Resonance Raman Spectroscopic Studies of Surface-derivatized TiO$_2$

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Raman spectroscopic evidence has established the nature of the surface species on [Ru^{II} (etcbpy)$_2$]$^{2+}$ derivatized TiO$_2$ [etcbpy = 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine].

Surface derivatization of large band gap semiconductors has been used to shift their absorption into the visible region for efficient harvesting of sunlight in solar energy conversion.[1] TiO$_2$, which has a band gap edge at *ca.* 380 nm, has been the most widely studied semiconductor. Recently, surface derivatization of TiO$_2$ by various inorganic complexes such as [Ru(bpy)$_3$]$^{2+}$,[2] [Ru(etcbpy)$_3$]$^{2+}$,[3] [Co(tsp)]$^{2+}$ [bpy = 2,2'-bipyridine; etcbpy = 4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine, tsp = tetrasulphophthalocyanine],[4] and [Fe(CN)$_6$]$^{4-}$,[5] has been reported. Of these, surface derivatization by the ruthenium ester complex has been shown, by Grätzel *et al.*,[3,6] to yield an efficient and stable system for visible light energy conversion. Unlike other Ru complexes this carboxylate ester is reported to bind chemically to the TiO$_2$ surface *via* one or two oxygen bridges. This proposal has, however, been challenged by Furlong *et al.*[7] In this communication we present new results relating to this controversy, these being obtained from our resonance Raman spectroscopic studies of surface-derivatized TiO$_2$.

Colloidal suspensions of TiO$_2$ were prepared by slowly adding 1.5 cm^3 of TiCl$_4$ to 100 cm^3 of vigorously stirred water at 0 °C.[8] The sols were dialysed until the pH reached *ca.* 2. TiCl$_4$ (GPR) from BDH was used as received. The water used was doubly distilled and deionized. The size of TiO$_2$ particles was determined by transmission electron microscopy (T.E.M.) using a Hitachi HU12A microscope with an accelerating voltage of 100 kV. The average particle size was found to be of radius *ca.* 43 Å. The complex [Ru(etcbpy)$_3$]$^{2+}$ used was a gift from Professor M. Elliott.

Surface-derivatized TiO$_2$ samples were successfully pre-

pared as described by Grätzel *et al.*[3] Completion of the reaction was confirmed by recording the u.v.—visible spectrum of the supernatant solution. The solid particles formed were pale red in colour, distinct from the orange colour of the parent Ru complex itself. The sample preparation procedure was found to be reliably reproducible, as were the resulting Raman spectra of the products. We note that Furlong *et al.*[7] have stated that they were unable to reproduce this procedure for preparing the surface-derivatized TiO$_2$, although they did prepare a red coloured sample by equilibrating TiO$_2$ with the ruthenium–tris(2,2'-bipyridyl-4,4'-dicarboxylic acid) complex in the presence of 10 mM ethylenediaminetetra-acetic acid (H$_4$ edta) at pH 4 for 48 h. The reason for the red colour of their product and the need for the edta could not be explained. It is interesting to note that Furlong *et al.*[7] found that the Ru ester complex appeared to bind electrostatically to TiO$_2$ through the carboxylate groups only after hydrolysis. Grätzel *et al.*[3] also recognised that the hydrolysis of the free ligand might occur under their reaction conditions.

Raman spectra were recorded using a Spex Model 1403 double monochromator fitted with a cooled photomultiplier tube, RCA type C31034–A02, linked to a Spex DPC-2 digital photometer. The spectrometer was controlled by a Compudrive and Scamp minicomputer. Spectra Physics model 170 Kr$^+$ or Series 2000 Ar$^+$ lasers were used for excitation. Solid samples were placed on a microscope slide and the laser radiation was focused onto various parts of the sample through the use of a Nikon OPTIPHOT microscope and a video camera coupled to the spectrometer.
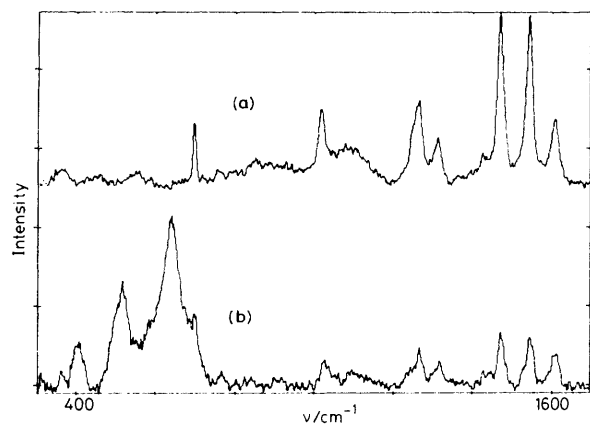
The u.v.–visible spectrum of the surface-derivatized TiO$_2$

Figure 1. (a) Resonance Raman spectrum of [Ru(etcbpy)₃]²⁺ solid: 488 nm, *ca.* 5 mW, 6 cm⁻¹ slits, 0.5 s integration, 1 cm⁻¹ steps, 50 scans. (b) Resonance Raman spectrum of surface-derivatized TiO₂: 514.5 nm, *ca.* 3 mW, 6 cm⁻¹ slits, 1 s integration, 1 cm⁻¹ steps, 47 scans.

