Resonance Raman and Luminescence Spectra from Colloidal Semiconductor Surfaces

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Spectra are reported for the surface-adsorbed free radical anion of methylviologen ($MV^{+\cdot}$) formed from MV^{2+} by electron transfer from colloidal CdS particles following photoexcitation by continuous wave Raman lasers.

Cadmium sulphide is a semiconductor which absorbs light in the visible region at wavelengths <520 nm; in colloidal form it is of current interest as a photocatalyst for the cleavage of water.[1] The lifetime of the electron-hole (e^-/h^+) pair formed by band-gap excitation in colloidal CdS is 10^{-9} s.[2] Electron transfer from the conduction band and/or hole transfer from the valence band to electron acceptors or donors, respectively, adsorbed on the CdS prolongs the life of the separated e^-/h^+ pair, providing more time for the diffusion-limited redox reactions with water to occur. Methylviologen (MV^{2+}) dichloride is commonly used as an electron acceptor in photocatalytic systems; in this communication we report for the first time the resonance Raman spectrum (r.R.s.) of the methylviologen radical cation $MV^{+\cdot}$ adsorbed on colloidal CdS. In addition, we present preliminary findings on the photochemistry of aqueous colloidal CdS systems stabilized by hexametaphosphate ions $(PO_3^-)_6$.

CdS colloids were prepared by passing H_2S gas slowly over the surface of a stirred aqueous solution of $Cd(NO_3)_2$ (5×10^{-3} M) containing sodium hexametaphosphate (10^{-2} M). Complete reaction took 1—2 h. Excess of H_2S was displaced from solution by N_2 and MV^{2+} then was added to the colloid so as to give a final concentration of 10^{-3} M. The final solution pH in each case was found to be 6. Raman and luminescence

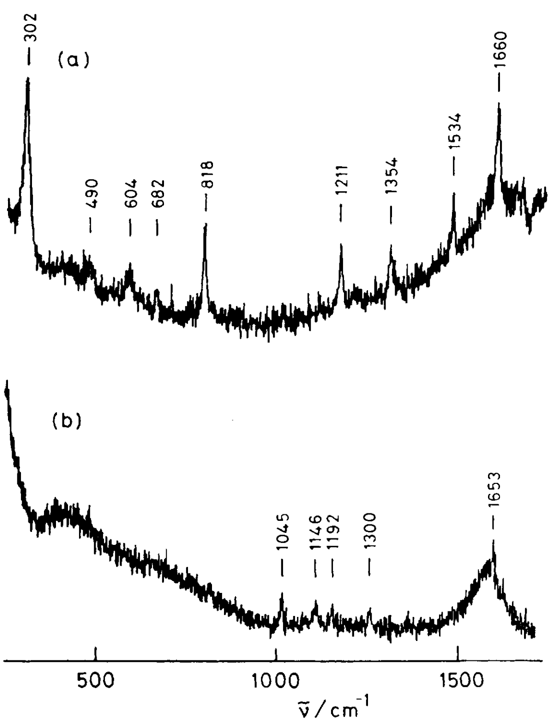

Figure 1. (a) The resonance Raman spectrum of MV^{2+} (reduced to $MV^{+\bullet}$) (10^{-3} M) adsorbed on hexametaphosphate-stabilized colloidal CdS (5×10^{-3} M) and (b) the non-resonance Raman spectrum of MV^{2+} (10^{-3} M) in aqueous $Cd(NO_3)_2$ (5×10^{-3} M) solution containing 10^{-2} M hexametaphosphate. Closed recirculating continuous flow systems with $\lambda_{ex.}(Kr^+) = 406.7$ nm at *ca.* 150 mW, 1 cm^{-1} steps, 5 cm^{-1} slits, 0.2 s integration, and 4 scans. Solutions were N_2-saturated and recirculated at 40 cm^3/min giving a linear flow velocity at the laser focus of 3.8 m s^{-1}.

spectra were recorded using a Spex model 1403 spectrometer equipped with a cooled phototube, RCA type C31034-A02, Compudrive, and Scamp minicomputer, used in conjunction with Spectra Physics model 170 Kr^+ and Coherent Radiation model CR4 Ar^+ lasers. Experiments were performed using continuously flowing samples (flow rate 40 cm^3/min) with recirculation through either a 1.5 mm bore spectroscopic cell or an open jet into which the laser beams were focused with conventional 90° illumination optics.

