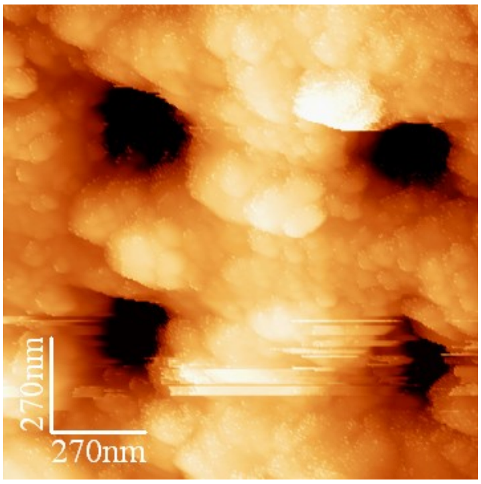
Controlling Anataste Coating of Diatom Frustules by Varying the Binding Layer

Electronic Supporting Information

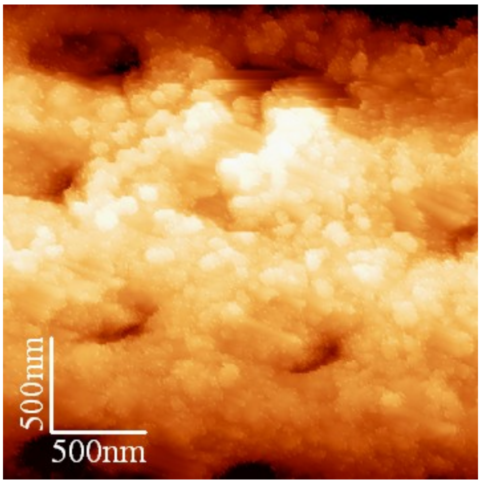
AFM :

P4VP

Before heat treatment

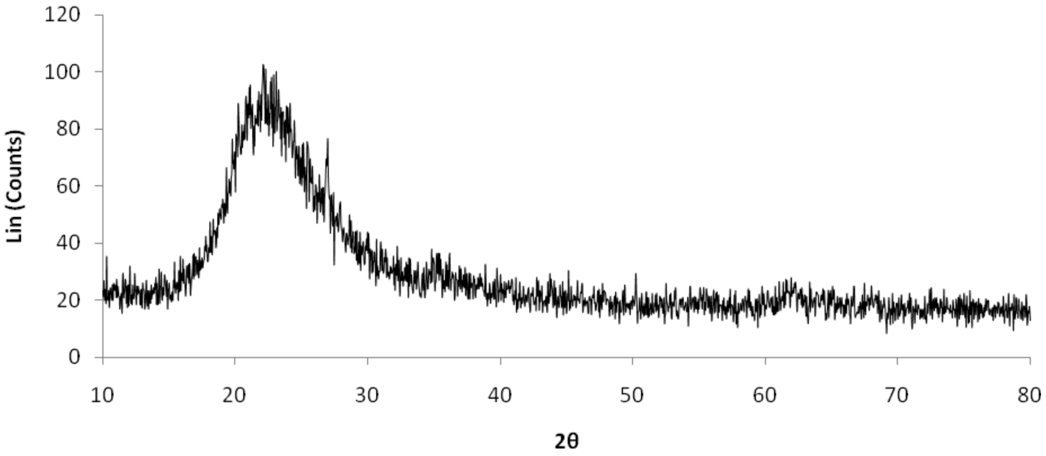


Post heat treatment (450^{o}C)



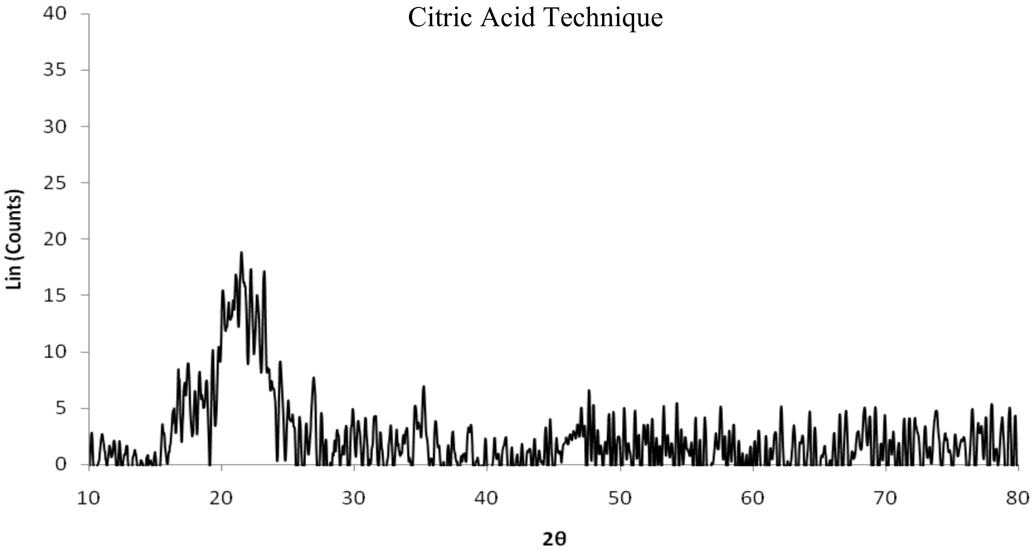
XRD:

