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Abstract: Fluidised Bed Chemical Vapour Deposition (FBCVD) has been widely used for the industrial production of corrosion resistant and mechanically robust coatings. Laboratory-based FBCVD rigs are less common, however, this technique is ideal for the high-throughput production of core-shell and multi-shelled materials, allowing large areas to be coated in a fast and cost effective way. The method is also convenient for the optimisation of advanced materials with tuned structural, electronic and functional properties. In this work, the synthesis of double-shelled rutile-anatase TiO2 particles is presented as a case study. Electron transfer mechanisms at the junction level of the two polymorphs have been reported as responsible for the high efficiency of TiO2-based materials, such as the well-known Evonik P25 standard. The photocatalytic performance of the double-shelled particles was evaluated during the mineralisation of a model organic pollutant (stearic acid) and compared with that of the individual components. To the best of our knowledge, this is the first time that multi-shelled particles have been synthesised from a chemical vapour deposition route.

Introduction

In recent years, a wide range of advanced core-shell and multi-shelled materials have been successfully used as antimicrobial1-3 and medical treatment systems,4-6 photocatalysts,7-9 thermochromic materials,10-12 quantum dots13-15 and battery compounds.16-19 These multi-component systems take advantage of the synergistic interaction between different layers (electron transfer processes, lattice matching, etc.) to suit particular functional properties. For instance, there have been many reports on core-shell arrays for use as high performance capacitance materials.19-22 Core-shell particles have also been reported for their excellent photonic properties.23, 24

Unfortunately, the main techniques reported for the synthesis of core-shell and multi-shelled materials are currently solution based, which can be undesirable for industrial scale-up production due to the long reaction times (3-4 days), expensive solvents, refining of the product and batch-like nature of the reactions. Thus, an alternative scalable approach is crucial for the introduction of these advanced materials into the market.
Multi-shell systems such as the case study introduced here are of increasing interest. A CVD approach allows successive shells to be deposited and the samples can be coated as many times as it is required. The thickness of each layer and concentration of dopants can be carefully tailored to achieve the desired properties in the final product. In the case of core-shell particles, there have been many reports on the synthesis of Au@SiO$_2$ core-shell materials which typically involve aqueous routes. This is a relatively slow process and is not easily scalable for industrial applications. Again in the latter case, CVD offers a convenient way to dope both the core and shells of such a structure, with the ability to control the dopant level by the concentration of the dopant in the precursor mix.

### Experimental

#### Chemical precursors

Titanium (IV) chloride (TiCl$_4$, 99.9%) and ethyl acetate anhydrous (C$_3$H$_6$O$_2$, 99.8%) was purchased from Sigma Aldrich UK. Mica (Symic CO01, synthetic fluorophlogopite:TiO$_2$ 80:20) was purchased from Eckert, the particle size range was 10-40 μm. All chemicals/substrates were used as received with no additional workup. Oxygen-free nitrogen (99.9%) was purchased from BOC. Octadecanoic (stearic) acid was purchased from Sigma Aldrich (CH$_{17}$CH$_2$COOH, ≥ 95%).

#### The Fluidised Bed CVD apparatus

The samples were produced using a specially designed hot-walled Fluidised Bed Chemical Vapour Deposition (FBCVD) reactor. Error! Reference source not found. (a,b) shows a schematic design of the FBCVD rig and a photograph of the system. The precursors were contained in stainless steel cylinders (bubblers) with brass jackets and heating bands. Nitrogen (N$_2$) was used as a carrier gas. All the stainless steel lines were heated using heating tapes (Electrothermal 400 W, 230 V) and the temperature of all the components of the rig controlled using k-type thermocouples with Thermodon controllers. The precursors were pre-mixed in a stainless steel mixing chamber. The hot-walled reaction chamber was created using a tube furnace, fitted with a Eurotherm controller. Fluidisation of the mica support was achieved by carrier gas flow only (Figure 1(c)). The design presented here is a fixed bed; there are no moving parts within the reactor. In general, fluidisation occurred at flow rates above ~7 L min$^{-1}$ but total flow rates of >10 L min$^{-1}$ are typically used to ensure complete fluidisation of the particles. Stainless steel gauzes (diameter size: 0.1 mm) are placed at the two ends of the reactor in order to prevent excess mica escaping the reaction chamber during deposition.

