Sand Supported Mixed-Phase TiO$_2$ Photocatalysts for Water Decontamination Applications**

By Dorian A. H. Hanaor* and Charles C. Sorrell

Using an organometallic precursor, TiO$_2$ coatings were fabricated on surfaces of quartz, zircon, and rutile sands. X-ray diffraction, X-ray fluorescence, UV–vis spectroscopy, and surface area measurement were used to characterize support materials. The phase composition and morphology of the coatings were characterized by laser Raman microspectroscopy and scanning electron microscopy, respectively. A packed bed reactor was used to study the inactivation of Escherichia coli in recirculating water by the supported photocatalysts. It was found that the sand grains were well coated with a homogenous layer of TiO$_2$ and coatings were well adhered, exhibiting a mixed anatase-rutile composition after firing at 850 °C. Photocatalytic activity was highest in coatings applied to quartz sand, although sterilization of the recirculating water was not achieved with any of the materials investigated. The advantages of quartz as a TiO$_2$ photocatalyst support material are likely a result of this material’s higher purity and optical transmittance. Potential enhancement through Si doping cannot be ruled out.

1. Introduction

TiO$_2$ photocatalysts are of increasing interest owing, in part, to their potential applications in solar-driven environmental remediation. In recent decades, TiO$_2$ has been shown to facilitate the decomposition of organic pollutants and pesticides and the inactivation of bacteria in water through the formation of adsorbed radicals by photogenerated electron–hole pairs at the photocatalyst surface.[1–3] The anatase phase of TiO$_2$ is the first phase formed through most synthesis routes and undergoes rutile transformation through thermal treatment.[4] Rutile, which exhibits a lower band gap relative to anatase, generally exhibits lower effective surface area and consequently, lower photocatalytic activity than anatase.[3–5] It has been widely reported that anatase-rutile mixtures exhibit enhanced photocatalytic activity, relative to single phase TiO$_2$, through enhanced electron–hole separation (improved exciton lifetime), allowing higher levels of radicals to be generated.[6–9]

Water purification by semiconductor photocatalysis has most commonly been studied using suspensions of TiO$_2$ powders in treated water,[10–12] this approach entails a catalyst recovery step to remove dispersed powders from treated water, rendering such systems unsuitable for significant upscaling. For large capacity water purification, the use of immobilized TiO$_2$ on catalyst supports of high surface area is an attractive approach for eliminating the requirement of complex liquid/powder separation processes.

Various catalyst support materials of increased surface area have been utilized to enhance the available surface area of immobilized TiO$_2$ photocatalysts for water purification applications. These support materials include glass fibers,[13,14] porous silica,[15] silica gel,[16] amorphous silica nano-particles,[17] carbon particles,[18,19] and zeolites.[20]

Sands are attractive as enhanced-surface-area catalyst support materials for large-scale water purification as a result of their low costs and the ease with which they can be separated from water. Through differing compositions and structures, different types of sand as catalyst supports may enhance or impair photocatalytic activity of TiO$_2$ immobilized on the sand grain surfaces.

The present work investigates the fabrication of nano-crystalline mixed-phase TiO$_2$ coatings on quartz, zircon, and rutile sand for use in water purification. TiO$_2$ immobilized on...
quartz sand (SiO₂) was investigated as such materials may exhibit enhanced photocatalytic performance caused by the diffusion of Si atoms from the underlying sand into the TiO₂ coating. Doping by Si has been reported to improve the performance of TiO₂ photocatalysts in water purification applications.[21–23] This has been reported to be a result of improved charge carrier separation at TiO₂–SiO₂ interfaces.