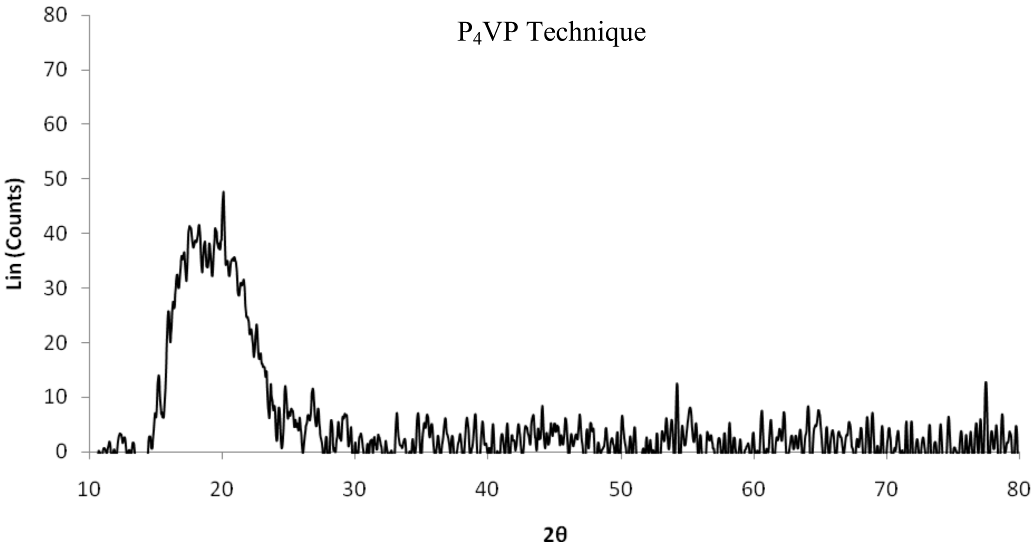
Diatoms only.



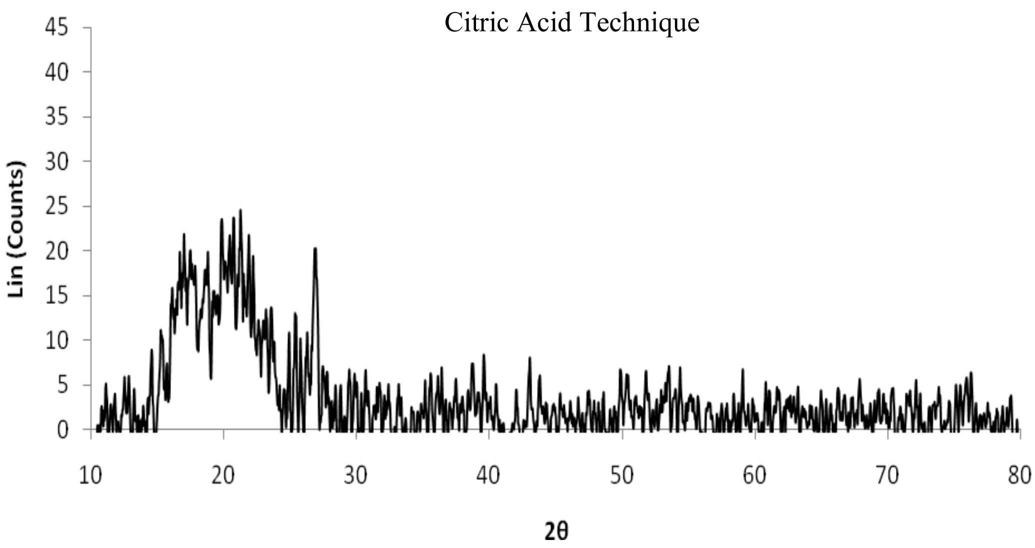
Titania coated diatoms.