#### Synthesis of double-shelled TiO$_2$ materials

Titanium dioxide (TiO$_2$) was deposited from reaction of titanium chloride (TiCl$_4$) and ethyl acetate (C$_3$H$_6$O$_2$)$_{55}$ as described in equation (1), on ~3 g of mica under the conditions described in Table 1. The temperature ramp rate of the reactor was 20 °C min$^{-1}$ and it was kept at the target temperature for at least 30 min before deposition. The TiCl$_4$ and C$_3$H$_6$O$_2$ bubblers were set to 75 and 40 °C, respectively.

\[
\text{TiCl}_4 (g) + \text{CH}_3\text{COOC}_2\text{H}_5 (g) \rightarrow \text{TiO}_2 + \text{byproducts} \quad (1)
\]

#### Film Characterisation

X-ray diffraction (XRD) studies were carried out using a Stoe (Mo) StaniP diffractometer. The instrument operates with a Mo X-ray source (Mo tube 50 kV 30 mA), monochromated (Pre-sample Ge (111) monochromator selects Kα1 only) and a Dectris Mython 1k silicon strip detector covering 18° (2θ). Samples were run in transmission mode, with the sample being rotated in the X-ray beam. The diffraction patterns obtained were compared with database standards. Raman spectroscopy was carried out using a Renishaw 1000 spectrometer equipped with a 633 nm laser. The Raman system was calibrated using a silicon reference. UV/vis...
Physical and optical characterisation

A series of double-shelled rutile@anatase, single-shelled anatase-rutile mix and individual pure anatase and rutile coatings were deposited on mica particles by Fluidised Bed Chemical Vapour Deposition (FBCVD). The TiO$_2$ films were synthesised by reaction between TiCl$_4$ and ethyl acetate as described above (vide supra).

The as-deposited pure anatase TiO$_2$ films were transparent and thus looked greyish on the mica substrate, which was originally of white/silvery colour. On the contrary, the powders annealed at 750 and 1000 °C, which contained the rutile phase, had a golden/cream colour.

Diffuse reflection UV/vis spectra (Figure 2) showed a red-shift of the absorption spectra for those samples containing the rutile phase, in agreement with the literature. Close inspection of Figure 2 suggests that the single-shelled anatase-rutile mix sample was predominantly anatase, since the absorption spectrum of the former is similar to that of pure anatase TiO$_2$, whilst the double-shelled rutile@anatase material had a clear rutile component. Tauc plots were calculated from absorbance data in order to estimate the corresponding band-gap energies of these materials (Figure 2, inset). The pure anatase and rutile phases had band-gap energies of 3.11 and 2.84 eV, respectively, which are lower than literature values. As expected, the mix and double-shelled rutile@anatase samples showed band-gap energies within these two extreme values (3.10 and 2.90 eV, respectively).

XRD analysis confirmed the presence of pure crystalline anatase and rutile TiO$_2$ phases (Figure 3(a)). The individual rutile and anatase samples were compared to standard samples (ICSD database) and the additional peaks observed in the patterns were due to the mica substrate. The intensity and sharpness of the diffraction peaks are in contrast with the typical broadening observed in XRD patterns of CVD TiO$_2$ thin films. The single-shelled mix and double-shelled samples showed the presence of both anatase and rutile phases. Surprisingly, the XRD pattern of the single-shelled mix sample (Figure 3(a)) showed similar peak intensity ratios of the two polymorphs, which was unexpected considering that the absorption properties of this sample were similar to pure anatase (Figure 2).
The crystallite size in the samples was roughly estimated using the Scherrer equation within the range of 58 – 65 nm.

Further structural studies were carried out using Raman spectroscopy (Figure 3(b)). Consistent with the XRD results, the pure anatase and rutile samples showed bands associated with these phases, and no impurity phases were identified. The characteristic Raman-active modes of the anatase TiO$_2$ structure were observed at 144, 197, 634 (E$\text{g}$), 525 (A$\text{ig}$$+$$B$\text{ig}$) and 400 (B$\text{g}$) cm$^{-1}$. Some additional bands were observed in the pure anatase spectrum, which were assigned to the mica substrate. The corresponding modes for the rutile polymorph were found at 150 (B$\text{g}$), 236, 444 (E$\text{g}$) and 610 (A$\text{ig}$) cm$^{-1}$. As expected, the characteristic Raman bands of the two polymorphs were also observed in the case of the single-shelled mix sample, although the anatase bands dominated the spectrum (Figure 3(b)). It is worth noting that the double-shelled material showed anatase bands only and no traces of the rutile phase were detected. The fact that rutile was clearly observed in the XRD studies but untraceable in the Raman analysis of the double-shelled material is strong evidence of the full coverage of the particle by an homogeneous anatase TiO$_2$ overlayer.