Immobilized TiO₂ on zircon sand (ZrSiO₄) was studied in the present work as this system has the potential to impart enhanced photocatalytic performance through the nucleation of elongated prismatic rutile crystallites on zircon surfaces alongside residual anatase as reported previously.[24] Further, diffusion of Zr from the underlying sand may enhance performance as suggested by reports that Zr doping enhances surface area and photoactivity of TiO₂.[25,26]

Finally, the use of rutile sand for the immobilization of TiO₂ may improve charge carrier separation through the previously reported synergism between large rutile grains and fine anatase particles in the coating.[9,27]

2. Experimental

Glassmaking quartz sand and naturally occurring rutile and zircon sands (Wallerah Minerals, Doyalson North, Australia) were used as support materials. Fifty grams samples of sand were ultrasonically cleaned successively in acetone and ethanol, and subsequently dried in air by heating at 110 °C. The crystallography of the sands was examined by X-ray diffraction (XRD) carried out using a Phillips X’pert MPD XRD system with Cu Ka X-ray emission. Surface area of the sands was evaluated by BET analysis of N₂ adsorption isotherms using a Micromeritics ASAP 2020 Physisorption Analyzer. Impurity levels in the sands were analyzed by wavelength dispersive X-ray fluorescence (XRF) using a Philips PW2400 XRF spectrometer.

A coating method using an organometallic derived colloidal suspension was employed. In this method, subsequent to washing, the sands were added gradually to a solution of 0.5 M titanium tetra-isopropoxide, TTIP (97%, Sigma–Aldrich) in 50 ml of isopropanol (100%, Univar), a commonly used solvent for TTIP. This was carried out under rapid stirring by a magnetic stirrer. By the dropwise addition of water diluted to 10 ml with the appropriate volume of isopropanol, the rapidly stirring slurry of sand in TTIP solution was hydrolyzed at a hydrolysis ratio of R = 4, giving a ratio of H₂O:TTIP of 4:1. The use of this moderately low hydrolysis ratio was chosen in order to avoid the formation of large and dense agglomerates that would not be able to adhere to sand surfaces. The additional isopropanol and dropwise addition were used for the purpose of moderating the rapidity of the hydrolysis and condensation reactions. After ≈5 min of continued stirring colloidal particles of amorphous TiO₂ were formed in similarity to earlier work,[28] and deposited onto sand surfaces.

Coatings on the different types of sands were crystallized and adhered by firing in air using a muffle furnace at 850 °C with heating/cooling rates of 2° min⁻¹. These firing parameters were chosen as they were found to yield a mixed phase composition of TiO₂ coatings on single crystal quartz substrates in previous work.[29] The slow rates of heating/cooling were chosen in order to reduce spalling.

Laser Raman microspectroscopy was carried out in conjunction with optical microscopy to ascertain the phase composition of the coatings using an InVia Raman Microspectrometer with laser excitation at 514 nm. Scanning electron microscopy (SEM) was carried out using Hitachi s900 and s3400 microscopes in order to examine the quality of TiO₂ coatings on the sand particles and the morphologies of TiO₂ grains within these coatings.

The photocatalytic performance of the supported TiO₂ materials prepared in the present work was evaluated by studying the inactivation of Escherichia coli AN180 (School of Biotechnology and Biomolecular Sciences, UNSW, Australia), using the bactericidal reactor illustrated in Figure 1. The apparatus was sterilized by recirculating 80 vol% ethanol and subsequently the system was flushed with autoclave-sterilized deionized water. A reservoir of 1 L of sterilized-deionized water was used for recirculation. Recirculating water was inoculated with 1 ml of overnight-incubated E. coli culture in Tryptone Soy Broth (Oxoid, Basingstoke, UK). Recirculating water flowed through a packed bed of 40 g of coated sand which was irradiated over a length of 350 mm and width of 20 mm placed 50 mm below a 15 W UV light source with an emission peak at 350 nm (Sylvania BL350) giving an irradiance level of ≈3.7 W m⁻² at the catalyst surface as determined using a Digitech QM 1587 light-meter.

