Voltammetry of Metal Oxide Nanoparticle Films

Surface processes at *Mono- to Multi-Layer Deposits*

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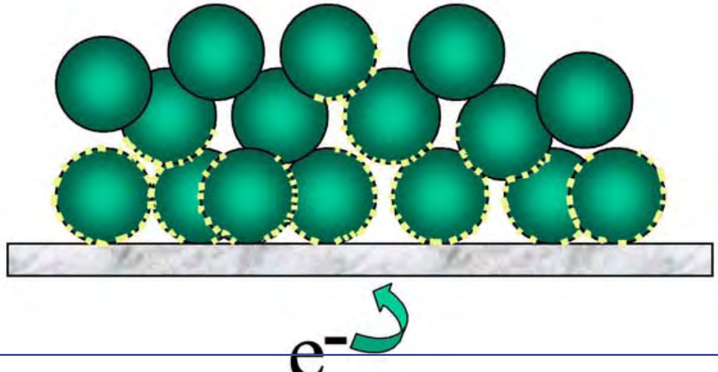
Overview:

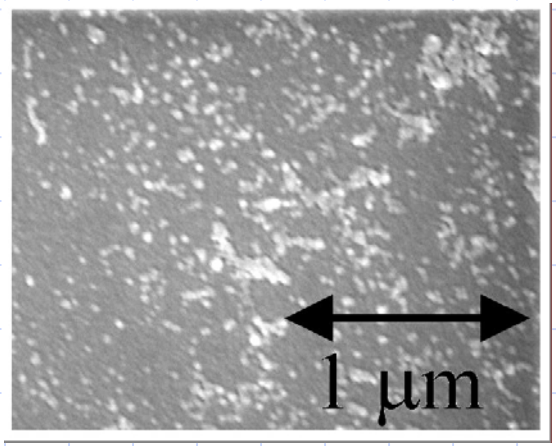
- Aims & Introduction
- I. Thin film voltammetry with nano-particle mono-layers: Fe_2O_3 – TiO_2
- II. Multi-layer structures: TiO_2
- III. Underpotential reduction: CeO_2
- IV. Surface stabilisation effects: Fe_2O_3
- Summary & Outlook

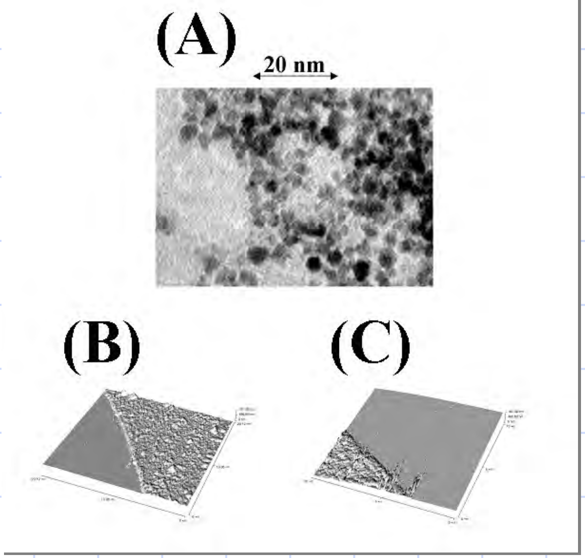
Electrochemical Characterisation of Nanoparticle Thin Films: Aims

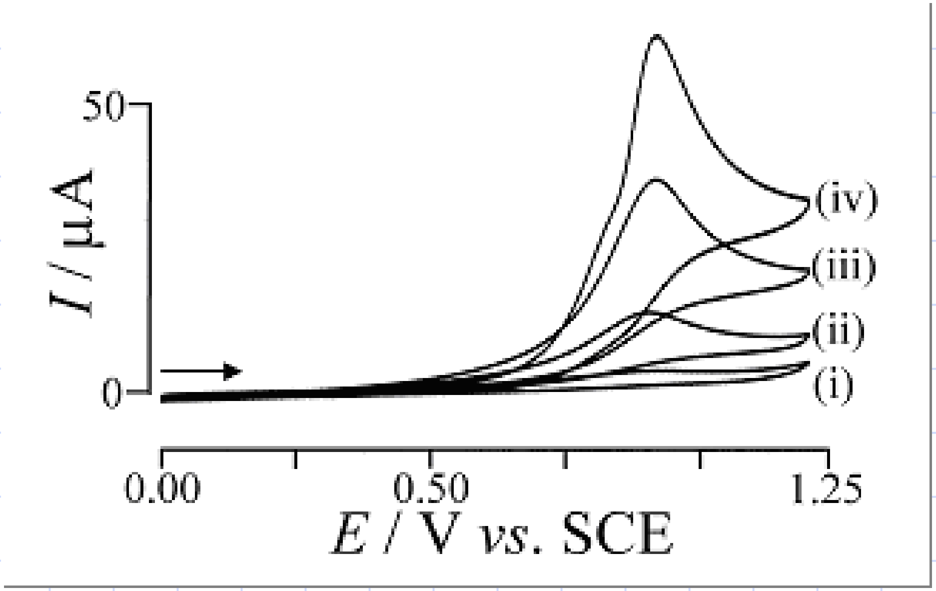


- To explore the surface (electro-)chemistry of “insulator” materials in nano-dimensions
- To exploit the use of the film thickness in the study of surface processes.
- To investigate **triple phase boundary processes** at contact points.
- To develop strategies for the assembly of novel thin film materials for electrocatalysis and electroanalysis.

Hydrous Iron Oxide Adsorbed onto BDD and Immersed in Aqueous Media:



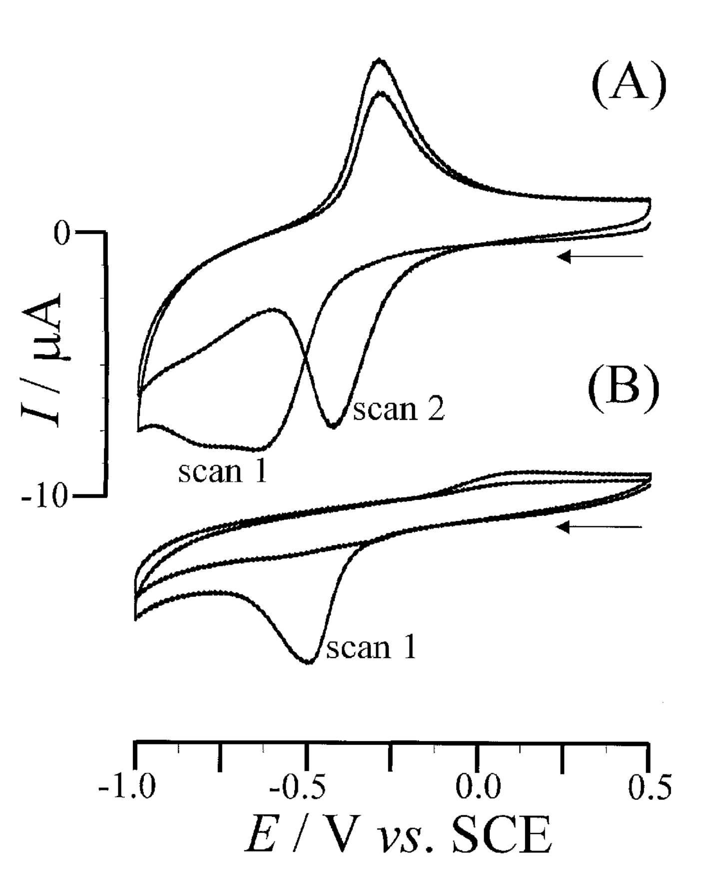


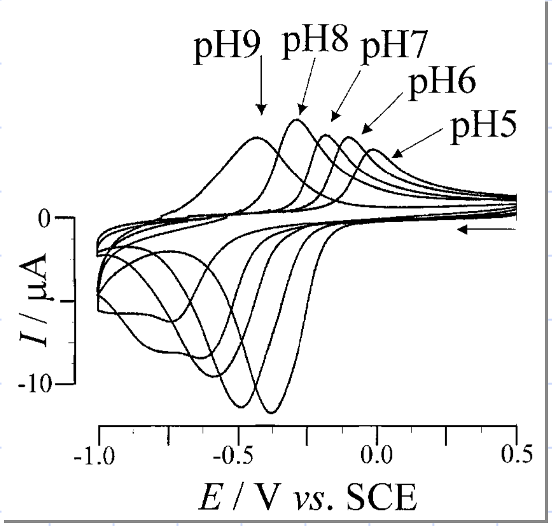


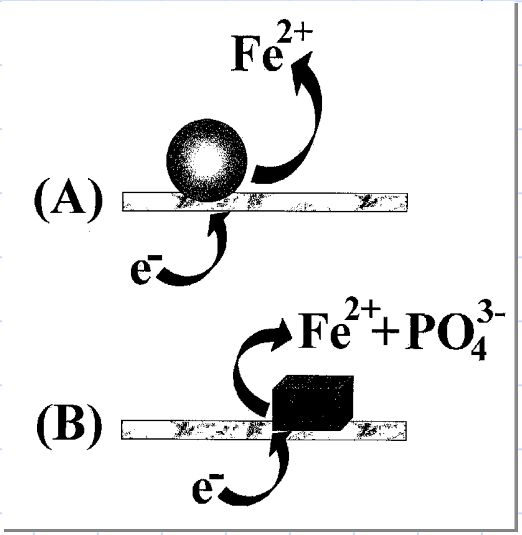
Cyclic voltammograms (scan rate 0.02 V s^{-1}) for the oxidation of 1 mM hydrogen peroxide in the presence of (i) 0.1 mM, (ii) 0.4 mM, (iii) 1.0 mM, and (iv) 2.0 mM KOH in aqueous 1.0 M KNO_3 at a boron-doped diamond electrode (0.25 cm^2) modified with hydrous ferric oxide.