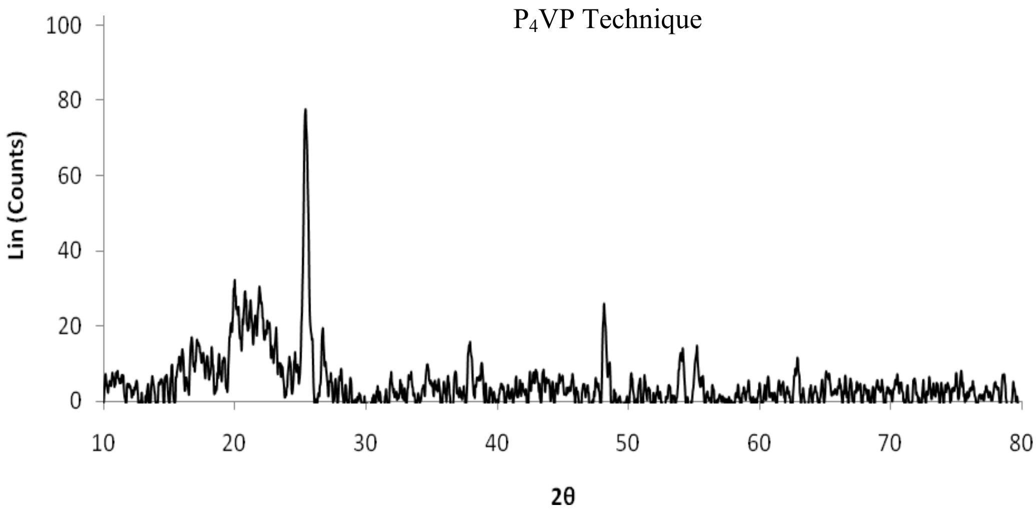
Before heat treatment





Post heat treatment





Peaks correspond to known peaks for anatase[1]

2θ = 25.40° (101), 2θ = 48.12° (200), 2θ = 54.12° (200)

The large noise is likely due to the small amount of titania relative to silica, which is particularly evident in the citric acid pattern, where only the main peak at 25.25° is observed.

The broad peak at 2θ = 20° present before heat treatment XRD pattern is associated with the amorphous silica of the diatom frustule as shown in the first presented XRD pattern.

Scherrer Equation:

$D=0.9\lambda/\Delta\cos\theta$

λ = 0.154 nm

$\Delta\ (2\theta)$ = 0.44°

Δ (rad)= 0.00384 rad

2θ = 25.4°

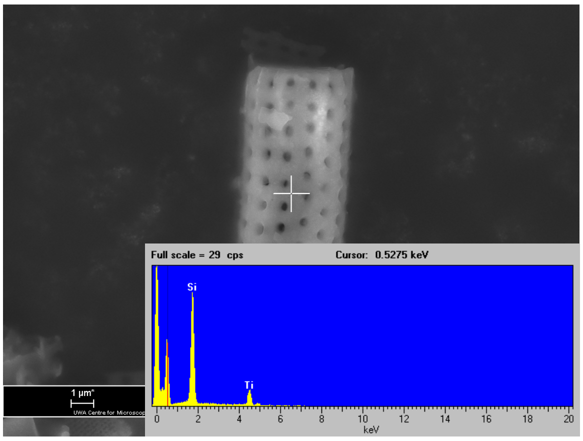
θ = 12.7°

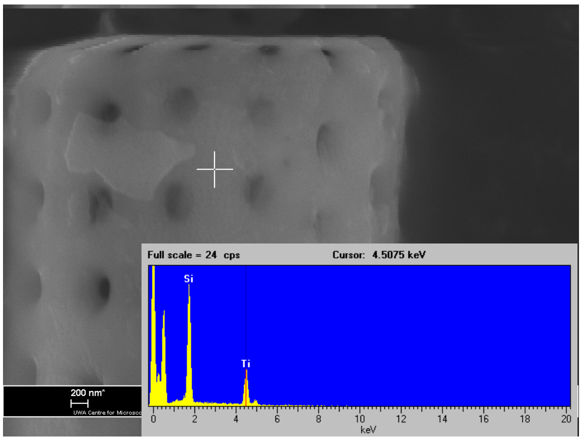
D = (0.9x0.154)/(0.00384xcos(12.7))

