A novel route for waste water treatment: photo-assisted Fenton degradation of dye pollutants accumulated in natural polyelectrolyte microshells

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The efficient accumulation of dyes in constructed natural polyelectrolyte microshells under moderate conditions, combined with the photo-assisted Fenton reagent, opens a new route for the effective elimination of dye pollutants from waste water.

The elimination of refractory dye pollutants from continual waste water effluent flows of the textile dyeing industry and colorant manufacturing plants, *via* green chemical processes, has been an active research topic in recent years.[1] The Fenton reaction (Fe^{2+}or Fe^{3+}/H_2O_2), as an efficient and environmentally benign choice, has shown high efficiency in the degradation of organic pollutants.[2] The process involves the generation and reaction of active species such as the hydroxyl radical ($^{\bullet}OH$), hydroperoxyl radical ($^{\bullet}OOH/O_2$) and/or high-valence iron complexes (FeO^{3+}, (L)Fe(IV)=O or ($L^{\bullet+}$)Fe(IV)=O), where L is a tetradentate porphyrin or trisbipyridine ligand.[3] However, the Fenton reaction, upon treating pollutants at lower concentration levels, suffers from the drawback of an excessive loss of the generated active species prior to reacting with pollutants. In this case, the question arises whether there is any possiblity of creating a green micro-device capable of accumulating pollutants, and then to degrade them efficiently in a defined region by means of Fenton reagents.

Recently, layer-by-layer (LBL) self-assembly[4] of oppositely-charged polyelectrolytes onto dissolvable colloidal particles has been utilized to create ultrathin nano- and microshells. The assembled shells, composed of synthetic polyelectrolytes, have been shown to be able to encapsulate dye molecules. In order to avoid secondary contamination originating from the shell components, we herein construct a natural and biocompatible polyelectrolyte microshell by using sodium alginate (ALG) and chitosan (CHI) as building blocks with the LBL self-assembly technique.[4,5] We find that the resulting microshells can accumulate dye pollutants efficiently in water under moderate conditions (room temperature, pure water medium) *via* a simple mix processing. The dye-accumulated shells can be separated from the solution by simple filtration. More remarkably, the Fenton reagent (Fe^{3+}/H_2O_2) can cross the wall of the shells[6] and under visible irradiation degrade rapidly the accumulated dye pollutants inside them. This finding provides a new economical route for the effective elimination of dye pollutants from waste water.

Confocal laser scanning microscopy (CLSM, Zeiss LSM 510 META) imaging directly verified the successful assembly of the (ALG/CHI) shells templated onto melamine formaldehyde (MF) colloidal particles (Fig. 1a). When a suspension of the (ALG/CHI) shells was added to a solution of rhodamine B (RhB) or fluorescein (Flu) overnight at room temperature, more intense fluorescence was observed from the shell interior than from the bulk solution (Fig. 1b and c). This indicates that an efficient accumulation of dyes inside the shells occurs. The amount of dyes accumulated in the interior of the shells could be determined by the

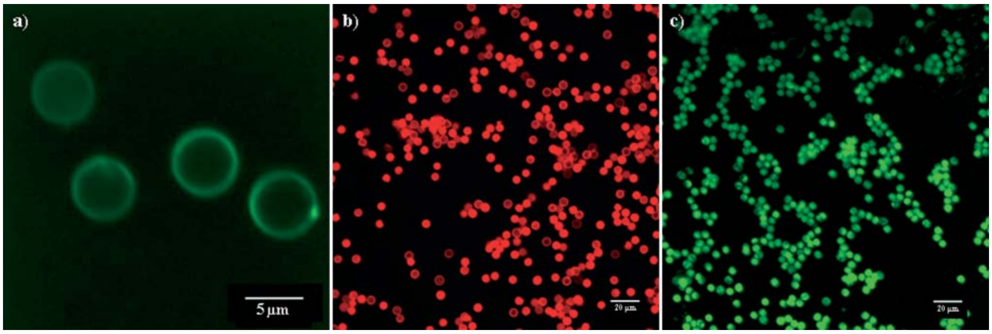

Fig. 1 (a) CLSM image of hollow microshells composed of $(ALG/CHI)_5$ templated onto 4.3 μm MF particles, where FITC–albumin was used to label the shells (FITC = fluorescein isothiocyanate). After being mixed with the shells overnight, RhB (b) and Flu (c) were accumulated inside the shells. Scale bars: (a) 5 μm, (b) 20 μm and (c) 20 μm.