Catalytic Species?

Hydrous Iron Oxide (Fe_2O_3) Monolayer Reactivity in Aqueous Phosphate Media:

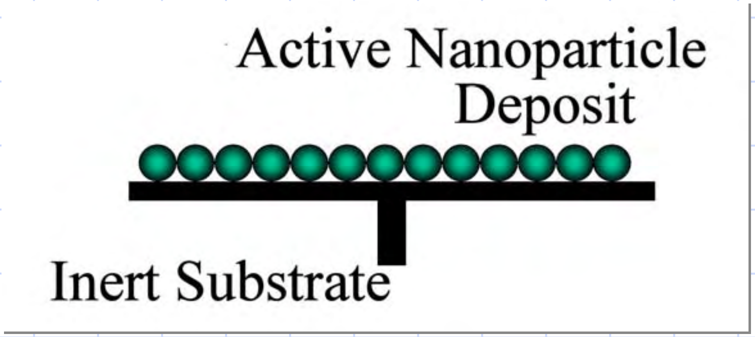


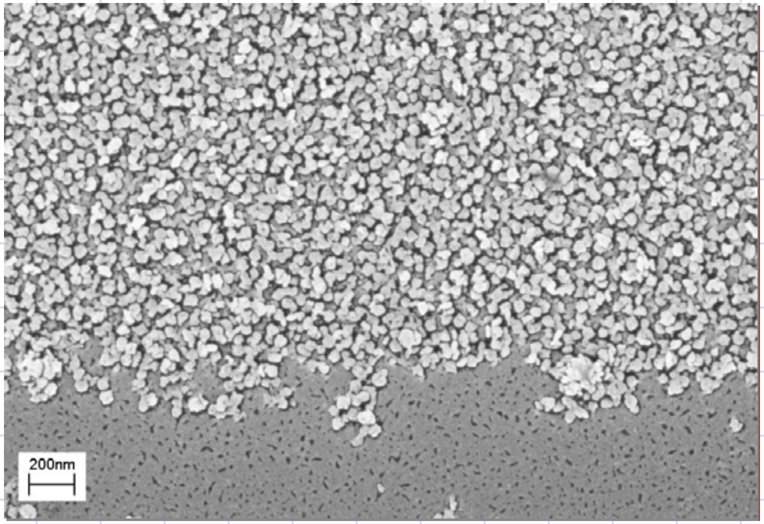


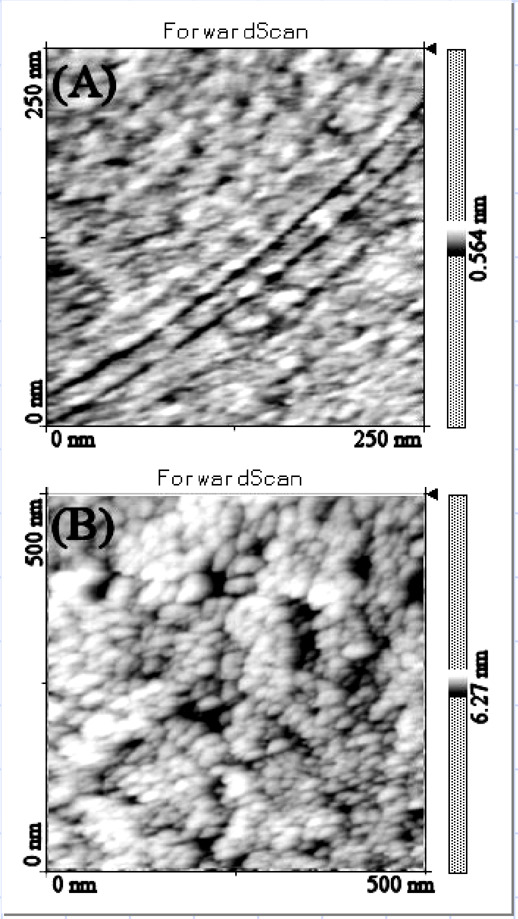


Cyclic voltammograms (two cycles, scan rate 0.1 V s^{-1}) obtained for the reduction of Fe_2O_3 nanoparticles adsorbed (by immersion into a Fe_2O_3 solution 2 mM in Fe) onto a 3 x 4 mm^2 tin-doped indium oxide electrode and immersed (A) in aqueous 0.1 M phosphate buffer at pH 8 and (B) in aqueous 0.1 M phosphate buffer at pH 8 containing 10 mM EDTA.

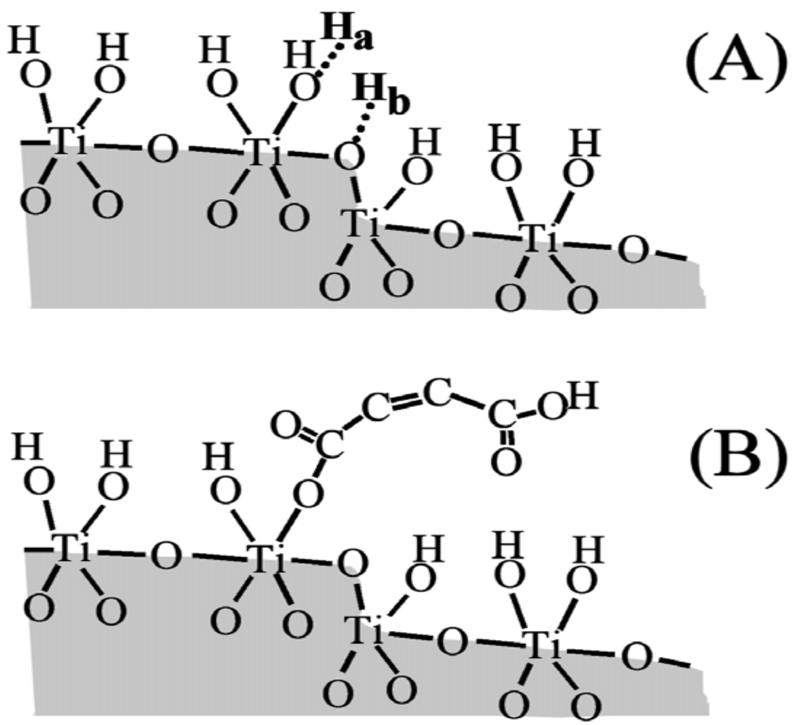
Titanium (IV) Oxide Reactivity in Aqueous Phosphate Media:

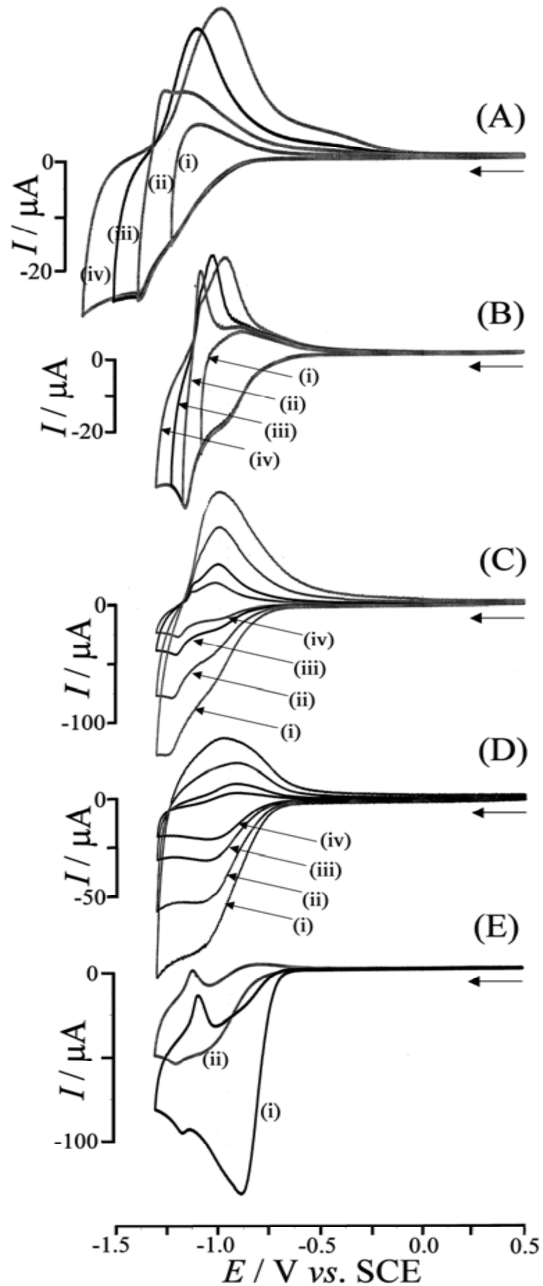






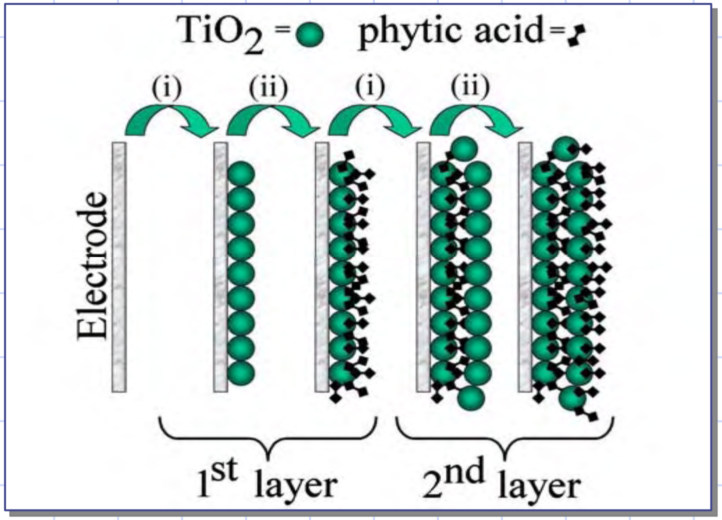
Titanium (IV) Oxide Reactivity in Aqueous Phosphate Media:

