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Latex-supported, Dye-sensitised, TiO_2 Core Shell Spheres, for the Photocatalytic Generation of Hydrogen from Water

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A sustainable method of hydrogen production for use as a fuel for energy generation is one area of research aimed at reducing carbon emissions from fossil fuels. Photo-catalytic hydrogen generation from water is attractive from an environmental perspective as harvesting solar energy and converting it into chemical energy is a sustainable natural process (photosynthesis). The facile release of energy stored in the H−H bond upon reaction with oxygen, yielding water as the only chemical product of the reaction, makes hydrogen an attractive, clean energy carrier and a possible, ideal solution for energy- related issues in the long-term [1].

Conventional electrolysis of water requires the generation of electricity in a separate process, leading to gross overall inefficiencies of the reaction system. Direct water splitting avoids this issue.

TiO_2-based materials are expected to play an important role as photocatalysts [2], both for the removal of organic pollutants from water and for the photocatalytic generation of hydrogen from water. An issue that needs to be overcome is the fact that TiO_2 predominantly absorbs ultra-violet light, which constitutes only 4% of the solar spectrum. For this reason it is necessary to sensitise crystalline titania towards visible wavelengths, an aim that can be achieved either by doping [3,4] the crystalline structure or coating its surface with organic [5,6] or metallorganic dyes [7,8]. The issues with these enhancements are that firstly, the insertion of dopant into the crystalline structure can create defects which become good recombination sites for the electron and hole pair formed by the absorption of a photon, and secondly, dyes could be desorbed from the surface of the TiO_2.

Here we report a novel core-shell TiO_2 structure, containing a dye supported on a polymeric sphere, enabling direct evolution of H_2 gas from an aqueous solution using light of visible wavelengths.

The basis of this concept is to covalently bind a dye-sensitiser to a support and the support/dye combination is then encapsulated by a thin layer of TiO_2, which serves as both the photocatalyst and as a physical barrier, preventing desorption of the dye.

Two different configurations of sensitised TiO_2 structures were prepared. In the first configuration, polystyrene latex spheres were synthesised using emulsion polymerisation with 4,4'-azobis(4-cyanovaleric acid) as the initiator. This process leaves carboxylic acid groups on the surface of the latex sphere (diameter: ~500 nm) [9]. These carboxylic acid groups were then functionalised with an organic dye (Rhodamine B isothiocyanate) through NHS/EDC (NCS=N-hydroxysuccinimide; EDC=1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride), coupling [10]. Subsequently these latex spheres were suspended in dry butyl-1-methylpyrrolidinium bis-triflamide [11], under inert

atmosphere, to which titanium isopropoxide was added. The Ti-precursor was then hydrolysed at 80 °C upon addition of water. This hydrolysis reaction although at low temperature, allows the synthesis of nanocrystalline anatase TiO_2 (studies were performed at different temperatures in the range 60□100 °C, Fig.2). A second ruthenium dye (N3) was then adsorbed onto the surface of the titania crystals. For the second configuration the polystyrene spheres were functionalised with the ruthenium dye (N3), with a similar procedure followed for the organic dye and then the TiO_2 layer was hydrolysed onto the dye-functionalised polystyrene surface, again in the presence of the pyrrolydinium ionic liquid. The crystals were then platinised (0.5 wt.% Pt to TiO_2).

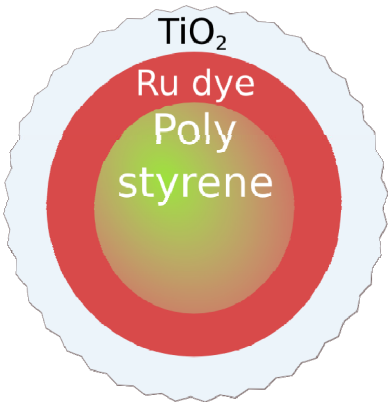


Figure 1: (a) Schematic illustrating of the core shell structure.