D = 36.4 nm

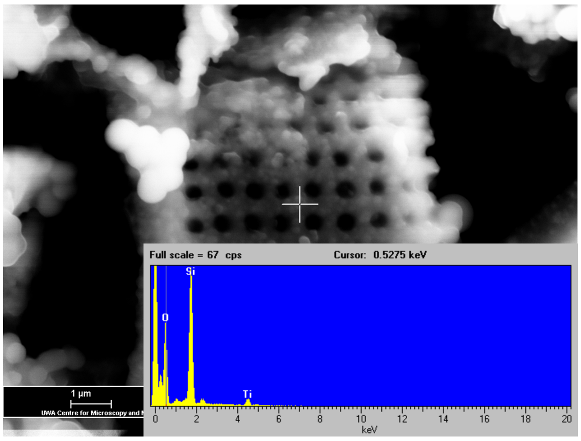
EDS:

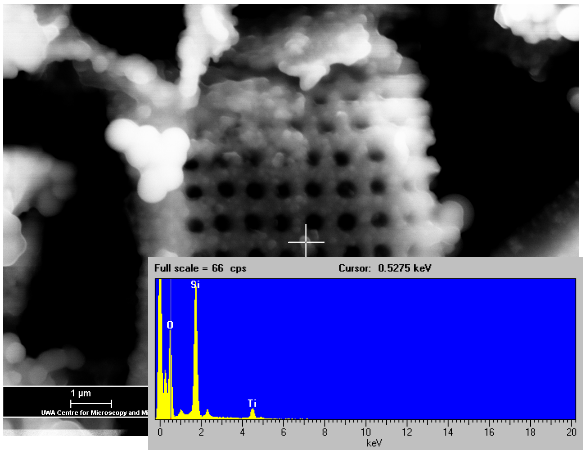
Titania coated diatoms citric acid method





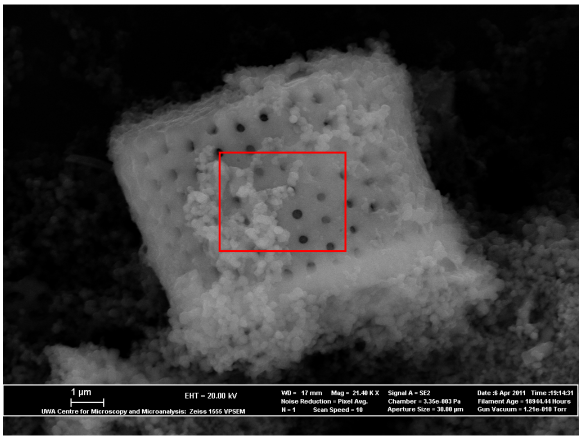
P4VP method

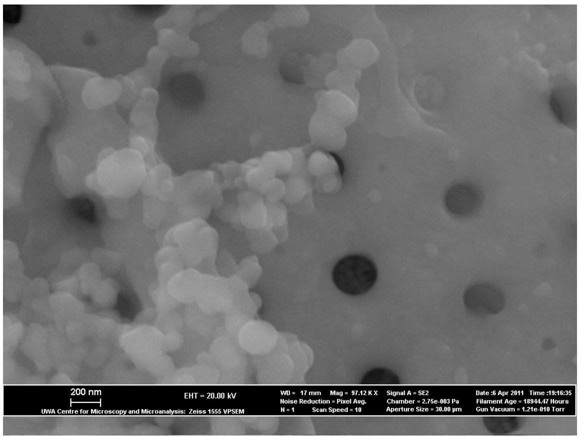


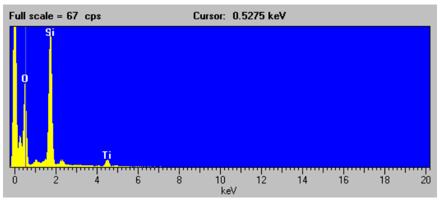


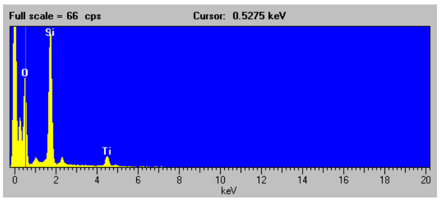
EDS confirmed the presence of titanium on the silica surface of the diatom frustules. When combined with XRD, which confirmed the presence of anatase titania, it can be inferred that the titanium peaks are representative of anatase titania.