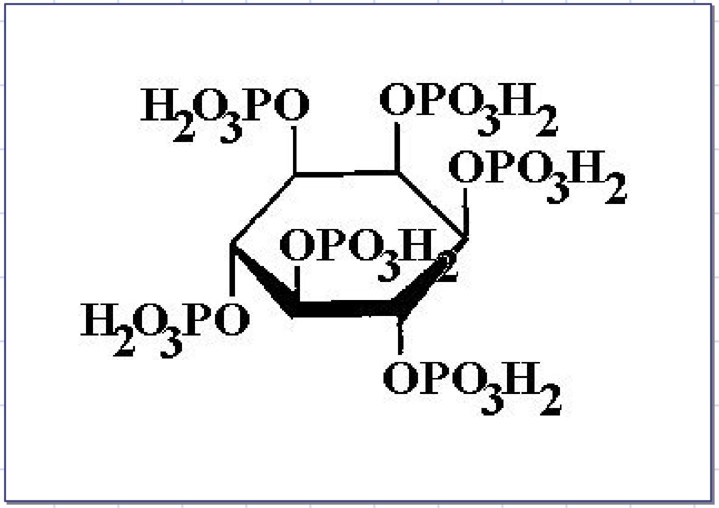




Multi-layer Film Preparation:

- two-component dip-coating of:
- (i) TiO_2 nanoparticle sol (anatase sol, TKS-202, typically 6 nm diameter, 30-37% acidified with HNO_3)
- (ii) 40 mM sodium phytate in H_2O, acidified with $HClO_4$ to pH 3.



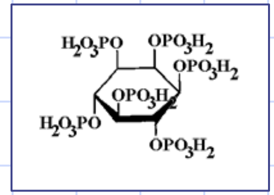


Robotic Dip-Coating Unit:

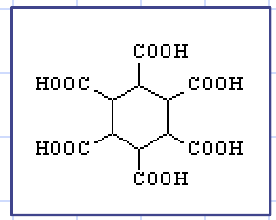
“Building Blocks”

Substrate	Metal Oxide
Glass	**<u>Fe_2O_3</u>**
Carbon	**<u>TiO_2</u>**
Diamond	ZrO_2
ITO	**<u>CeO_2</u>**
Au	Ru_2O_3
Pt	MnO_2
	SnO_2
	SiO_2

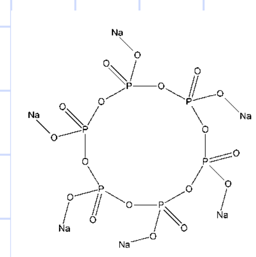
Binder



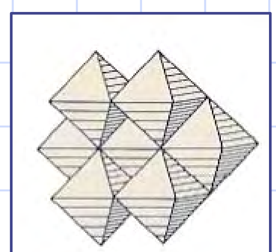
phytic acid



$C_6H_6(CO_2H)_6 \cdot H_2O$

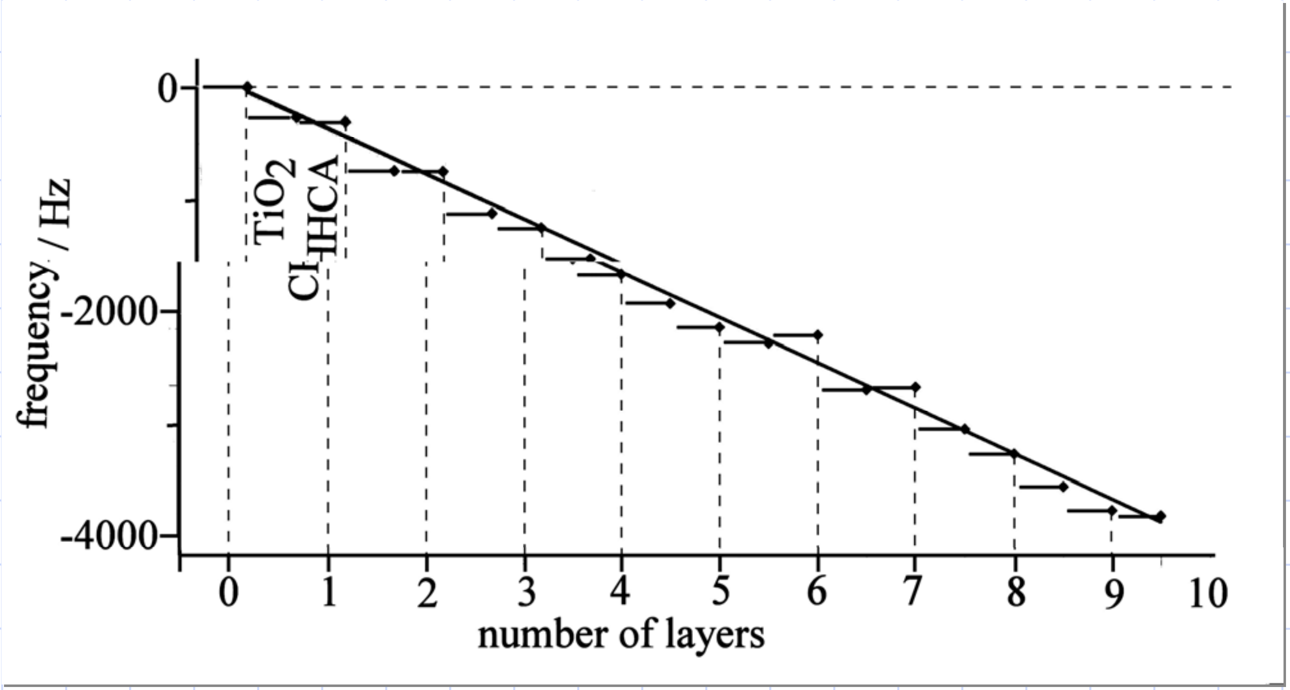


hexametaphosphate

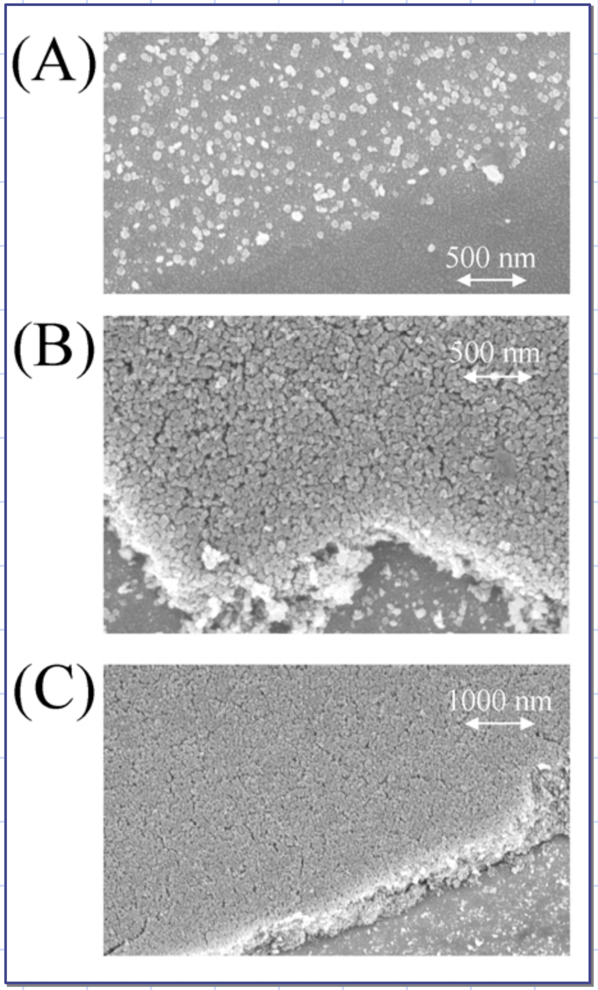


$[Mo_7O_{24}]^{6-}$

QCM monitoring of the layer-by-layer growth of a TiO_2 cyclohexane hexacarboxylic acid film