Inactivation of the bacteria in the recirculating water was examined by determining the concentration of viable colony forming units (CFUs) in the recirculating water according to ASTM D5465.[30] One milliliter aliquots of water were taken at fixed time intervals and serially diluted at 1:9 ratios in sterile 0.1% peptone water (Oxoid). Subsequently, 100 μl aliquots of

![Fig. 1. Diagram of bactericidal reactor.](http://www.aem-journal.com)
the appropriate dilutions were spread-plated on Tryptone Soy Agar gel plates (Oxoid) and these were incubated for 24 h at 37 °C. Subsequent to incubation, colonies were enumerated and the concentration of CFUs in the reactor water was determined. To evaluate the penetration of UV irradiation through the different types of sand in the packed bed reactor, UV–vis transmission, through 1 mm layers of sand, was measured using a Perkin–Elmer Lambda-35 UV–vis spectrometer, with grains of sands allowed to settle under gravity in the measurement cuvettes.

3. Results

3.1. Characterization of Support Materials

XRD patterns of sands are shown in Figure 2. Quartz sand is of the α-quartz structure, space group $P_3_121$. Zircon sand exhibits a tetragonal structure, space group $I_4_1/amd$ and Rutile sand exhibits a tetragonal structure, space group $P_4_1/mnm$. No secondary crystalline phases were identified in the sands by XRD (Figure 2).

The properties of the sands used as catalyst support materials are summarized in Table 1. It can be seen that quartz sand exhibits a lower surface area in comparison with zircon and rutile sands. This is a natural consequence of the larger sizes, smoother surfaces, and more spherical morphologies of grains of this type of sand. While no secondary crystalline structures were apparent through XRD analysis, XRF shows significant levels of impurities in zircon and rutile sands. The levels of impurities as determined by XRF show rutile sand has the highest levels of impurities while quartz sand exhibits low levels of impurities. This was expected as the quartz sand used in this work is of glassmaking specification.

UV–vis transmission spectroscopy of the sands used as photocatalyst support materials, (Figure 3) was carried out to ascertain the penetration of UVA and visible light through the packed bed of sand used in the bactericidal reactor. The UV–vis transmission through 1 mm of quartz sand was significantly higher than the transmission through a similar profile of the darker zircon and rutile sands.

![Scaled XRD patterns of sands used as catalyst support materials.](image)

![UV–vis transmission through 1 mm of the sands used in this work.](image)

**Table 1. Summary of support materials used in the present work.**

| Sand    | Formula     | Average grain size [μm] | Surface area (BET) [m² g⁻¹] | Crystal structure  | Impurities [wt%] |
|---------|-------------|-------------------------|----------------------------|-------------------|-----------------|
| Quartz  | SiO₂        | ≈250                    | 0.019                      | Trigonal          | Al₂O₃: 0.03%     |
|         |             |                         |                            |                   | ZrO₂: 0.05%      |
|         |             |                         |                            |                   | TiO₂: 0.04%      |
|         |             |                         |                            |                   | Fe₂O₃: 0.01%     |
| Zircon  | ZrSiO₄      | ≈120                    | 0.248                      | Tetragonal        | HfO₂: 1.54%      |
|         |             |                         |                            |                   | Al₂O₃: 0.56%      |
|         |             |                         |                            |                   | TiO₂: 0.24%      |
|         |             |                         |                            |                   | Fe₂O₃: 0.13%      |
|         |             |                         |                            |                   | SiO₂: 1.76%      |
|         |             |                         |                            |                   | ZrO₂: 0.73%      |
|         |             |                         |                            |                   | Fe₂O₃: 0.42%      |
|         |             |                         |                            |                   | Al₂O₃: 0.24%      |
|         |             |                         |                            |                   | Na₂O: 0.20%      |
| Rutile  | TiO₂        | ≈100                    | 0.105                      | Tetragonal        | Al₂O₃: 0.32%      |
|         |             |                         |                            |                   | ZrO₂: 0.35%      |
|         |             |                         |                            |                   | Fe₂O₃: 0.06%      |
|         |             |                         |                            |                   | SiO₂: 2.0%       |
3.2. Coating Morphology

Coatings on all types of sand were consistent in appearance, and coating thicknesses varied in the region of \( \approx 30-300 \) nm, with an average coating thickness of \( \approx 200 \) nm. The typical appearance of coatings is shown in Figure 4. Localized regions exhibiting the absence of TiO\(_2\) coating as a result of spalling were observed in rutile sand, as shown in Figure 5, however this was an infrequent observation and overall coatings were well-adhered. The microstructure of the coatings consisted of TiO\(_2\) grains of 30–50 nm as shown in Figure 6. Cracking was prevalent to a similar extent in all coatings. As shown in Figure 7, SEM images of unfired coated sand showed that cracking was present subsequent to drying rather than formed in the process of firing. The coatings were resistant to prolonged use in the recirculating bactericidal reactor and no significant deterioration in coatings was evident subsequent to use in the reactor shown in Figure 1.