Figure 2. Alternative binding models for surface-derivatized TiO₂: (a) strong covalent ligation; (b) electrostatic binding.

contains, in addition to its band gap edge at *ca.* 380 nm, a band at *ca.* 480 nm, a broad feature at *ca.* 600 nm, and a weak peak at *ca.* 670 nm.[3] The band at *ca.* 480 nm may be attributed to two transitions, *viz.* (i) the sub band gap transition of the modified semiconductor which results from derivatization and (ii) the metal to ligand charge transfer transition of the ruthenium complex itself[9] which is bound to the TiO₂ surface. Therefore, by selecting a laser excitation line near to 480 nm a double resonance enhanced Raman scattering due to both of these transitions is feasible. Thus the Raman spectrum may be expected to contain bands arising from the modified TiO₂ itself and from the surface bound species. [The resonance enhancement described here should not be confused with surface enhanced Raman (SERS) effects where resonance enhancement occurs with species adsorbed at certain metal surfaces, *e.g.* Ag, Au, *etc.*].

Figure 1 shows resonance Raman spectra of the pure complex (a) and that of the surface-derivatized TiO₂ (b). It is apparent that the high wavenumber region (>700 cm⁻¹) of both spectra look very similar and there is little change in the peak positions or the relative intensities. The bands in this region of the spectrum are associated with the vibrational features of the etcbpy ligand.[10] In the low wavenumber region (<700 cm⁻¹) there are three intense bands at *ca.* 404, 516, and 638 cm⁻¹. The spectrum of TiO₂ contains bands at *ca.* 420 and 630 cm⁻¹. Thus the peaks at *ca.* 404 and 638 cm⁻¹ may reasonably be assigned to vibrational modes associated with the phonon modes of modified TiO₂. The new band at *ca.* 516 cm⁻¹, and the shift in the 420 cm⁻¹ band of TiO₂, may be attributed to the surface binding of the complex. We assign the 516 cm⁻¹ band to a new type of metal–oxygen (Ti–O) bond vibration. There are two plausible ways in which one can model the complex binding at the surface of TiO₂ and these are shown in Figure 2. Grätzel *et al.*[3] have suggested that during photolysis the Ru complex loses one of its ligands and binds to the surface of TiO₂ *via* one or two oxygen bridges of the type Ru–O–Ti (Figure 2a). On the other hand, Furlong *et al.* have reported that on hydrolysis of the complex, the resulting dicarboxylate ligand could bind electrostatically to the TiO₂ surface to form binding of the type Ti–O–C (Figure 2b).

Considering Furlong's model, hydrolysis of the carboxylate ester groups at the 4,4′-positions of the pyridyl ring may be
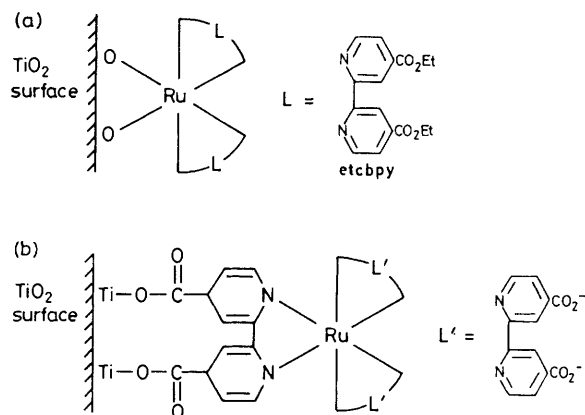
expected to influence the vibrational modes of these ligands. However, the band at *ca.* 701 cm⁻¹, which is attributed to the effect of substitution at the 4-position of the pyridyl ring,[10] has not shown any significant shift. Moreover, this ester hydrolysis would be expected to influence the high wavenumber bands associated with the ligand modes, but the resonance Raman spectra of the surface-derivatized TiO₂ and the Ru ester complex do not differ significantly in the high wavenumber region. Thus the evidence is firmly in favour of the band at *ca.* 516 cm⁻¹ being assigned to Ru–O–Ti type binding rather than the Ti–O–C type.

In conclusion, the new Raman spectroscopic evidence has been found to favour the structural model for surface-derivatized TiO₂ microheterogeneous photocatalysts wherein direct covalent bonds to ruthenium are formed (Figure 2a). Such bonding requires the loss of one ligand from the [Ru(etcbpy)₃]²⁺ species. No spectroscopic evidence for ester hyrolysis was found.

References

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