SEM images of the TiO_2 phytate nanofilm on ITO

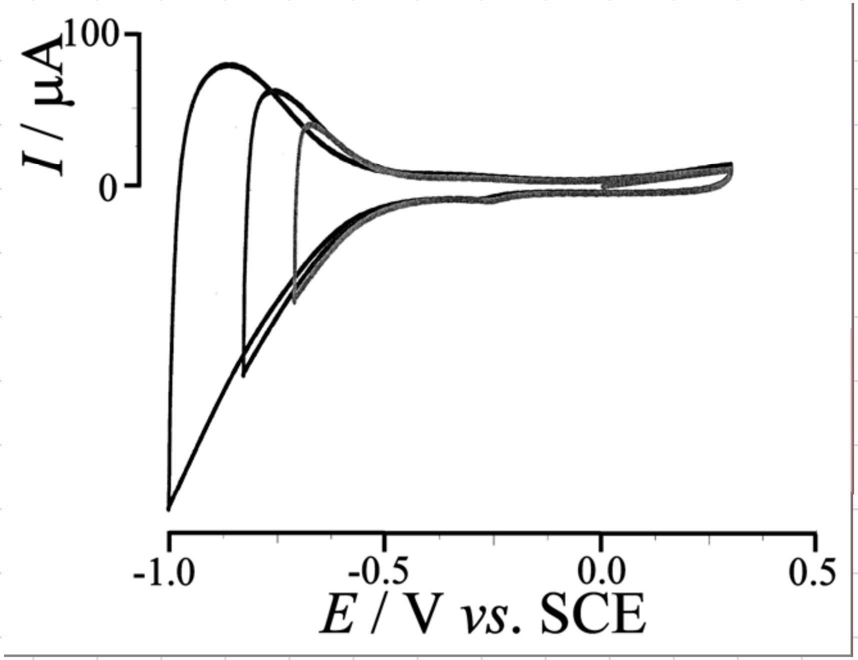


- (A) one layer TiO_2 nanoparticles – some agglomerates
- (B) 10 layers TiO_2 phytate
- (C) 30 layers TiO_2 phytate

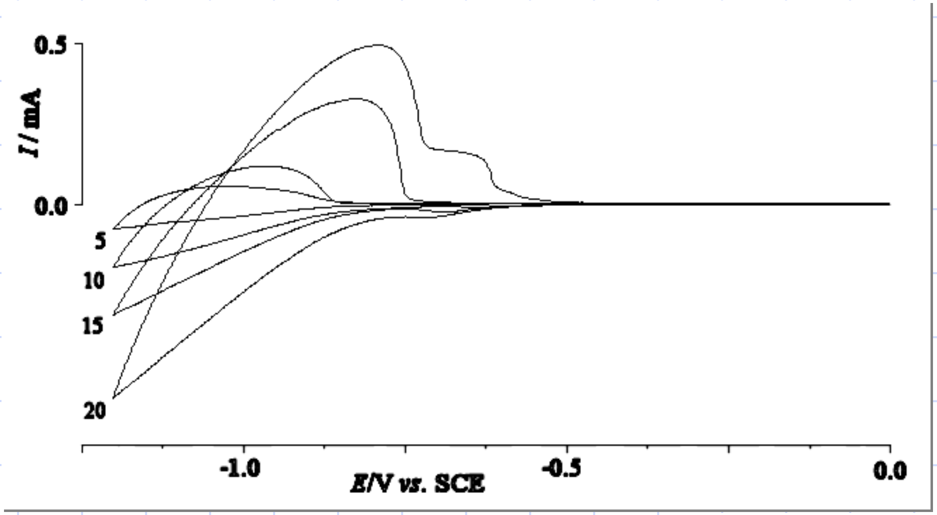
- Prior to imaging, surface scratched & gold coated

Titanium Oxide (TiO_2) Reactivity in Aqueous Phosphate Media:

Reversible charging processes in aqueous media at a potential negative of –0.5 V vs. SCE. No reaction in phosphate buffer media.

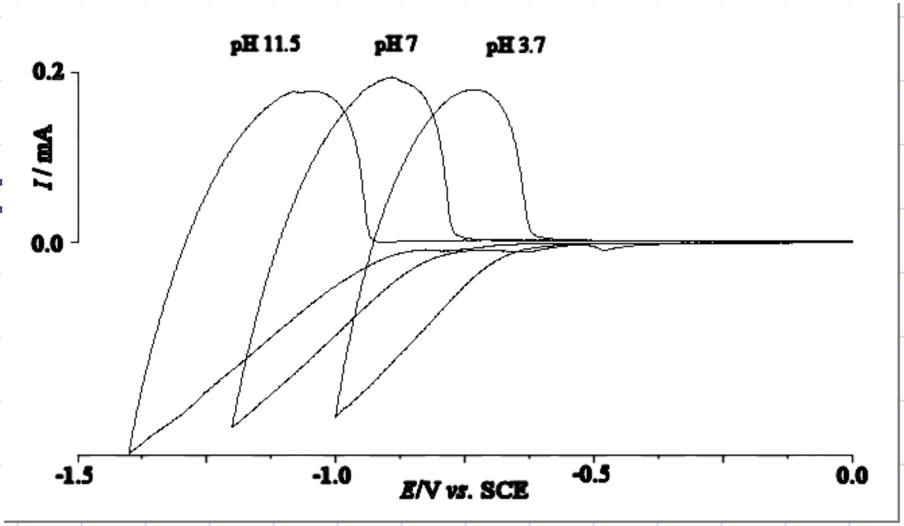


Titanium (IV) Oxide Reactivity in Aqueous Phosphate Media:

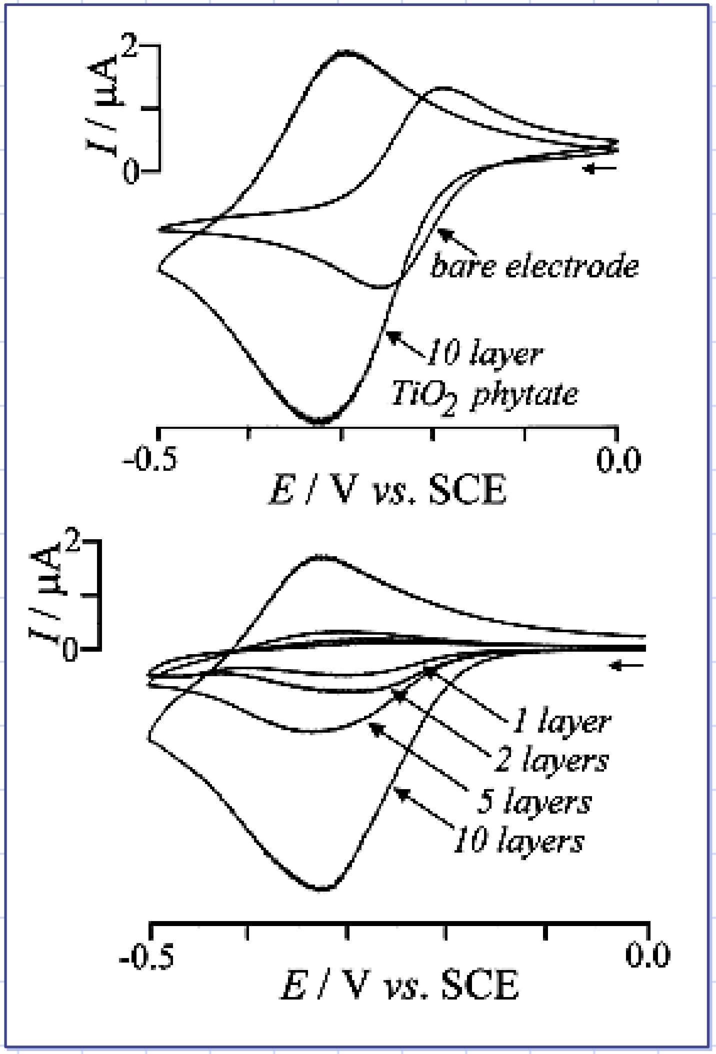


Effect of scan rate:

Effect of pH:

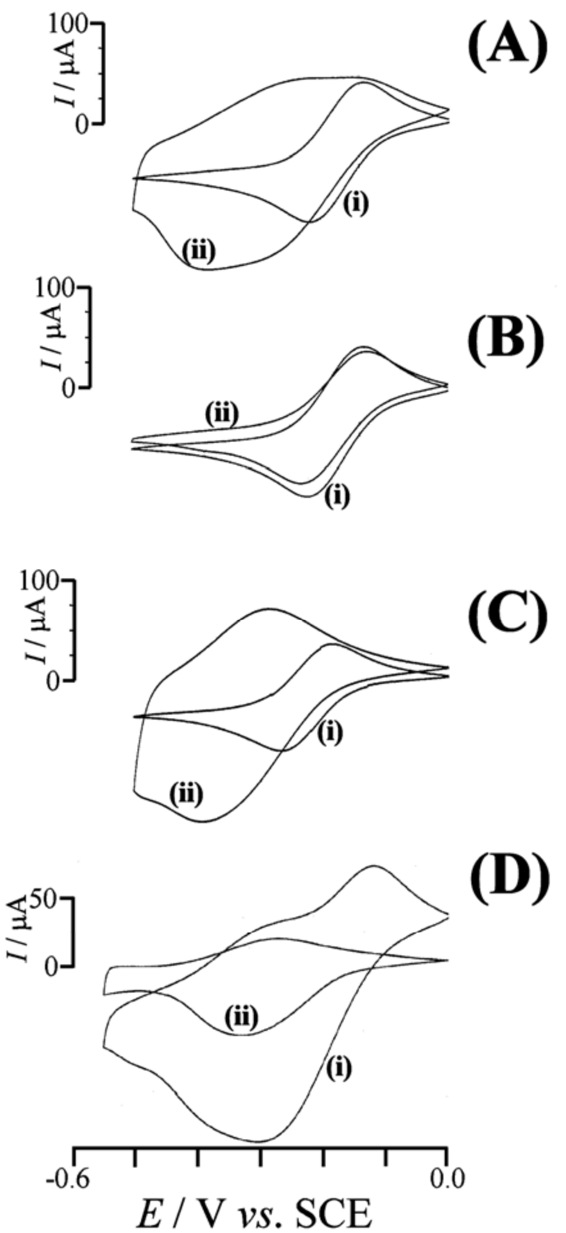


Electrochemical Characterisation of TiO_2 Films: Thickness Effects



- Reversible one electron process
- **$Ru(NH_3)_6^{3+}(aq) + e^- \rightarrow Ru(NH_3)_6^{2+}(aq)$**
- New voltammetric response at E_p^{red} = -0.33 V *vs.* SCE
- Adsorption of $Ru(NH_3)_6^{3+}$ into TiO_2 phytate film