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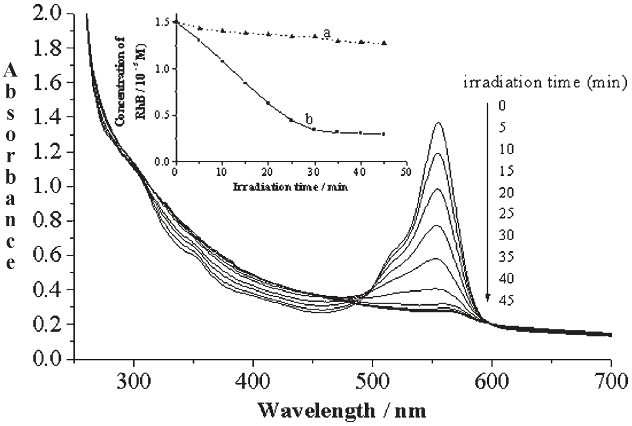

Fig. 2 UV/vis spectral changes of accumulated RhB (1.5×10^{-5} M) in a solution of Fe^{3+} (2×10^{-4} M) and H_2O_2 (5×10^{-4} M) under visible irradiation. Inset shows concentration changes of accumulated RhB both in the dark and under visible irradiation.

difference between the initial concentration of dyes added and the amount of non-accumulated dyes remaining in the supernatant liquid, combined with their respective standard curves, as well as the known physical parameters of MF particles, *i.e.* 6.0×10^{-11} g per shell for RhB and 4.2×10^{-11} g per shell for Flu.[7]

The dye-accumulated microshells, after simple separation by filtration, were dispersed in the Fenton reagent. The changes that took place to the temporal absorption spectra (Perkin-Elmer, Lambda Bio 20 spectrophotometer) in the presence of Fe^{3+} and H_2O_2 under visible irradiation are displayed in Fig. 2. Under light irradiation with a 500 W halogen lamp (light filter $\lambda < 420$ nm), the characteristic absorption band of accumulated RhB at about 555 nm decreased rapidly and nearly disappeared after irradiation for 45 min. A control experiment showed that accumulated RhB degraded to a small extent in the dark (see Fig. 2, inset) compared with the photoreaction, indicating that visible irradiation accelerated markedly the degradation process. We also carried out the photodegradation of free RhB in a homogeneous solution of Fe^{3+} and H_2O_2 under otherwise identical conditions to the Fig. 2 experiment. It was found that the degradation rate of free RhB was slightly faster than that of accumulated RhB. Two possible reasons can be considered to explain the decrease in the photodegradation rate of accumulated pollutants: (i) though the walls of the shells are very thin (nanometer scale[4]), to some extent the polyelectrolyte microshells block the visible light radiation, thereby leading to a decrease in photoefficiency, (ii) the photodegradation of dye pollutants in the defined microshells in the presence of Fe^{3+} and H_2O_2 might proceed *via* a reaction mechanism different from the simple Fenton mechanism ($^{\bullet}$OH mechanism),[3c] because no photodegradation of the polyelectrolyte shells was observed (see Fig. 3 below).

To gain further direct visualization of the changes to the accumulated dyes inside the shells before and after the photoreaction, the CLSM technique can be employed. Fig. 3a, b and c display CLSM images of the RhB-accumulated shells in a solution of Fe^{3+} and H_2O_2 before and after exposure to visible irradiation for 45 and 60 min, respectively. Evidently, under irradiation, the fluorescence intensity, which is proportional to the RhB concentration in the shell interior, decreases at a rapid rate. It is worth noting that during the whole photodegradation process, no fluorescence is observed in the bulk solution, indicating that the dye molecules are located in the interior of the shells. Fig. 3d shows a transmission electron microscopy (TEM, JEOL 2010 operating at 200 kV) image of the RhB-accumulated (ALG/CHI) shells in the presence of Fe^{3+} and H_2O_2 after 60 min. of irradiation. From Fig. 3 we can see that the RhB-accumulated shells keep their spherical shape intact, even during the photoreaction. This indicates that the assembled polyelectrolyte shells are stable against attack from highly active species and have potential application in recycling degradation. Although for the moment we cannot yet comment on which active species is predominantly involved in the current system, no corrosion induced by the highly oxidative species generated in a photo-assisted Fenton reaction has been observed for other substances such as Nafion, Nafion-glass mats and polyethylene block copolymers.[8]

