaded capsules, the content of Ti and Fe in the resulted capsules (Figure 8b) is considerably lower (about 1%) in comparison with initial composite particles. On the other hand, the content of Ti atoms is similar to that of the B3 capsule sample prepared with the same TiO2 loading and, considering only the Ti amount, these capsules should have the same photocatalytic properties.

Figure 8d shows the mobility of the TiO2/Fe3O4-loaded capsules in the nonuniform magnetic field of a permanent magnet. The capsule mobility was measured analogous to the experiment on TiO2 particle sedimentation (see Figure 1) except that the gravity field was substituted with a magnetic field applied alongside the cuvette. The capsule suspension became almost transparent in about 100 s after the magnetic field was applied because of the capsule attachment to the cuvette wall near the magnet. This clearly indicates the response of TiO2/Fe3O4 capsules to the applied magnetic field.

Finally, the photocatalytic properties of TiO2/Fe3O4-loaded capsules were figured out by incubation of the capsules in the Rho B solution under UV light. Figure 9a,b shows the comparison of the relative change of the concentration and percentage degradation curves for TiO2/Fe3O4-loaded capsules and B3 capsule samples loaded with the same type and amount of TiO2 nanoparticles. The acquired data reveal the concentration decrease of Rho B incubated with TiO2/Fe3O4-loaded capsules is half as much of those of Rho B incubated with the B3 sample after 3 h under UV light. The

Figure 7. Relative change of the concentration of the degradable fluorescent agent ($\Delta c/c$, %) for the capsules loaded with (a) anatase (A1−A4 samples) and (b) P25 anatase + rutile (B1−B4 samples) nanoparticles under UV light.

Figure 8. (a) SEM image of the CaCO3/TiO2/Fe3O4 composite particle (scale bar is 2 μm); (b) SEM image of the capsule assembled on CaCO3/TiO2/Fe3O4 composite particle (scale bar is 1 μm); (c) relative distribution of Ti and Fe in CaCO3/TiO2/Fe3O4 composite particles and corresponding capsules measured by EDX (SEM); (d) mobility of the capsules loaded with TiO2 and Fe3O4 nanoparticles in the magnetic field measured as time dependence of the capsule suspension transparency.

Figure 9. Relative change of the concentration (a) and percentage degradation of Rho B (b) in aqueous solution incubated with photoactive capsules loaded with TiO2 (B3) and TiO2/Fe3O4 (B3 + Fe3O4) nanoparticles under UV light; ln($C/C_0$) plots (c) and corresponding reaction rate constants (d) for TiO2 and TiO2/Fe3O4-loaded capsules.
**CONCLUSIONS**

For the first time, TiO$_2$ nanoparticles were loaded into mesoporous CaCO$_3$ microparticles with the FIL technique. Moreover, the FIL method was shown to be only effective for the preparation of CaCO$_3$/TiO$_2$ composite particles in mild aqueous conditions and potentially can be extended to any type of nanoparticles incompatible with CaCO$_3$ in an aqueous medium. The P25 anatase + rutile nanoparticles were found to be the most suitable for CaCO$_3$/TiO$_2$ composite preparation. The loading efficiency of P25 particles was found to be higher than that of anatase that may be associated with less sedimentation stability of anatase particles in aqueous solution. The EDXS analysis demonstrated that the nanoparticles are mostly located in the surface layer with an average penetration depth of about 100 nm.

The CaCO$_3$/TiO$_2$ composite particles may be employed as template cores for the preparation of photoresponsive polyelectrolyte microcapsules. The inclusion of TiO$_2$ nanoparticles effectively promotes the photodegradation of rhodamine B fluorescent dye into the capsule microvolume and TRITC fluorescent label adsorbed onto the surface bilayer of the capsule shell. Noticeably, the relative change of the concentration of the degradable fluorescent agent is higher for the capsules loaded with P25 anatase + rutile particles rather than anatase-loaded capsules because of the higher photocatalytic activity of anatase with rutile inclusions. Additionally, multifunctional photocatalytic and magnetically responsive microcapsules were prepared by iterative loading of TiO$_2$ and Fe$_3$O$_4$ nanoparticles to the CaCO$_3$ template. The capsules exhibit photocatalytic properties and can be easily collected by the magnetic field for further recovery and regeneration of the catalyst.