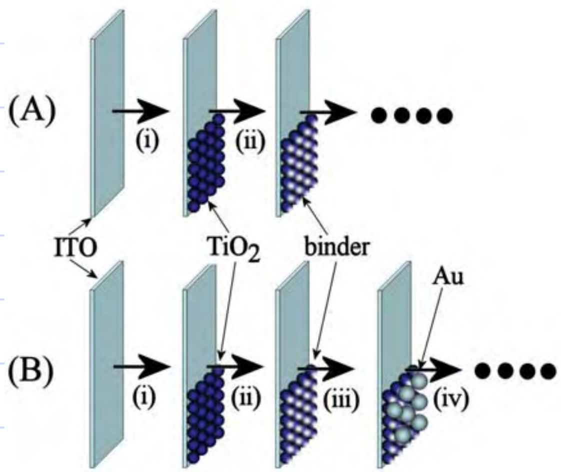
Electrochemical Characterisation
f 500 °C Calcined
iO$_2$ Films

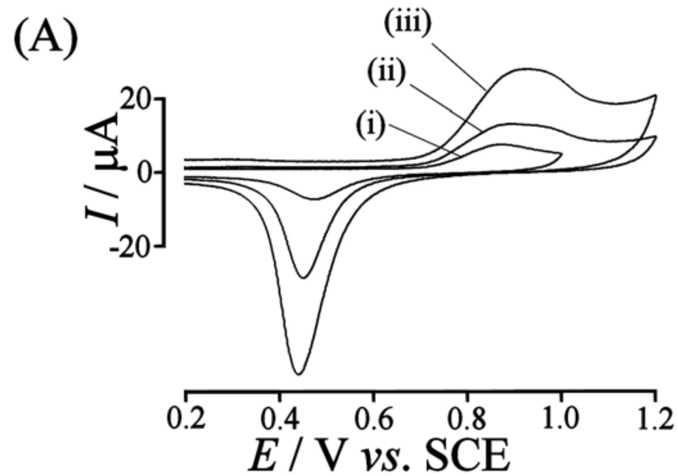


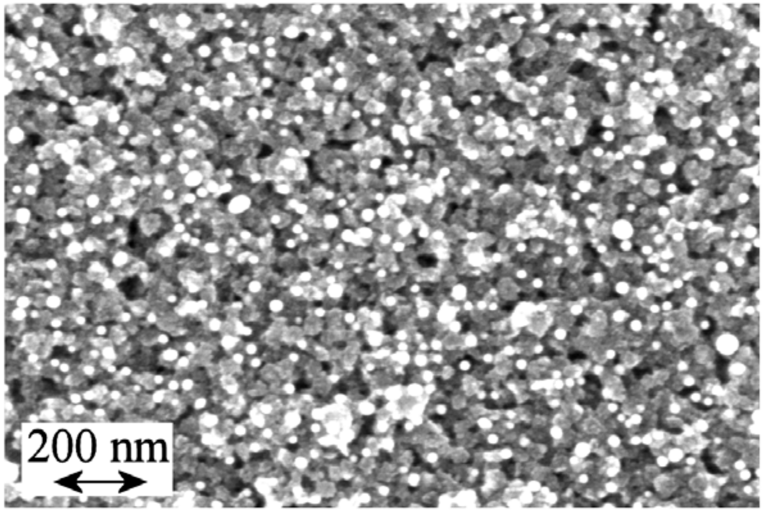
- Reversible one e$^-$ process
- **$Ru(NH_3)_6^{3+}(aq) + e^- \rightarrow$**

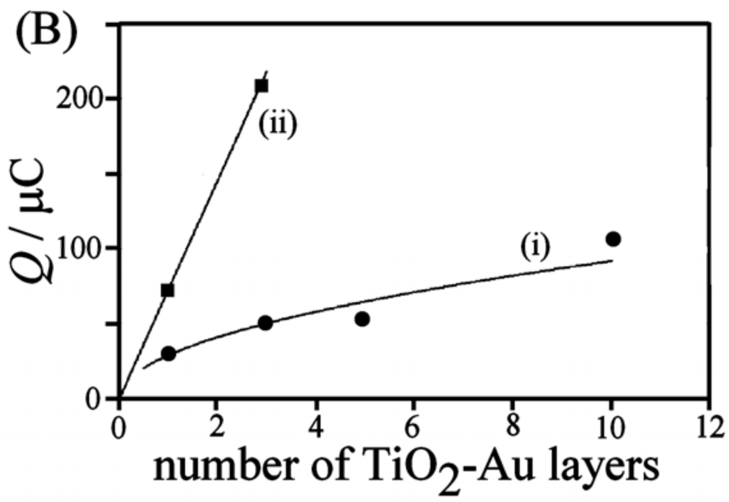
  $Ru(NH_3)_6^{2+}(aq)$
- (A) with phytate
  (B) no phytate/with CHHCA
  (C) in phosphate
  buffer at pH 7
  (D) effect of $Ru(NH_3)_6^{3+}$
  concentration

Processes within Nafion-TiO_2-Nafion-PDDA-Au-PDDA Films:



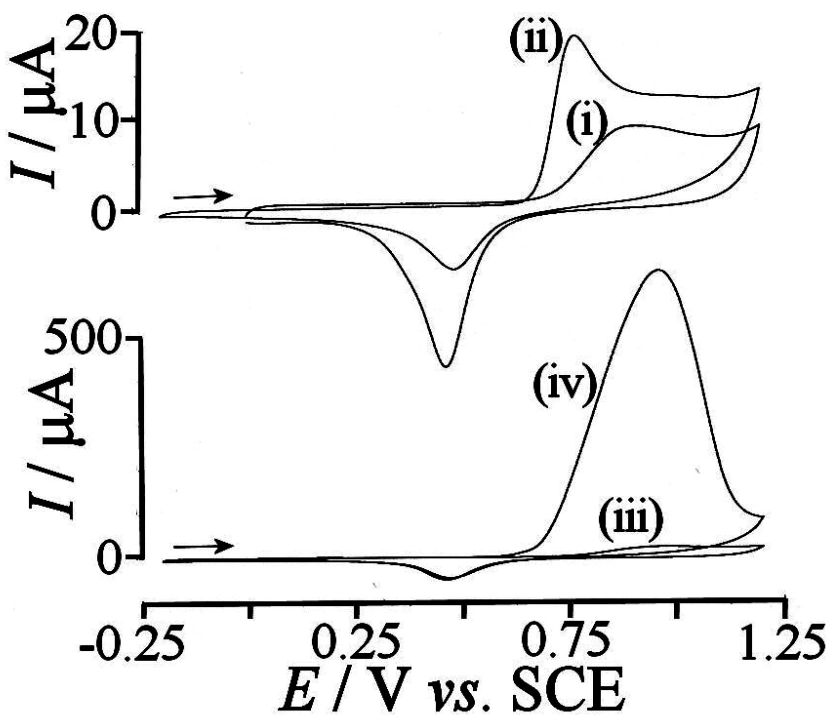


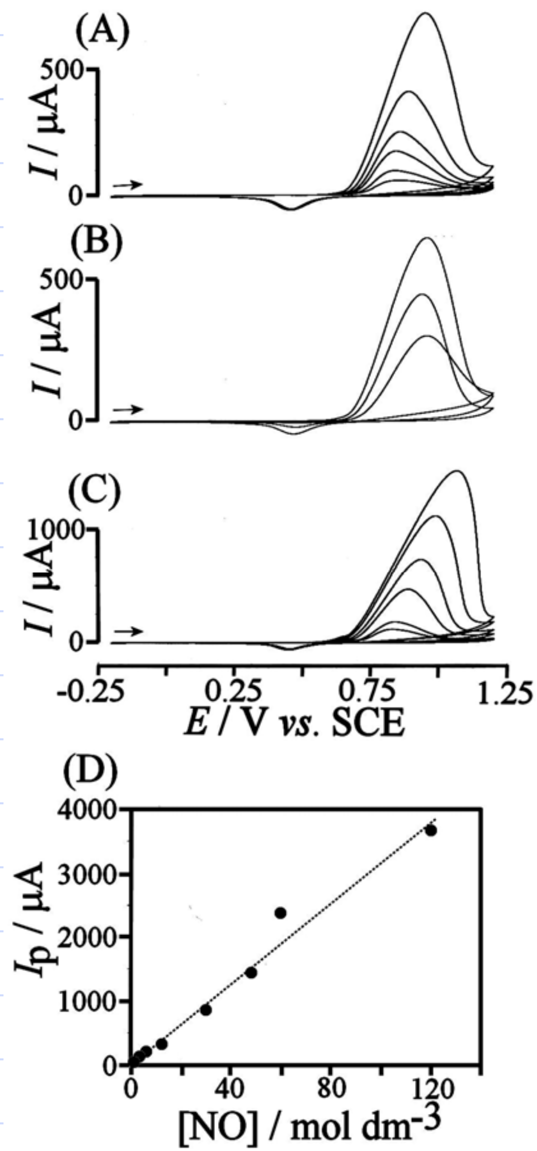




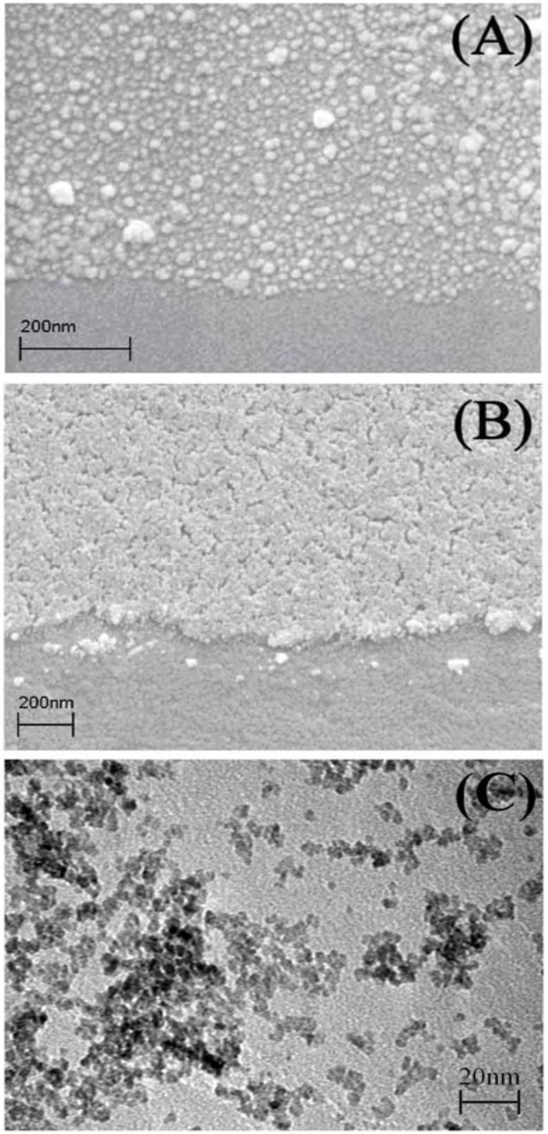
Processes within Calcined TiO_2-Au Films:

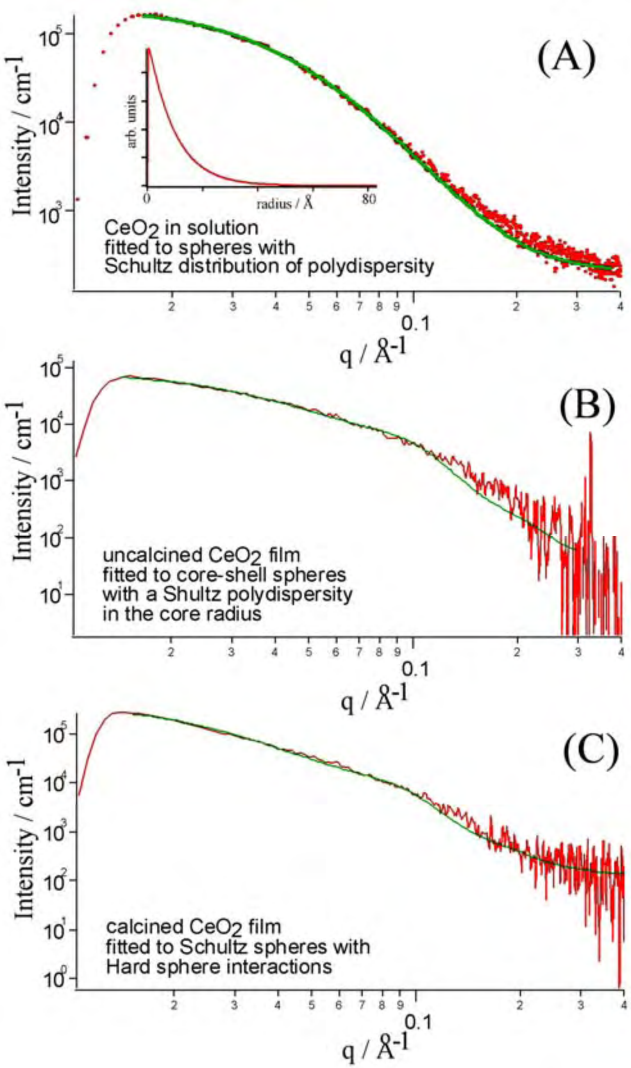
The determination of NO (nitric oxide) is possible at TiO_2-Au film electrodes:





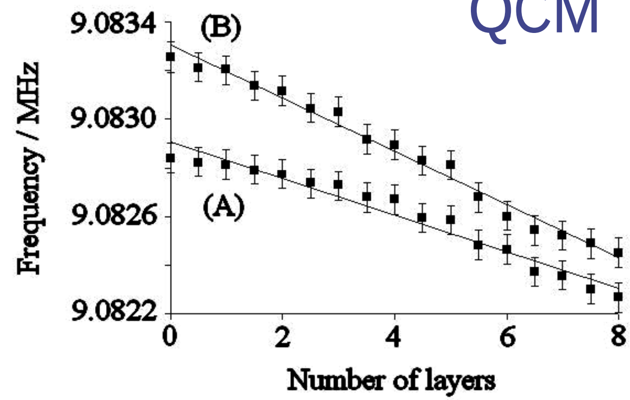
CeO_2 can be assembled with phytate or with cyclohexanehexacarboxylate



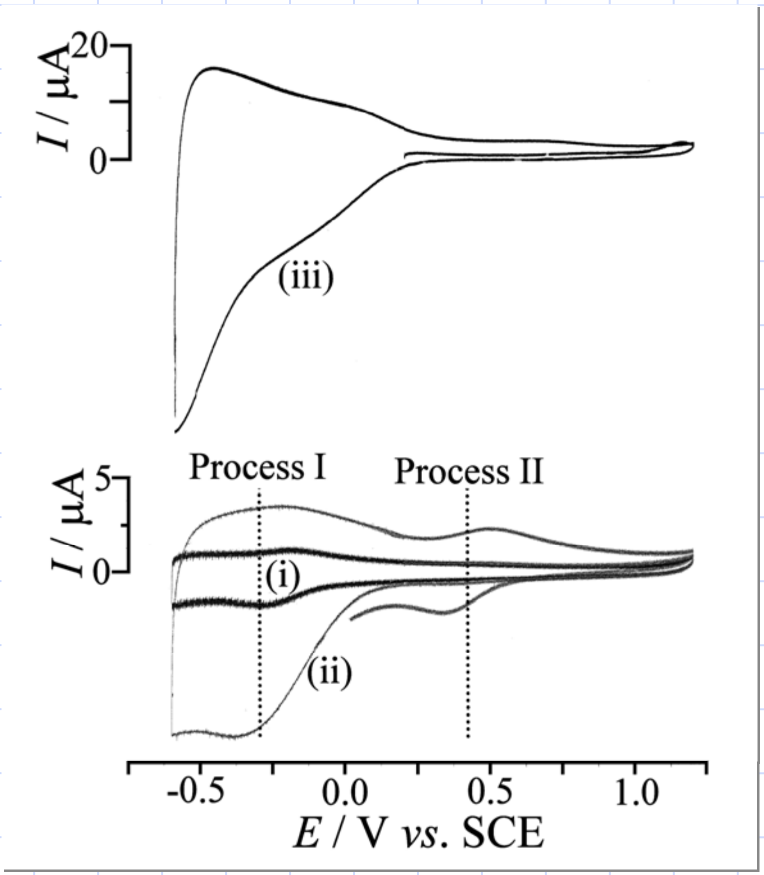


SAXS

QCM

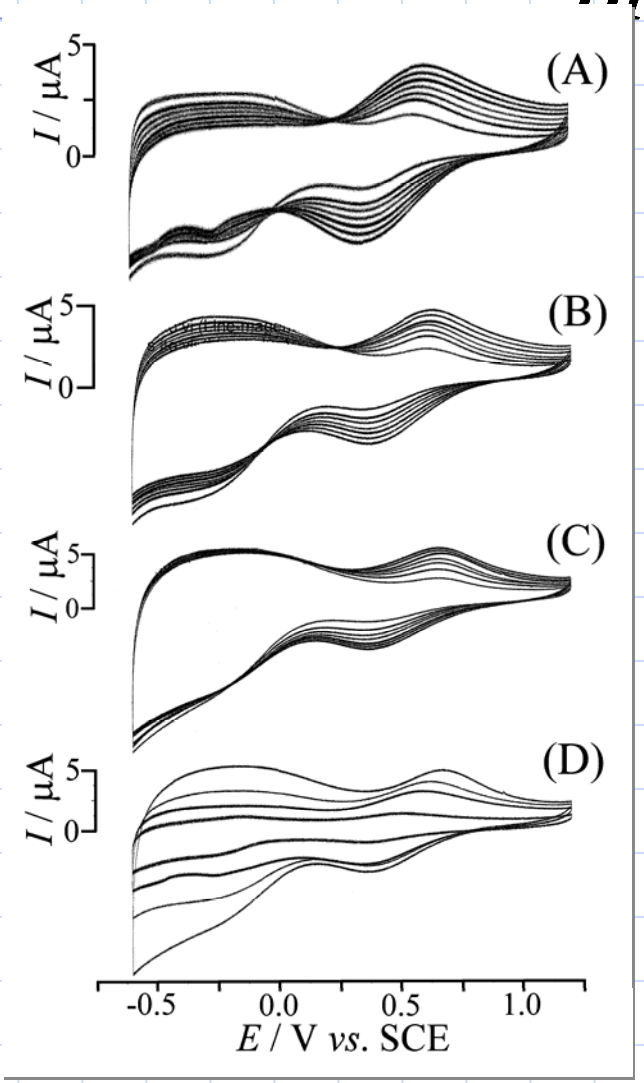


Cerium (IV) Oxide Reactivity in Aqueous Phosphate Media:



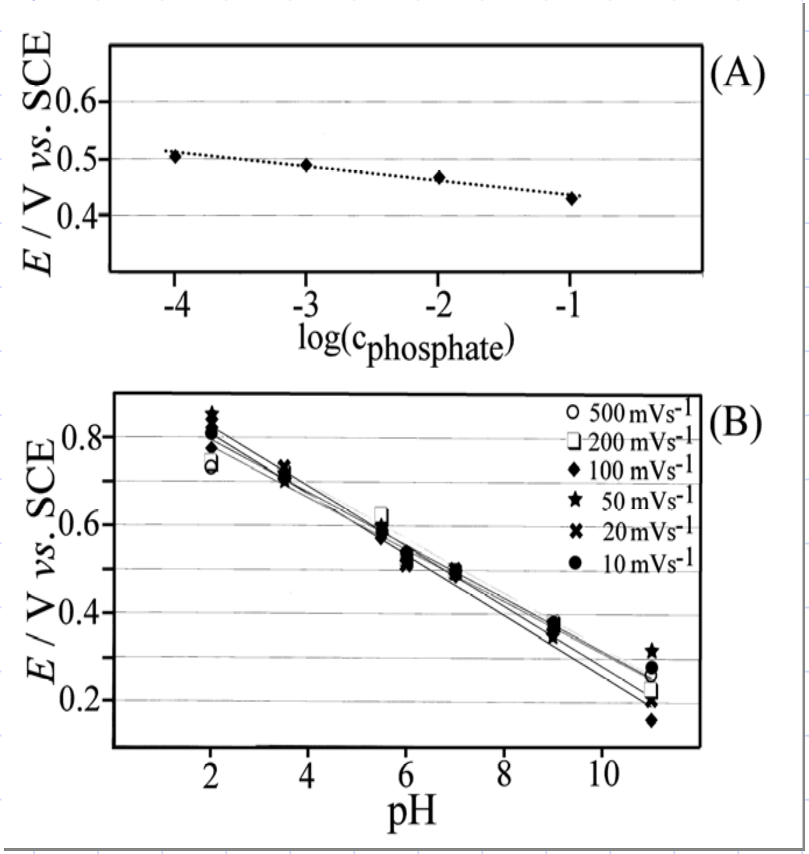
- (i) Background ITO only in 0.1 M PBS at pH 7
- (ii) one layer of cerium oxide in 0.1 PBS at pH 7
- (iii) one layer of cerium oxide in 0.1 M KCl

Electrochemical Characterisation of CeO_2 Films



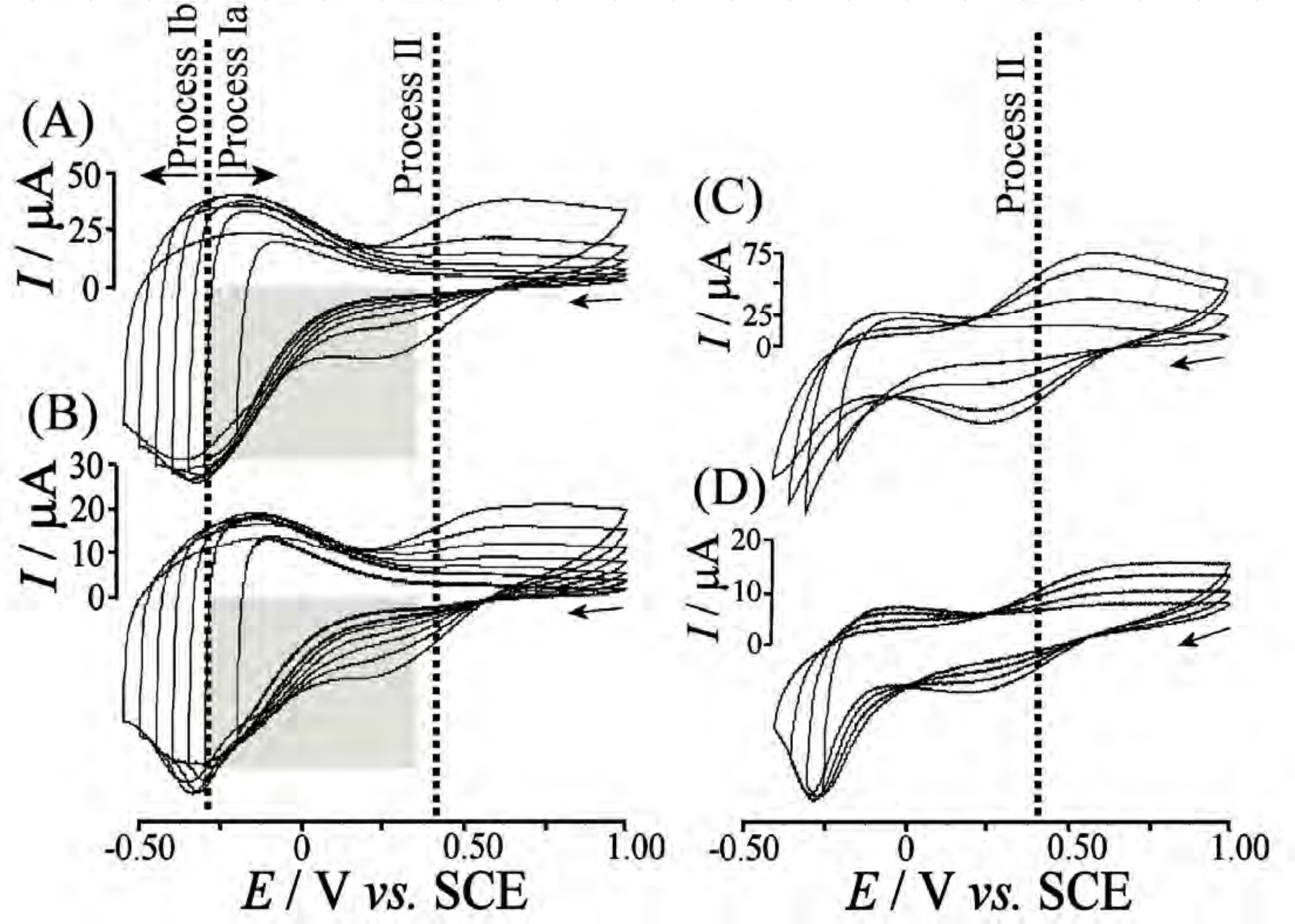
- Continued potential cycling causes PI to diminish and PII to appear
- Strong phosphate concentration effect
- Rate of $CePO_4$ formation is different, presumably due to more extensive phosphate adsorption and better electron transport

Electrochemical Characterisation of CeO_2 Films



- **Process I:**
  $2\ CeO_2(s) + H^+ + e^- \rightarrow CeO_2H(s)$
- **Process II:**
  $Ce_3(PO_4)_4(s) + 3\ H^+(aq) + 3\ e^-$
  $\rightarrow 3\ CePO_4(s) + H_3PO_4(aq)$
- More layers – more current

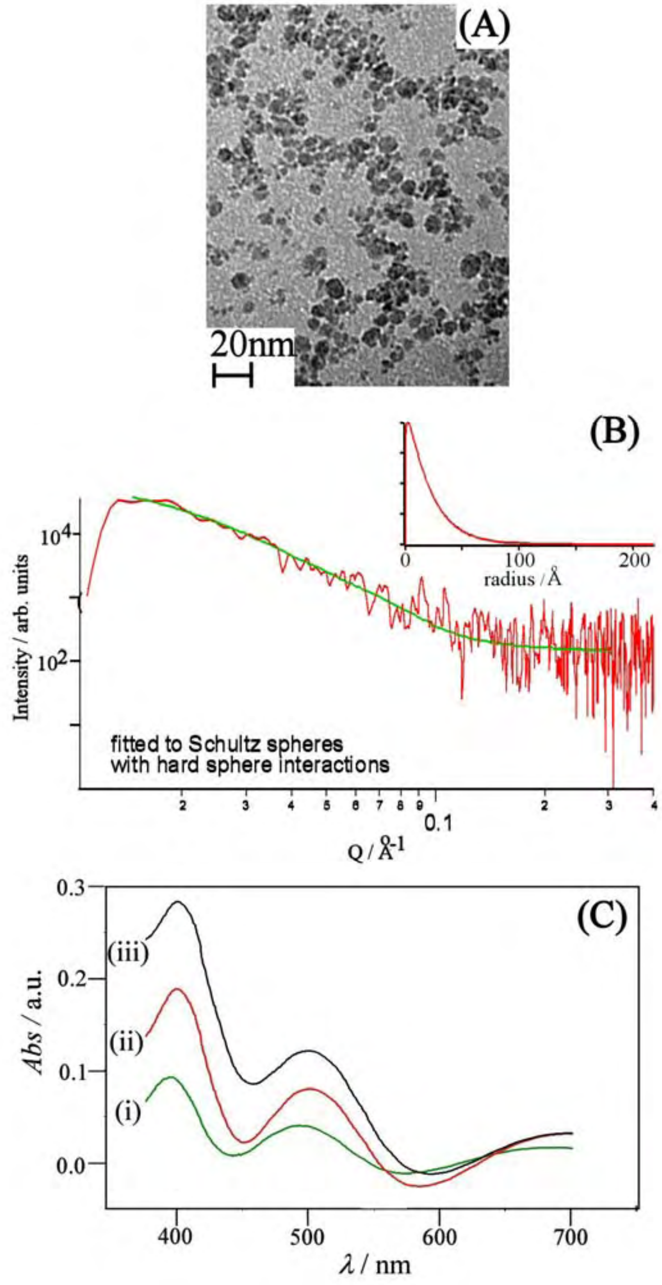
Electrochemical Characterisation of CeO_2 Films: Underpotential Reduction



Fe_2O_3 assemblies prepared from nanoparticles.