3.3. Phase Composition of Coatings

XRD analysis was deemed to be unsuitable for phase analysis of coatings as the peaks from the grains of sand are significantly more dominant in such analyses relative to peaks from the thin nanocrystalline coatings. For this reason, laser Raman microspectroscopy was used to differentiate the phases present in coatings using similar parameters to those reported elsewhere.\(^{[32]}\) Alongside varying significant levels of peaks from the underlying and partly exposed sands, Raman spectra of coated sands fired in air at 850 °C, shown in Figure 8, show biphasic anatase + rutile compositions in the coatings with anatase peaks being dominant (in part, a result of the stronger Raman shift by this phase). The rutile Raman shift in coatings on rutile sands is strong as a result of the combined effects from a rutile phase in the coating and from the underlying support material. The Raman spectra shown here are not appropriate for quantitative analysis, however it is likely that anatase is present in a larger quantity than rutile, owing to the weak Raman shift exhibited by rutile in these spectra.

3.4. Bactericidal Activity

The photocatalyzed inactivation of bacteria is shown in Figure 9. In order to determine the background bactericidal activity in the absence of a photocatalyst, uncoated quartz sand was used in the reactor with and without UV irradiation, in the UVA region (325–400 nm, emission peak at 350 nm). It can be seen that the inactivation of \textit{E. coli} in the absence of TiO\(_2\) coatings is negligible even in the presence of UV irradiation. This is a result of the longer wavelength of the UV source used in comparison with UV irradiation typically used in antimicrobial lamps.\(^{[33]}\) In the presence of TiO\(_2\) coated sand,
inactivation of bacteria under UV irradiation is evident, being significantly more pronounced for the coated quartz sand. No complete sterilization of the recirculating water was achieved within the timeframe of the experiments, rather the concentration of *E. coli*, as determined by counting CFUs, diminished to a level at which the bactericidal activity of the photocatalyst was in effect offset by the natural multiplication of the bacteria in the water.

4. Discussion

4.1. Coating Morphology

Using a colloidal-sol deposition method, sand grains exhibited reasonably homogenous coverage by TiO$_2$ coatings as shown in Figure 4. A reaction between surface adsorbed hydroxyl groups at the sand surfaces and the titanium tetra-isopropoxide precursor may result in the formation of (Si/Ti/Zr)-O-Ti bonding and further serve to enhance coating integrity and adhesion. Cracking was prevalent in all coatings and SEM micrographs of unfired material, such as that shown in Figure 7, have shown that this crack formation occurs during drying, likely as the result of shrinkage. Although most grains were well coated, infrequently occurring areas devoid of TiO$_2$ were observed, particularly in coatings on rutile sands. Spalling of TiO$_2$ coatings may have occurred as a result of differential shrinkage in combination with localized poor adhesion due to remaining contaminants. As rutile sand was of the lowest purity, poor coating adhesion on this material may have been the result of the combustion of residual organic material and/or other impurities on the sand surfaces. The nanocrystalline microstructure of TiO$_2$ grains resembles photocatalytic films synthesized on quartz substrates and subjected to a similar thermal treatment. Overall coating adhesion was good on all three-support materials with only slight deterioration of the coating evident after use in the bactericidal reactor. It is likely that localized poor adhesion allows a limited degree of coating removal through spalling and abrasion, however the results indicate that with appropriate synthesis parameters, adequately durable coatings are achievable to allow prolonged lifetime in a similar reactor, providing similarly low levels of support-material-agitation are present.