The reported data demonstrate the potential of TiO$_2$-loaded capsules prepared with the FIL method for photoinduced degradation of organic molecules, bacteria, and other water pollutants either diffusing into the capsule volume or attaching to their surface. Additionally, FIL allows for multiple loading of various functional materials and, thus, the application field may be extended with further capsule modification and preparation of multifunctional containers, which was demonstrated by the addition of magnetic nanoparticles. We believe, these capsules are promising for water treatment applications and antifouling materials.
CaCO₃/TiO₂ composites were also prepared by coprecipitation and adsorption from solution methods for comparison with FIL. For coprecipitation, 0.615 mL of 1 M CaCl₂ and 0.615 mL of 1 M Na₂CO₃ solutions were injected into 2.5 mL of titanium dioxide aqueous suspension with the concentration of 1 mg/mL under vigorous stirring. After 1 min, the stirring was stopped and the resulted suspension of particles was separated by centrifugation and washed two times with DI water. To obtain CaCO₃/TiO₂ composites by the adsorption method, 40 mg of CaCO₃ microparticles were suspended in 2 mL of titanium dioxide aqueous suspension with a concentration of 1 mg/mL. After 40 min of incubation, the particles were washed three times with DI water. After washing all types of particles were dried.

**Synthesis of Polyelectrolyte Composite Microcapsules.** Synthesis of polyelectrolyte composite microcapsules was carried out according to Sukhorukov et al. Alternating adsorption of polyelectrolytes (PAH and PSS, 1 mg/mL in 0.15 M NaCl) onto the CaCO₃/TiO₂ microparticles was carried out for 15 min with each layer followed by three DI rinsing/centrifugation steps (1 min, 1500 rcf). After assembly of four PAH/PSS bilayers, the CaCO₃ was dissolved with 0.1 M HCl, which resulted in the formation of composite PAH/PSS capsules loaded with TiO₂ nanoparticles. The HCl solution can be safely used to remove CaCO₃ because of the absence of the specific sorption of Cl⁻ ions onto the surface of TiO₂ particles. In the same manner, the shell was assembled onto CaCO₃/TiO₂/Fe₃O₄ cores. The control samples were assembled on regular CaCO₃ cores with the same shell surface, the PAH in the absence of the specific sorption of Cl⁻ ions onto the surface of TiO₂ particles.

**Hydrodynamic Diameter of Nanoparticles.** The hydrodynamic diameter of nanoparticles was measured by DLS with a Zetasizer Nano ZS analyzer (Malvern Instruments Co, United Kingdom).

**Stability of Aqueous Suspensions.** The stability of aqueous suspensions was estimated with respect to a sedimentation ratio measured with the homemade setup analogous to the one described in ref 21. In particular, a quartz cuvette was filled with 3 mL of aqueous nanoparticle suspension with a concentration of 1 mg/mL. The measured pH value was 6.2 for anatase and 6.5 for P25 anatase + rutile particle suspensions. The cuvette was placed between the laser diode and photodetector in a way that the laser light passed through the cuvette parallel to the air/water interface. The device measured the time dependence of the suspension transparency increasing along with the particle sedimentation. Prior to measurement, the nanoparticle suspensions were redispersed with a horn ultrasound (Bandelin, Germany) for 1 min. The ultrasound source operates at 20 kHz with a power density of 1 W/cm².

**Surface Morphology (SEM) and Elemental Analysis (EDX).** Surface morphology (SEM) and elemental analysis (EDX) were performed with a MIRA II LMU scanning electron microscope (Tescan, Brno, Czech Republic) equipped with the INCA Energy 350 energy-dispersive microanalysis system.