The particle morphology was investigated by TEM. Figure 4(a) shows a typical TEM image of the pure anatase sample, containing round particles within a range of sizes. The latter was attributed to the mica substrate. In contrast, the rutile coated particles seemed to crystallise/sinter into a hexagonal shape (Figure 4(b)). Interestingly, the single-shelled mix material (Figure 4(c)) combined features of both anatase and rutile particles, with a hexagonal structure clearly present but with rounded edges. Finally, the double-shelled particles, with the anatase phase deposited as an overlayer, showed very similar morphology to that of pure anatase (Figure 4(d)), which supports the conclusions based on the Raman studies. A close inspection of the TEM images showed an apparently homogeneous coating of the mica substrate and no obvious imperfections or porosity could be observed. The thickness of the outer shell in the double-shelled sample, Figure 4(d), was used to determine growth rates for the FBCVD process as $\sim$1.7 nm min$^{-1}$. Whilst this growth rate seems low in comparison to normal CVD TiO$_2$ deposition processes, which are typically in the range of $\sim$100 s nm min$^{-1}$, the former rate is expected once the surface area of the powder substrate is taken into account. The average particle size of the samples was estimated as 50 – 70 nm, in agreement with the crystallite size range estimated from the Scherrer equation (vide supra).

BET analysis was used to determine the surface areas of the samples, which ranged between 3 – 12 m$^2$ g$^{-1}$ (Table 1), which is in accordance with literature values for similar sized TiO$_2$ particles. These values are significantly lower than those for standard commercial powders, such as P25, with literature values of 56 m$^2$ g$^{-1}$. Interestingly, the BET results could be correlated with the particle sizes observed in the TEM images. The anatase and rutile nanoparticles had similar particle size and calculated surface areas, whilst the single-shelled mix sample contained small particles and large BET areas and the double-shelled material had the largest particles and correspondingly smallest area. The relatively low surface areas determined also suggested that the samples exhibited low porosity, giving further evidence of good surface coverage by the FBCVD route.

Photodegradation of organic pollutants

The photocatalytic activity of the TiO$_2$-based samples synthesised in this work was assessed during mineralisation of stearic acid, a model organic pollutant. Stearic acid is very stable under UVA irradiation in the absence of a photocatalyst. The mineralisation of the acid can be formulated according to equation (2) and it follows simple zero-order kinetics. The full mineralisation process requires 104 electrons.

$$\text{CH}_3(\text{CH}_2)_{n}\text{CO}_2\text{H} + 26\text{O}_2 \rightarrow 2n\text{CO}_2 + 18\text{H}_2\text{O} \quad (2)$$
The degradation of the acid can be easily monitored by FTIR, following the disappearance of C–H characteristic bands within the range of 2700–3000 cm\(^{-1}\) (Figure 5(a)). Typically, the degradation rates are estimated from linear regression of the initial 30–40% drop in integrated area of the acid characteristic IR-active bands. The degradation curves of stearic acid on the different TiO\(_2\)-based samples are shown in Figure 5(b). The initial concentration of the acid did not change under the illumination conditions of the experiment (UVA, 4 ± 0.2 mW cm\(^{-2}\)) in the absence of a photocatalyst (on plain glass). The photocatalytic activity can be expressed as formal quantum efficiency (\(\xi\)), defined as molecules degraded per incident photon (molec photon\(^{-1}\)). The corresponding \(\xi\) values are reported in Figure 5(c). In this case, it was assumed that all incident photos were absorbed by the photocatalyst and they all had the same energy, corresponding to 365 nm (E = 3.39 eV). As expected in the case of photodegradation reactions of organic pollutants, the pure rutile sample showed negligible activity whilst the pure anatase sample showed the highest degradation rate (Figure 5(c)).\(^{54}\) The \(\xi\) value of the anatase sample was consistent with those reported for thin films,\(^{53}\) considering the thickness of the layers (≤ 100 nm) deposited in this work. The activity rates of the single- and double-shelled materials were found as intermediate between the pure rutile and anatase behaviours. The small difference in BET surface areas (3–12 m\(^2\) g\(^{-1}\)) was not considered relevant to the activity rates observed here (Table 1). The highest surface area was estimated for the anatase-rutile-mix sample, however this sample did not show the highest activity. Similarly, both the double-shelled and pure anatase samples had similar surface areas (3 and 5 m\(^2\) g\(^{-1}\)) respectively but the photocatalytic activity of the latter was significantly higher.