SAXS shows particle properties before and after calcination.

UV/Vis evidence for film growth.



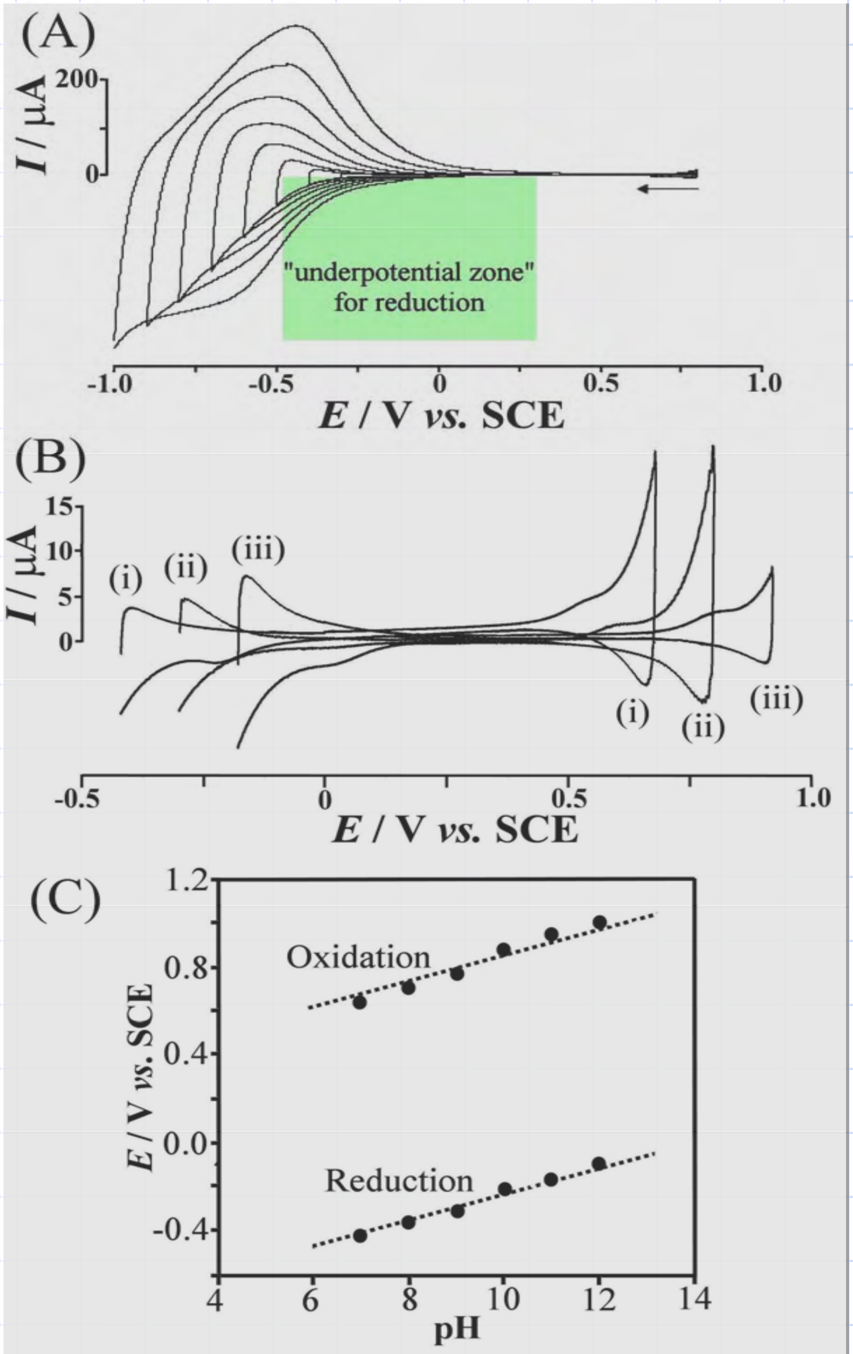
Nanoparticle Thin Film Voltammetry IV.: Reactivity of Fe_2O_3 Assemblies

Fe_2O_3 assemblies show two distinct types of surface processes:

Fe(III/II)

Fe(VI/III)

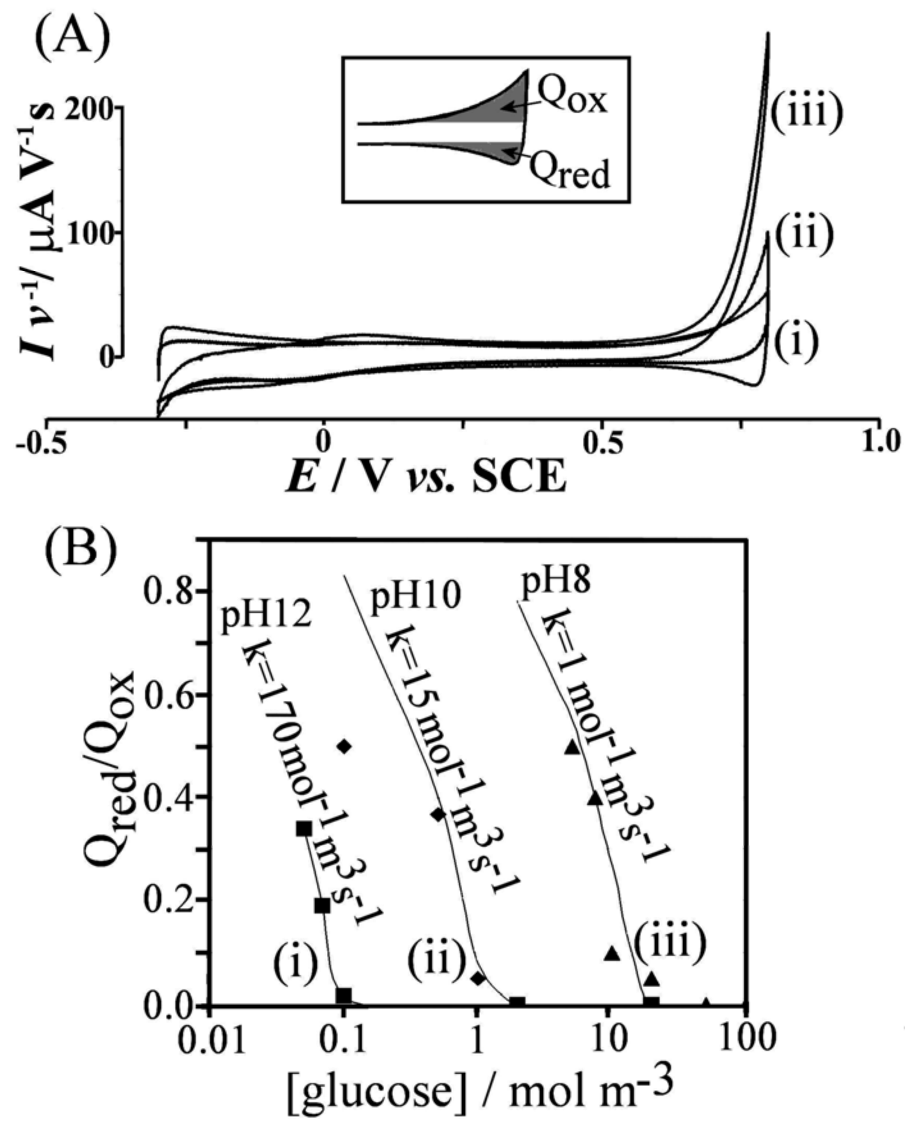
"SURFACE STABILISATION"



Fe(VI) Electrocatalytic Detection of Glucose:

Fe(VI) at the nanoparticle surface is a strong oxidant e.g. reacting with glucose in solution.

However, the anion controls reactivity.



Summary & Outlook:

- I. Thin film voltammetry with nanoparticle mono-layers: Fe_2O_3 – TiO_2
- II. Multi-layer structures: TiO_2
- III. Underpotential reduction: CeO_2
- IV. Surface stabilisation effects: Fe_2O_3
- V. Voltammetry is a tool for studying oxide surfaces

Nanoparticle thin film voltammetry offers a powerful diagnostic tool for both (i) bulk conducting and (ii) surface conducting materials.

THANK YOU FOR YOUR ATTENTION!