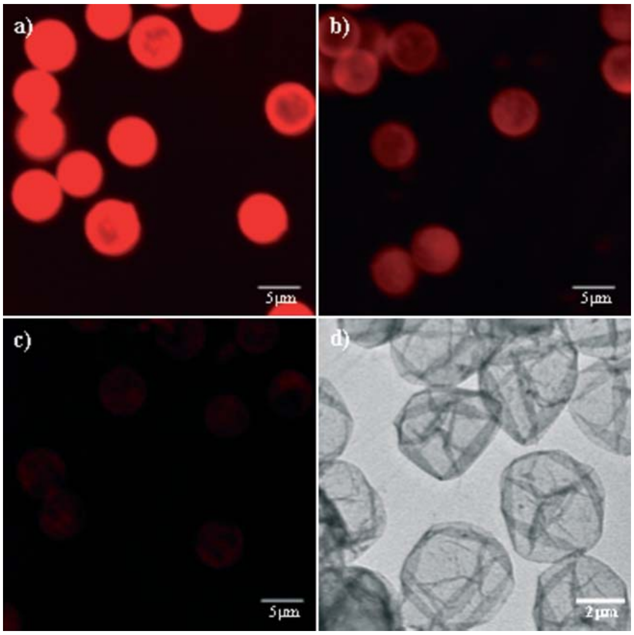

Fig. 3 Variations in CLSM fluorescence images of $(ALG/CHI)_5$ shells accumulated with RhB in the presence of Fe^{3+} (2×10^{-4} M) and H_2O_2 (5×10^{-4} M) before (a) and after irradiation for 45 (b) and 60 min (c), respectively. During the measurements the optical parameters of the CLSM remained unchanged. (d) TEM image of the RhB-accumulated shells under the same conditions as (c).

In addition, we find that other dyes such as methylene blue, acridine orange, 6-carboxyfluorescein and rhodamine 6 G can also be efficiently accumulated inside ALG/CHI shells, indicating that spontaneous accumulation is a general phenomenon instead of an occasional finding. Furthermore, all accumulated dyes can be easily degraded in a solution of Fe^{3+} and H_2O_2 under visible irradiation.

In summary, a natural polyelectrolyte microshell, constructed *via* the LBL self-assembly technique, has been introduced into dye-polluted systems. Efficient accumulation of dyes in the prepared shells, combined with photo-assisted Fenton reagent, opens up a new route to the effective elimination of dye pollutants from water. This work may also provide a useful insight into the selective (photo-)oxidation and synthesis of optical materials in micrometer-sized containers.

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Notes and references

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5 The procedure for the preparation of hollow microshells was as follows: 1.5 cm^3 of alginate solution (1 mg cm^{-3} in 0.5 M NaCl) or 1.5 cm^3 of chitosan solution (1 mg cm^{-3} in 0.2 M NaCl at pH 3.8), with a charge opposite to that of MF templates (Microparticles GmbH, Germany) or the last layer deposited, was added to a template colloidal solution (0.3 cm^3), and left to absorb for 1 h. The excess of added species was removed after each layer was deposited by 3 repeated centrifugation (2500 g, 3 min)/washing/redispersion cycles using dilute aqueous NaCl. Subsequent layers were deposited until the desired number of multi-layers (5 double layers were assembled here) was achieved. Hollow microshells were obtained by dissolving the MF cores in HCl (0.1 M), centrifugation (2500 g, 5 min) and washing 3 times with water.

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7 Unless otherwise noted, 300 μl of MF microparticles (diameter 4.3 μm, density 1.51 g cm^{-3}, solid content 10 weight%) were used in the preparation of the microshells and in subsequent experiments. All the resulting shells were aged for approximately 2 d. The RhB/Flu standard curve was obtained by measuring the absorbance of several known concentrations of RhB/Flu at their respective maximum absorption wavelengths (555 nm for RhB, 485 nm for Flu).

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