**TEM and STEM.** Transmission (TEM) and scanning/transmission (STEM) electron microscopy imaging was performed with a Titan 80-300 TEM/STEM (FEI, USA) electron microscope equipped with a Schottky field emission gun, spherical aberration corrector (Cs probe corrector) and EDXS (EDAX, USA).

**Absorption Spectra.** The absorption spectra of TiO₂ suspensions were measured with a Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) with an acquisition step of 1 nm. The measured UV–vis absorption spectra were further processed to estimate the band gap of anatase and P25 anatase + rutile particles by Tauc plot of $(huα)^2$ versus $(hu)$ and extrapolation of linear plot region to the energy axis. α is the absorption coefficient that is calculated from the measured absorbance $A = \alpha x d$, where $d$ is the path length of the cuvette (1 cm).

**Confocal Laser Scanning Microscopy.** CLSM images were obtained with a Leica TCS SP8 X (Leica, Germany) microscope equipped with immersion objective ×100 (numerical aperture of 1.44). A 552-nm laser was used to excite the TRITC–PAH fluorescence.

**Photocatalytic Properties of TiO₂ Loaded Microcapsules.** The photocatalytic properties of TiO₂-loaded microcapsules were evaluated under UV light of Camellion LH9-U 9W lamp ($λ = 367$ nm, the spectrum is given in Figure S1 in the Supporting Information). To do this, the capsules were mixed with Rho B solution (0.01 mg/mL) and dispersed in a 96-well plate that was constantly shaken by a mini-shaker with a speed of 260 rpm. The lamp was set 5 cm above the irradiated surface, whereas the irradiated area of the single well was 38.5 mm². The absorption spectra of Rho B and the capsule mixture were measured using the Synergy H1 Multi-Mode Reader UV–vis spectrometer (BioTek Instruments, Inc., USA). The data were collected before UV exposure and after every 30 min of irradiation, whereas the total irradiation time was 3 h. The absorption spectra were measured from 480 to 620 nm range with a 1 nm step. The same experiment was carried out with aqueous suspension of TRITC-labeled capsules.

Afterward, the obtained data were processed with the standard data processing software and were presented as dependences of the relative absorbance change ($ΔA/A$) on the irradiation time. The time dependence of $ΔA/A$ was derived as the ratio of the absorbance intensity change measured before and after irradiation to the initial absorbance intensity

$$\frac{ΔA}{A} = \frac{A_{after} - A}{A} \times 100, \% \sim \frac{Δc}{c}$$

where $A$ is absorbance measured before UV exposure, whereas $A_{after}$ is that measured after UV exposure, $Δc/c$ is a relative change of the degradable fluorescent agent concentration. The values were figured out as an absolute peak magnitude at 560 nm. According to the Beer–Lambert law, the absorbance is directly related to the concentration (except extremely low or high analyte concentrations), and, therefore, the measured time dependence of $ΔA/A$ can be associated with the relative change of the concentration $Δc/c$ of the degradable fluorescent agent.

Additionally, the percentage of degradation of Rho B was figured out. To do this, the Rho B standard plot was measured first. Afterward, the corresponding decrease in Rho B concentration depending on the UV irradiation time was plotted.
The spectrum of the employed UV lamp, the comparison of measured TiO$_2$ nanoparticle properties, the TEM images and XRD patterns of TiO$_2$ nanoparticles, the SEM image of CaCO$_3$ vaterite template particle, the detailed description of the mechanism of acceptors’ photoreduction and donors’ photooxidation processes in TiO$_2$ nanoparticles, the UV–vis absorption spectra of TiO$_2$ nanoparticle suspensions with corresponding Tauc plots and calculated band gap values, calculation of reaction rate constants for Rho B degradation, and the Rho B standard plot (PDF).

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