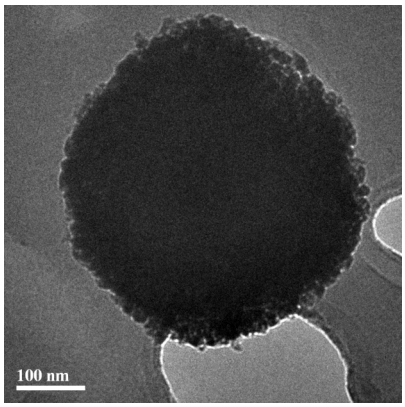


Figure 1: (b) TEM micrograph of a polystyrene sphere coated with TiO_2 nanocrystals.

The coating of the polystyrene sphere with TiO_2 in the ionic liquid was required to obtain a crystalline structure without the need for calcination at 450 °C, which would have destroyed both the polystyrene substrate and the organic sensitisers.

Photochemical testing of the materials for hydrogen generation was performed in a double walled quartz reactor, thermostated to 25 °C. The catalyst was suspended in a water:methanol (10:1) solution and deoxygenated with nitrogen before irradiation with a mercury lamp (350 W, Oriel) equipped with a water filter and cut-off filters (305, 395, 430 nm). Argon was used as a carrier gas to convey any hydrogen produced into an online GC for quantification with a TCD detector.

The preliminary studies for the synthesis of TiO_2 at low temperatures, allowed the formation of crystalline titania even at temperatures as low as 60 °C (Fig. 2), significantly lower than the ones previously reported in the literature [11].

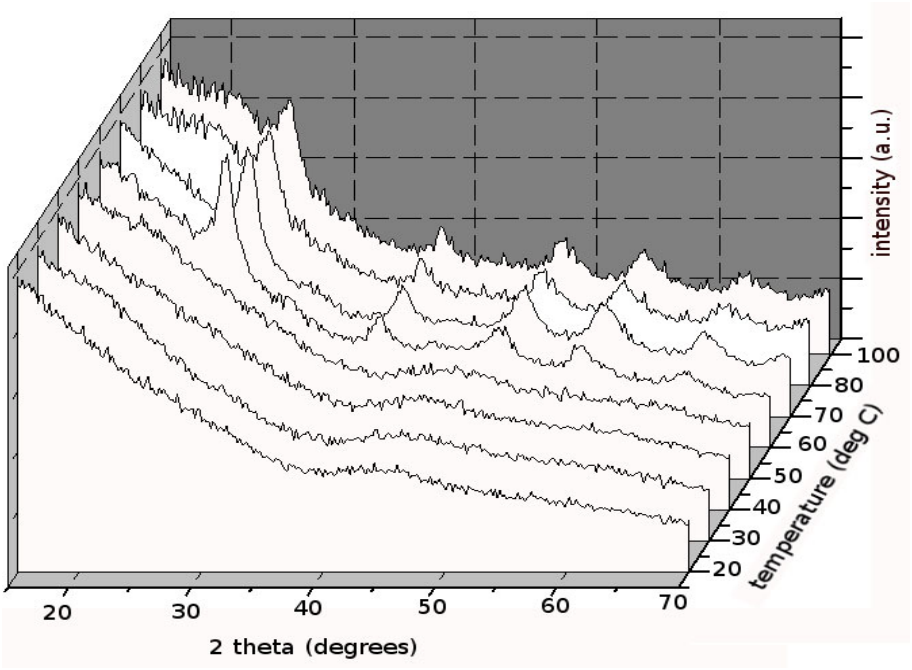
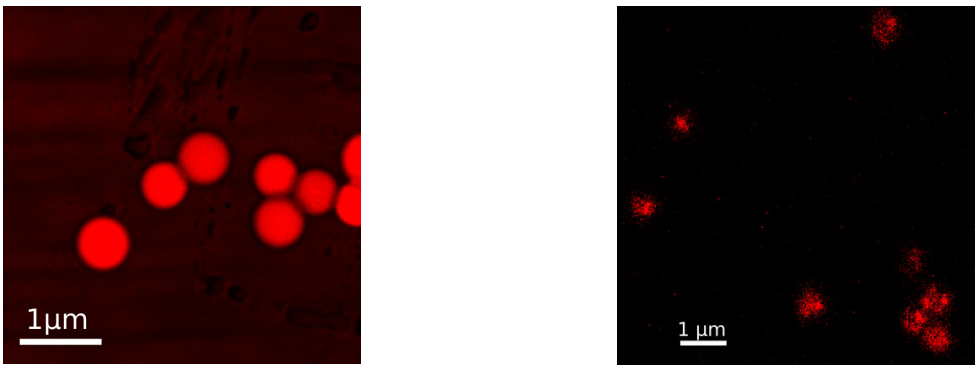


Figure 2: XRD diffractograms of TiO_2 hydrolysed at different temperatures.

