Laser Raman spectroscopy of colloidal semiconductor photosensitizers

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Abstract. Colloidal semiconductor photosensitizers have been used as heterogeneous catalysts for the chemical solar energy conversion processes. The use of Raman spectroscopy to address the problems related to colloidal semiconductors and photosensitization reactions is reviewed. In particular, the adsorption characteristics of various secondary sensitizers and their electron-transfer reactions are studied using resonance Raman and time-resolved resonance Raman spectroscopy. Finally, the importance of the quantum size effect of colloidal semiconductors in relation to their catalytic effects is presented with particular reference to their influence on photosensitizing properties.

Keywords. Laser Raman spectroscopy; colloidal semiconductor photosensitizers; heterogeneous catalysts; chemical solar energy conversion processes.

1. Introduction

Photosplitting of water into hydrogen and oxygen using heterogeneous catalysts has been the objective of many of the chemical solar energy conversion processes. In particular, there has been considerable activity in developing suitable colloidal semiconductors to sensitize and to mediate the water-splitting redox reaction (Grätzel 1985). In spite of the rapid progress made in this area of research, there are still many features that require further investigation (Kalyanasundaram et al 1986). In this article we review the use of Raman spectroscopy in solving problems related to colloidal semiconductors and their use in solar energy conversion.

Solar energy conversion in this present context is defined as the splitting of water to hydrogen and oxygen by sunlight in the presence of colloidal semiconductors. Electron–hole pairs created in the semiconductor by absorption of light may take part in surface redox reactions. For such redox processes to be efficient, it is important to effectively separate the electrons and holes to prevent their recombination. Therefore, relay compounds, such as methylviologen (an electron acceptor), are used to separate the photoinduced charges. The electrons formed in the semiconductor move to the surface where they are transferred to the relay species adsorbed on the surface. This electron-transfer process can be efficient only if (a) the absorption of sunlight by semiconductor is strong enough to produce a large number of electrons and holes, (b) the electron-transfer across the interface is fast enough to prevent electron–hole recombination, and (c) the relay species is adsorbed directly on the semiconductor surface. Raman spectroscopy has been used to study adsorption characteristics of the relay and electron transfer reactions at the semiconductor/adsorbate interface.

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2. Raman methods

The application of Raman spectroscopy to studies of surface adsorbed species has recently been reviewed (Bartlett and Cooney 1987; Hester 1988). Surface spectroscopies were formerly dominated by the use of ion and electron beam methods, viz. Auger electron spectroscopy, ultraviolet and X-ray photoelectron spectroscopy, electron energy loss spectroscopy and secondary ion mass spectrometry (see Clark and Hester 1988). Infrared and Raman spectroscopies provide alternative tools for probing the molecular structure of surface species. For the study of solid surfaces in contact with the aqueous phase, Raman methods are more favourable than infrared due to (a) low interference from water itself, (b) selective enhancement of vibrational modes associated with different chromophoric parts of molecules through resonance Raman methods, and (c) time-resolution into the picosecond regime.

Normal Raman scattering is an inherently weak process, with typically only one in $10^7$ photons resulting in Raman scattering, and therefore requires an intense light source. Although strongly scattering samples are easily amenable to normal Raman spectroscopy, one has to invoke other Raman methods such as resonance Raman (RR) or surface enhanced resonance Raman (SERR) spectroscopies for weak scatterers. RR spectroscopy and its relevance to the present work are discussed below; SERR spectroscopy is not relevant to this work since worthwhile surface enhancement is observed only on certain metal surfaces, viz. mainly gold, silver and copper.

2.1 Resonance Raman scattering

The intensity of a Raman band associated with a transition from state $m$ to $n$ for randomly oriented molecules is given by (Clark and Dines 1986)

$$ I = K I_0 v^4 \sum |\alpha_{\rho\sigma}|_{mn}^2, $$

where $K$ is a constant which takes into account the permittivity of free space, $I_0$ is the irradiance of the incident radiation, $v$ is the scattered light frequency and $\alpha_{\rho\sigma}$ is the $\rho\sigma$th element of the transition polarizability tensor. When the excitation frequency is in resonance with a vibronic transition from the ground state to an excited state, the transition polarizability tensor can be written as

$$ [\alpha_{\rho\sigma}]_{mn} = A + B + C + D. $$

The terms $A, B, C$ and $D$ are responsible for different types of resonance Raman scattering. The most commonly found resonance effect due to the $A$-term is discussed here. The full description of the term involves the variable

$$ 1/(v_{ik} - v_0), $$

where $v_{ik}$ is the frequency associated with the energy gap between the lowest vibrational level of the ground state and the $k$th vibrational band of the excited electronic state, and $v_0$ is the incident exciting frequency. As $v_0$ approaches $v_{ik}$ the resonance condition is reached and the intensities of the $A$-type Raman bands increase dramatically. Thus, by selecting the appropriate excitation frequency which is in resonance with the electronic transition of a given chromophoric part of a molecule one can obtain the