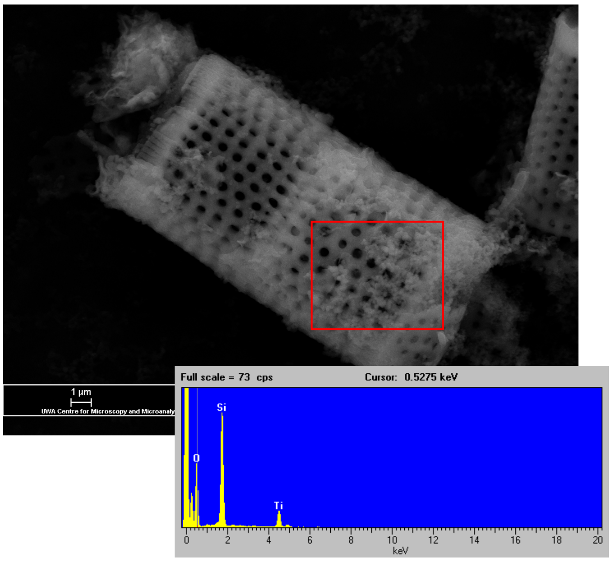
Control Experiment

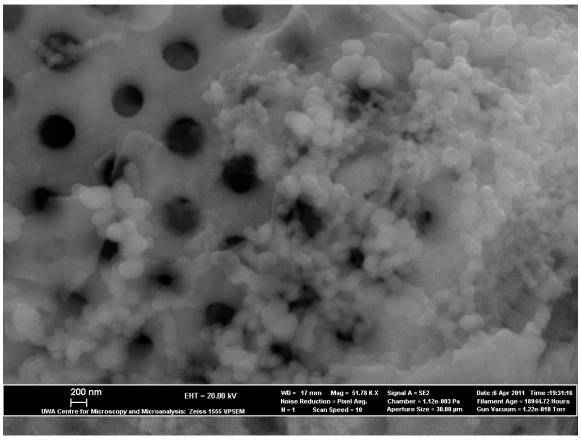












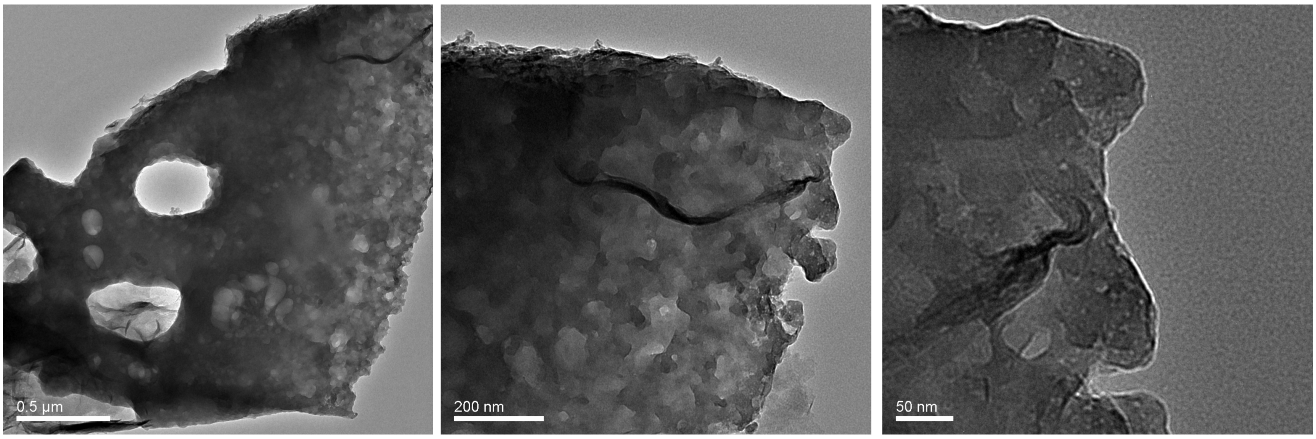
Control experiment:

Nitrogen was bubbled through a dispersion of plasma cleaned diatoms (15 mg) in ethanol (15 mL) for 15 minutes. Titanium(IV) isopropoxide was added (50 µL) and mixed for 15 minutes in air. The coated diatom frustules were then centrifuged and collected.