Inspection of the corresponding UV/vis spectra (Figure 2) allowed correlation of their respective activities with the content of anatase and rutile phases in the single-shelled mix and double-shelled samples, provided any synergistic interaction between the polymorphs is ignored. However, the fact that the rutile-anatase systems showed poorer activities than that of pure anatase and anatase-rutile mix nanoparticles was surprising, since the synergistic interaction between the two TiO\(_2\) polymorphs has been extensively reported.\(^{33, 55-58}\) It is important to highlight that the arrangement of the polymorphs in anatase-rutile systems should contribute to a vectorial separation of photogenerated charge pairs, as in a layered arrangement, and in any random anatase-rutile mixture the overall effect may be hindered.\(^{35}\) When arranged appropriately, the anatase-rutile interaction contributes to an efficient charge separation and thus enhanced activity in these systems. The latter argument has been used to explain, for instance, the high photocatalytic efficiency of the commercial standard Evonik TiO\(_2\) sample, formerly Degussa P25.\(^{46}\) The mechanism of this interaction and in particular the band structure and electron transfer between the rutile and anatase phases is still a matter of debate. It has been generally accepted that rutile acts as an electron sink in anatase-rutile systems. However, evidence of electron transfer from rutile to anatase has been observed by EPR analysis.\(^{56}\) The latter observation was also supported by recent calculations.\(^{54}\) These authors suggested that the widely observed electron transfer from anatase to rutile is due to defects at the heterojunction level, which represent deep electron trap levels (1 eV below the conduction band) in rutile. This has been recently confirmed by transient spectroscopy studies on anatase-rutile mixtures which revealed hole transfer occurring from rutile to anatase.\(^{59}\) This is relevant since it has been postulated that hydroxyl and hydroperoxyl radicals (\(\cdot\)OH, \(\cdot\)O\(_2\)H), formed in the reactions with participation of photogenerated holes and water molecules, are key species in the photodegradation of organic molecules.\(^{60}\)

Here, the surprisingly low activity of the double-shelled sample could be due to the efficient coverage of the rutile layer by the deposition of the anatase overlayer, as inferred from the Raman results (Figure 3(b)) and the discussion around the TEM/BET analysis. The exposure of both anatase and rutile phases to the medium also seems to play a crucial role in the activity enhancement observed for anatase-rutile samples. Zhang et al.\(^{58}\) observed an enhanced activity of anatase-decorated rutile particles during H\(_2\) evolution up to approximately 15 wt.% anatase loading, but the activity of the samples dropped once the rutile phase was fully isolated from the medium. Similar observations were independently reported by Kandiel et al.,\(^{55}\) for anatase-decorated rutile nanorods. The latter showed optimum photocatalytic activity in the gas-phase degradation of acetaldehyde under UVA irradiation, however the nanorods became inactive once they were embedded in anatase nanoparticles. In the current work, an attempt was made towards the decoration of rutile components with anatase nanoparticles by changing the deposition times of the anatase phase (5, 10, 20 min). However, this approach resulted in homogeneous coatings with variable thicknesses and the activity of the resulting samples was similar to that of the double-shelled rutile@anatase material discussed here. In the case of the single-shelled mixed sample, its relatively high photoactivity could be explained considering that anatase will initially transform into rutile in the bulk of the particles, but the surface could still remain as anatase at the deposition temperature used in the synthesis (750 °C), according to previous studies in the literature.\(^{58}\)

**Conclusions**

A laboratory-scaled fluidised bed chemical vapour deposition (FBCVD) system has been introduced as an easily scalable, fast and cost effective route to produce multi-shelled and core-shell particles with the ability to tailor the core and shells to obtain desirable chemical properties. Single-shelled mix and double-shelled rutile@anatase TiO\(_2\) particles were successfully synthesised and investigated as a case study. The TiO\(_2\) shells were deposited on mica particles. The photocatalytic activity of these materials was studied during photodegradation of stearic acid. It was interesting to observe that the double-shelled rutile@anatase material showed a surprisingly low activity, which corroborates a number of reports that state
both rutile and anatase polymorphs must be exposed to the medium for a photocatalytic efficiency enhancement in mixed-phase materials. This seemingly negative result is actually perceived as evidence for the coverage efficiency of the FBCVD method, as inferred from TEM, BET measurements and particularly Raman studies.

Acknowledgements

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Notes and references

Figure 5: a) IR spectra of stearic acid during UVA illumination on TiO$_2$ anatase particles over 38 h. b) Integrated areas of characteristic stearic acid IR-active bands (2700 – 3000 cm$^{-1}$) on rutile:anatase core-shell, anatase/rutile mixed-phase, pure rutile and pure anatase nanoparticles under UVA irradiation (4 ± 0.2 mW cm$^{-2}$). The integrated areas of the acid on plain glass (no catalyst) are included for reference. c) Corresponding formal quantum efficiencies ($\xi$), defined as molecules of acid degraded per incident photon (molec photon$^{-1}$).

<table>
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<th>Name</th>
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<th>Deposition Conditions</th>
<th>Annealing Conditions</th>
<th>Size (nm)</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$E_g$ (eV)</th>
<th>$\xi$ (molec photon$^{-1}$) x10$^{-6}$</th>
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<td>500</td>
<td>10</td>
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Table 1: Synthesis conditions and surface areas of single- and double-shelled TiO$_2$ samples on mica support.

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