In Figure 1 the Raman spectra of MV^{2+} in N_2-saturated solutions together with (a) $(PO_3^-)_6$-stabilized colloidal CdS and (b) $Cd(NO_3)_2$ (aq.) and $(PO_3^-)_6$ (aq.) are shown for excitation by Kr^+ 406.7 nm radiation. The conditions of the experiment are given in the caption to Figure 1. In the presence of CdS the r.R.s. of $MV^{+\bullet}$ is observed and found to be identical to that obtained by Forster *et al.*[3] for $MV^{+\bullet}$ formed by the reduction of MV^{2+} by zinc. The spectral region shown in Figure 1(a) contains many Raman bands which may usefully be regarded as constituting a molecular 'fingerprint' and both the band wavenumbers and their relative intensities correspond closely with those reported for $MV^{+\bullet}$ in solution. Pulsed laser studies[4] of surfactant-stabilized CdS colloids show the electron transfer from CdS to MV^{2+} to occur in 10^{-9} s while the subsequent $MV^{+\bullet}/h^+$ recombination occurs in *ca.* 10^{-6} s; it would appear that electron transfer only occurs to species located on the CdS surface. Thus the spectrum shown in Figure 1(a) is of $MV^{+\bullet}$ adsorbed on CdS. The absence of shifts in the positions of Raman bands or changes in their relative intensity for $MV^{+\bullet}$ formed by photoreduction on the surface of CdS or by chemical reduction by zinc indicates that the interaction of $MV^{+\bullet}$ with the surface of colloidal CdS does not result in any significant change in its vibrational structure. The non-resonance Raman spectrum of MV^{2+} shown in Figure 1(b) is considerably weaker than the r.R.s. of $MV^{+\bullet}$. This intrinsic intensity difference, together with the onset of fluorescence, as seen in Figure 1(a), prevents us from determining the extent of conversion of MV^{2+} into $MV^{+\bullet}$ in the colloidal system.

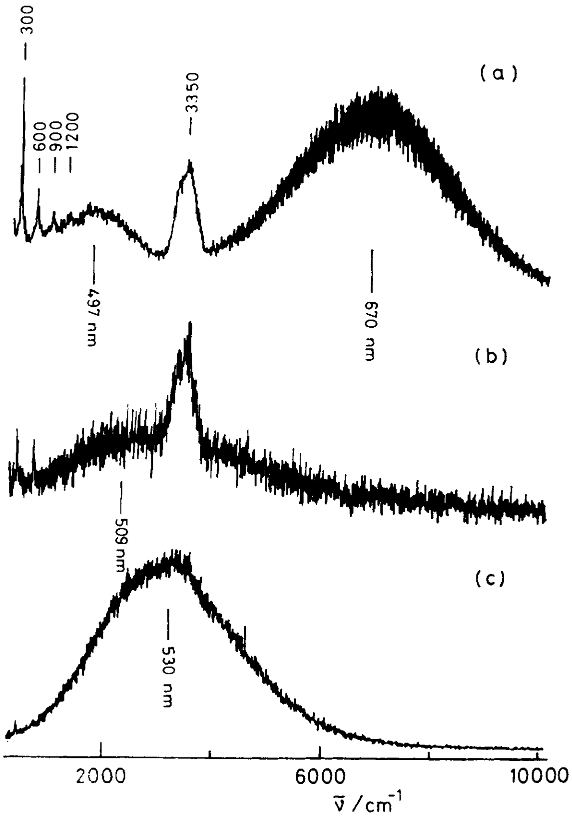

Figure 2. Raman and luminescence spectra obtained from N_2-saturated CdS colloids (5×10^{-3} M) in (a) a closed recirculating flow system, (b) an open-jet recirculating flow system, and (c) as for (b) but with MV^{2+} (10^{-3} M) added to the colloid. $\lambda_{ex.}(Ar^+) = 457.9$ nm at *ca.* 70 mW; single scans were made with the other conditions as in Figure 1.

In Figure 2 are shown Raman and luminescence spectra obtained for N_2-saturated CdS colloids in (a) a closed recirculating flow system, (b) an open-jet recirculating flow system, and (c) as for (b) but with MV^{2+} added to the colloid, using excitation by Ar^+ 457.9 nm radiation. The spectra of Figure 2(a) and (b) might be expected to be identical. Both show the CdS optical phonon band and its overtones with relative intensities 300 cm^{-1} > 600 cm^{-1} > 900 cm^{-1} > 1200 cm^{-1}, a fluorescence band at *ca.* 500 nm and the water Raman band at 3350 cm^{-1}. However, the intense fluorescence at 670 nm present in Figure 2(a) is absent in Figure 2(b). The reason for this is believed to be associated with the fact that yellow CdS deposits were found on the walls of the spectroscopic cell (a) where the laser beam had entered and left the cell. It is known that solid CdS gives fluorescence bands at 515 and 700 nm which have been attributed to e^-/h^+ recombination and anion vacancies, respectively.[5] In the presence of MV^{2+}, Figure 2(c), an increase in the intensity and a red shift of the e^-/h^+ recombination band to 530 nm is observed. Duonghong *et al.*[2] have reported results similar to those shown in Figure 2(a) and 2(c), but have argued that luminescence centred at *ca.* 700 nm in colloidal CdS arises from surface states acting as radiative recombination sites and that the shift to 524 nm in the presence of MV^{2+} implies that MV^{2+} interacts with the surface states, preventing their radiative recombination. However, our observations suggest that the red fluorescence in our experiments arises from CdS deposits on the walls of the spectroscopic cell, since the fluorescence disappears in the absence of the cell walls. Thus we are left with the conclusion that the e^-/h^+ recombination band shifts from 500 to 530 nm upon addition of MV^{2+} to the colloid and we suggest that this may be associated with (i) some aggregation of CdS particles[5] and/or (ii) a lower energy gap for the $MV^{+\bullet}/h^+$ recombination process than for e^-/h^+ recombination.

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