The coating of the polystyrene spheres was performed in a buffered solution at pH 7.4 (phosphate buffered saline), after activation with NHS/EDC, ethylendiamine was added to the suspension in order to obtain an amino terminated chain, which could readily react with isothiocyanate groups present onto the rhodamine B dye. Confocal microscopy images confirm the presence of the dye on the surface of the PS spheres, before (Fig. 3a) and after coating with the TiO_2 layer (Fig. 3b). The second image shows that although the spheres are almost uniformely coated, the dye underneath is still capable of absorbing visible light.



(a) before coating with TiO_2. (b) after coating with TiO_2.

Figure 3: Confocal microscopy images under irradiation at 530 nm.

The expected spherical morphology of the TiO_2 coated spheres was confirmed by TEM (Fig. 1b) and the crystallinity of the titania was verified by X-ray diffraction analysis. The diameter of the composite was slightly larger than of the uncoated spheres (~500 nm), showing a layer

roughly 20□30 nm thick. Occasionally larger agglomerates of TiO_2 crystals were observed to protrude from the surface of the beads.

Tests for photochemical hydrogen production show that the visible light sensitised structure is still active under irradiation at 430 nm (Fig. 4) , in contrast with the standard P25 which is active only in the UV region.

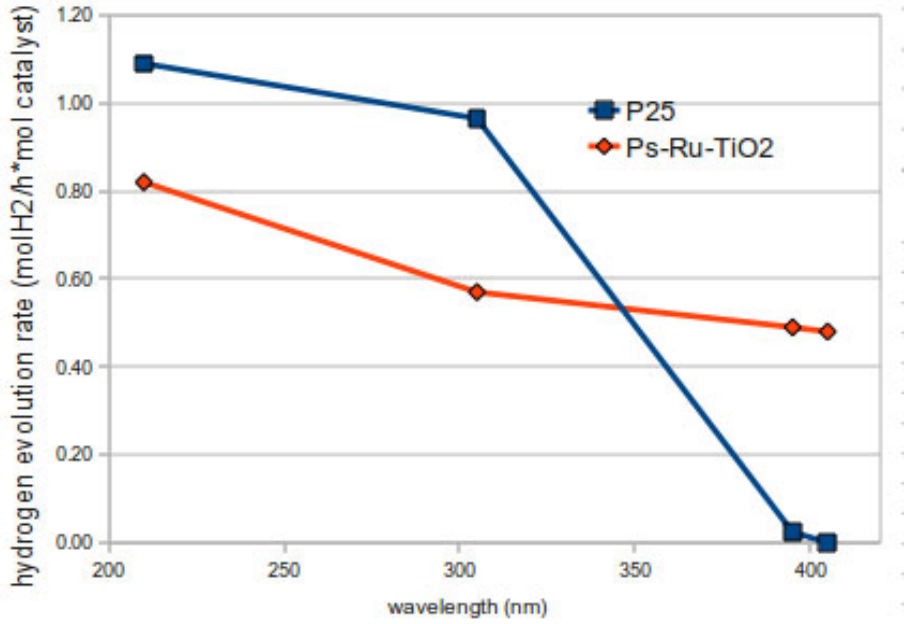


Figure 4: Hydrogen evolution rate of P25 and the N3 sensitised PS-dye-TiO_2 structure.

In conclusion, the step-wise process allowed the synthesis of supported, dye-sensitised TiO_2 core shell structures, which benefit from both crystallinity and dye encapsulation for photo-catalytic hydrogen production.

The TiO_2 structures will have to be further optimised and then tested for recyclability and stability of the dyes to photo-degradation. A newly acquired solar simulator will be used for more accurate testing of the catalyst.

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