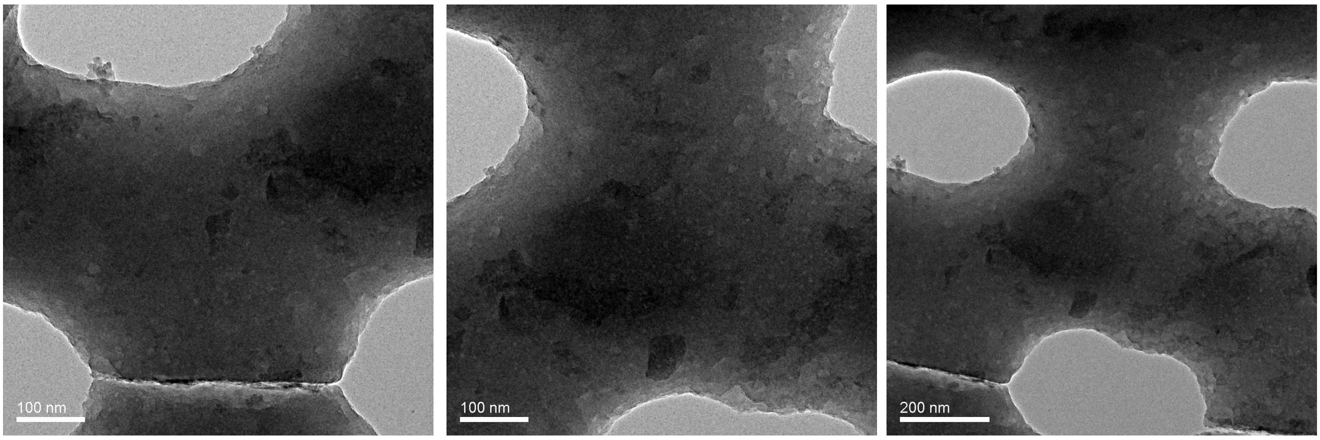
SEM shows uncontrolled attachment of titania with large particles obstructing the pores of the frustules.

TEM:

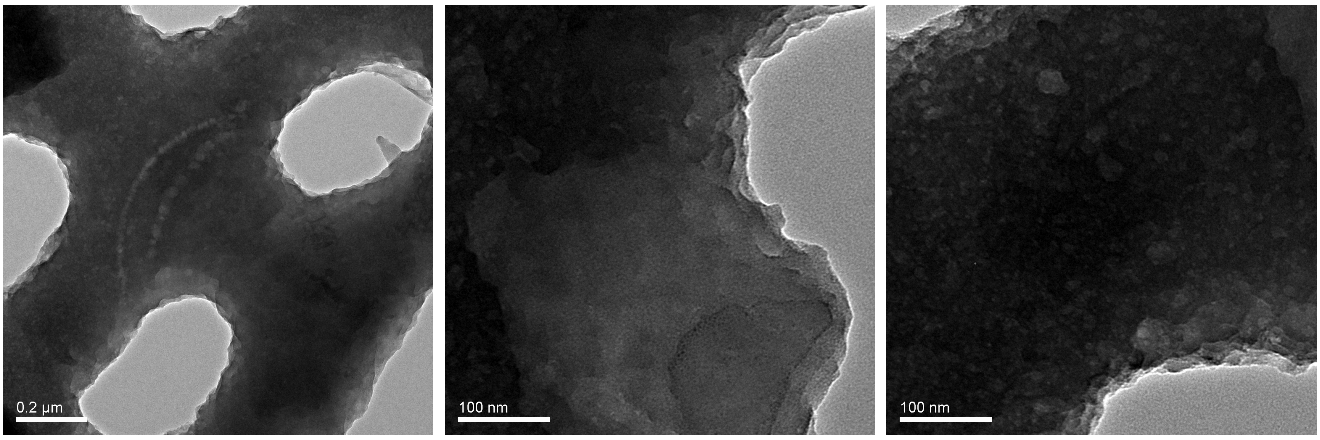
Citric acid method



P4VP method



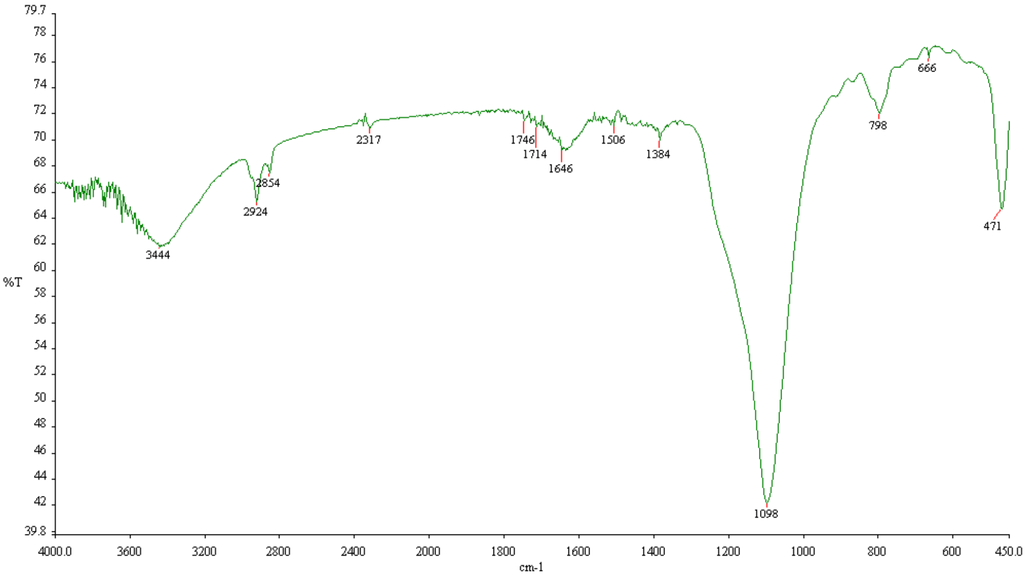
Pristine Diatom



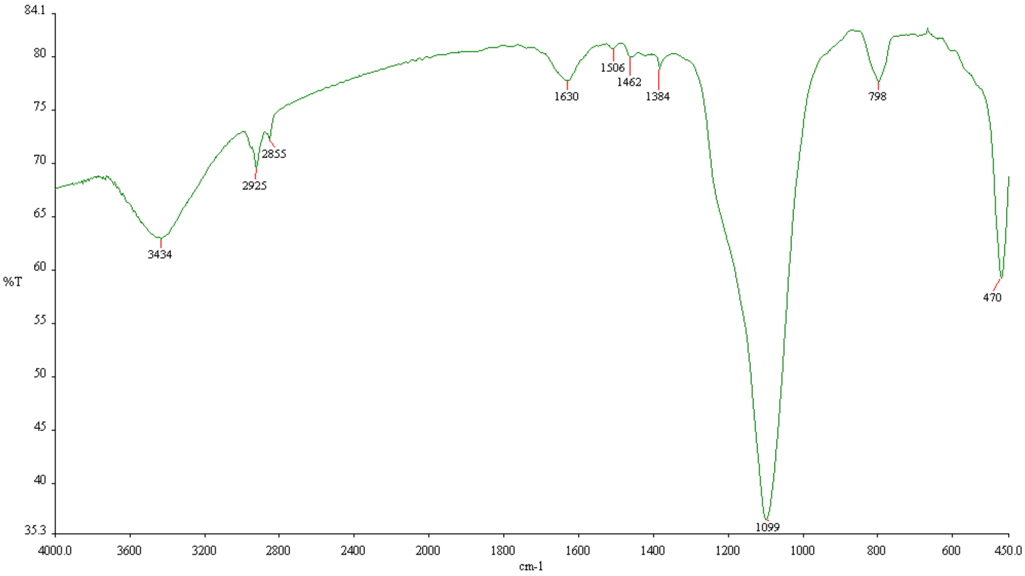
TEM of the pristine diatoms show clear similarities to the titania coated diatoms made via both methods. It was for this reason that TEM was not seen as the most reliable tool for the analysis.

FT-IR:

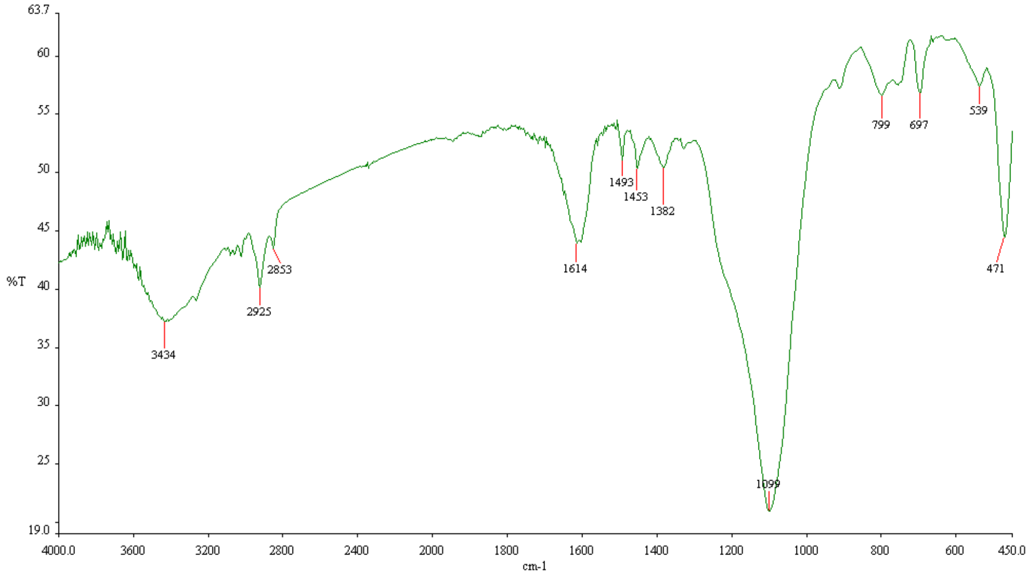
Citric acid coated diatom



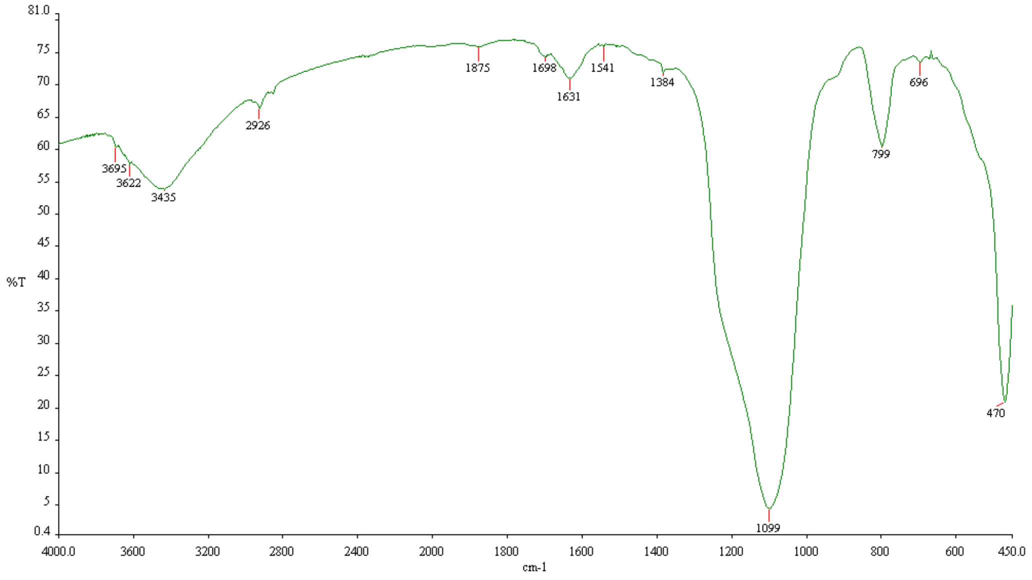
Citric acid coated diatom with titania



P_4VP coated diatom



P_4VP coated diatom with titania



The FT-IR was expected to show three main absorption bands at about 1099, 950 and 470 cm^{-1}. The band at 1099 is consistent with the Si-O stretching mode, which is present throughout the silica diatoms. The band at 950 cm^{-1} could be assigned of Ti-O-Si stretching mode, however can not clearly be observed due to the masking by the Si-O stretching band at 1099 cm^{-1}. The band at 470 cm^{-1} can be assigned of the Ti-O stretching or the Si-O bending modes.[2, 3]

Heat Treatments:

120°C stabilisation:

Polymer coated samples were placed in an oven that was already at 120°C resulting in the sample quickly reaching this temperature. The sample was then maintained at this temperature for four hours after which it was removed and left to cool to room temperature covered on the benchtop.

450°C anatase conversion:

The samples were placed into a furnace at 200°C and this temperature was ramped up to 450°C over approximately 30 minutes. It was then left at this temperature for at least four hours to ensure complete conversion to anatase.

1. Porkodi, K.; Arokiamary, S. D., Synthesis and spectroscopic characterization of nanostructured anatase titania: A photocatalyst. *Materials Characterization* **2007,** 58, (6), 495-503.
2. Bertaux, J.; Frohlich, F.; Ildefonse, P., Multicomponent analysis of FTIR spectra: Quantification of amorphous and crystallized mineral phases in synthetic and natural sediments. *Journal of Sedimentary Research* **1998,** 68, (3), 440-447.
3. Xu, L. P.; Zhao, Y. X.; Wu, Z. G.; Liu, D. S., A new method for preparing Ti-Si mixed oxides. *Chinese Chemical Letters* **2003,** 14, (11), 1159-1162.