4.1.1. Phase Composition

As indicated by Raman spectra, TiO$_2$ coatings exhibited a mixed phase composition after firing at 850 °C. The phase transformation behavior of these coatings is similar to what has been observed in coatings fabricated on single crystal quartz substrates. The anatase to rutile phase transformation is inhibited in coatings on the sands used in this work in comparison with unsupported anatase, which is generally reported to transform to rutile at temperatures around 600 °C. The stabilization of the anatase phase in coatings on sand is likely a result of the diffusion of Si, Zr, and Al into the TiO$_2$ coatings. These elements are reported to inhibit the formation of rutile through the restriction of the atomic rearrangement involved in the phase transformation. Lower firing temperatures for similar coatings may result in similar mixed phase coatings if anatase-to rutile transformation promoting dopants, such as V, Co, and Ni, are added. However, the use of lower firing temperatures may impede the formation of good coating adhesion. Higher temperatures are likely to improve adhesion, however these are likely to result in single phase
rutile coatings exhibiting poor performance resulting from crystal growth. The use of a sol-gel micelle nanostructure precursor as reported elsewhere[39] may be applicable in order to facilitate the use of high temperature adhesion processes while maintaining nanostructured coatings.

4.1.2. Photocatalytic Performance

From studying the inactivation of E. coli in recirculating water, it is apparent that quartz sand is a superior support material despite exhibiting a lower surface area as determined by BET analysis. This may be the result of higher purity and thus lower levels of contamination of the photocatalyst by secondary phases, which could act as charge carrier recombination centers. Rutile sand, and to a lesser extent zircon sand, exhibited significant levels of iron impurities as shown by XRF analysis. Under certain conditions, Fe, and other transition metals[40–43] and alkali impurities[44–46] have been reported to impair photocatalytic activity and it is possible the presence of such impurities in rutile and zircon sands contributed to the poor bactericidal performance of TiO\textsubscript{2} coatings supported on these materials. It should be noted that the presence of very low levels of transition metal dopants/impurities, such as the levels observed in quartz sand by XRF, has been reported as being beneficial for photoactivity.[47]

Diffusion of Si from the quartz sand into the TiO\textsubscript{2} lattice may enhance photoactivity in similarity to observations reported elsewhere.[21–23] While this effect is likely also in zircon sand and in rutile sand (owing to the SiO\textsubscript{2} impurities in this material), it is possible that the levels of diffusion from quartz are greater, and/or the beneficial effects of Si doping are outweighed by detrimental levels of transition and alkali metal impurities. Conclusive evidence of the presence of Si in the coatings was not achieved as XRD, Raman and other spectroscopic techniques are not sensitive enough to ascertain with confidence whether interstitial Si is present in the TiO\textsubscript{2} lattice.

Further impairing the performance of rutile and zircon sands in the bactericidal reactor is the poor UV–vis transmittance of these materials, as seen in Figure 3. This leads to low penetration of the UV irradiation into the packed bed and thus lower levels of irradiated TiO\textsubscript{2} coated surfaces.

A packed bed reactor such as the one used in this work suffers the drawback of poor catalyst exposure as only the top layer of grains is exposed directly to the UV source. This demonstrative reactor was chosen due to its simplicity and the ease with which experiments could be repeated. A more effective reactor would involve greater levels of coated surfaces subjected to impinging UV irradiation. The low cost of the raw materials used in the present work mean that large scale fabrication can be undertaken inexpensively.

5. Conclusions

Thin well-adhered coatings of nanocrystalline TiO\textsubscript{2} can be fabricated on various types of sand enabling the cheap production of an enhanced-surface area supported photocatalyst.

The anatase to rutile phase transformation is inhibited in TiO\textsubscript{2} supported on sand grains as a result of the diffusion of structure-stuffing cations, which restrict the atomic rearrangement involved in the formation of rutile from anatase.

The use of glass-making quartz sand as a photocatalyst support material appears to bring about superior photocactivity in comparison with naturally occurring zircon and rutile sands, likely as a result of higher purity and optical transmittance.

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