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Adsorption and electronic states of morin on TiO_2 nanoparticles

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ABSTRACT

Low temperature Stark effect spectroscopy has been used to investigate the changes in the electronic charge distribution in the flavonoid morin caused by adsorption to colloidal TiO_2 nanoparticles in ethanol. The differences in the permanent dipole moment, $\Delta\mu$, and in polarizability, $\Delta\alpha$, between the ground and excited state were determined. Adsorption causes an increase in both $\Delta\mu$ and $\Delta\alpha$ of morin but the vector $\Delta\boldsymbol{\mu}$ remains nearly perpendicular to the Ti-dye direction, like in the free molecule. This picture of electron movement on electronic excitation is supported by semiempirical calculations. In contrast to other dyes adsorbed on TiO_2, it indicates the indirect effect of chelated Ti atom on morin electronic structure which does not involve the atomic orbitals of the metal, and the electronic structure of adsorbed morin similar to that of the anion.

1. Introduction

New trends in photovoltaics and photocatalysis stimulate research on new generation of solar devices based on dye sensitization of semiconductor surface. The dye-sensitized solar cells (DSSC) that exhibit high performance and have relevant advantages over traditional silicon solar cells have been constructed [1,2]. The main goal of a large number of studies in this area is the detailed understanding of fundamental processes influencing DSSC efficiency. One of these basic phenomena is the mechanism of interfacial electron transfer between electronically excited dye molecule and semiconductor surface which is of basic importance for DSSC [3–6] as well as for solar water splitting [7] and photocatalysis [8].

Typical dyes that function well in DSSC when adsorbed on TiO_2 nanoparticles are Ru complexes that have shown good efficiency [9]. Moreover, other numerous dyes and pigments have been investigated in this respect, including synthetic metal-free derivatives of coumarin, squaraine, carbazole, perylene, triarylamine, anthracene dyes and their derivatives, as well as naturally occurring photosensitizers [10].

Our investigations focus on the interaction of dye molecules with the adsorption sites on TiO_2 nanoparticles and its effect on electronic excited states, as reflected by the electronic charge redistribution in the electronic transitions. This study is devoted to the morin dye (Fig. 1) that belongs to the group of flavonoid compounds. Flavonoids commonly occur in higher plants and are well known for their antioxidant activity. Morin which is nonfluorescent in free form [11] becomes fluorescent in the association with some metal ions, and this property has been widely investigated with the prospect of its use in analytical methods for the detection of metal traces and ligand identification [12–15]. Morin interaction with metals involves its dissociated hydroxy groups coordinating the metal ion with their oxygens [16,17]. The method used in this work for investigating the redistribution of electronic charge over the morin–TiO_2 system is the Stark effect spectroscopy, which provides information on the changes in permanent dipole moment and molecular polarizability that occur on electronic excitation of the free or adsorbed dye molecule.

2. Methods

In Stark effect spectroscopy, the external electric field **F** applied to the sample induces a change in energy of the electronic transition between the ground and excited states given by:

$$\Delta E = -\Delta\boldsymbol{\mu}\cdot\mathbf{F} - \frac{1}{2}(\mathbf{F}\cdot\Delta\hat{\boldsymbol{\alpha}}\cdot\mathbf{F}). \quad (1)$$

where $\Delta\boldsymbol{\mu}$ and $\Delta\hat{\boldsymbol{\alpha}}$ are the dipole moment vector and polarizability tensor differences in the electronic states involved. This is equivalent to a field-induced spectral shift, and the experimentally measured quantity is the electric field-induced change in absorbance, $\Delta A(\nu)$. For an isotropic sample, $\Delta A(\nu)$ is proportional to the square of the electric field and can be expressed as a linear combination of

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the absorption spectrum itself and its first and second derivatives according to the following formula [18,19]:

$$\Delta A(\nu) = a_0 \cdot A(\nu) + a_1 \nu \frac{d(A(\nu)/\nu)}{d\nu} + a_2 \nu \frac{d^2(A(\nu)/\nu)}{d\nu^2}. \quad (2)$$

Here, ν is the wavenumber, the coefficients a_1 and a_2 depend on $\Delta\alpha$ and $\Delta\mu$ and are expressed by:

$$a_1 = \frac{f^2 \Delta\alpha}{10\sqrt{2}hc} F^2 \left[(3\cos^2\gamma - 1)\cos^2\chi + 2 - \cos^2\gamma\right] \quad (3)$$

$$a_2 = \frac{f^2 (\Delta\mu)^2}{10\sqrt{2}h^2c^2} F^2 \left[(3\cos^2\delta - 1)\cos^2\chi + 2 - \cos^2\delta\right]. \quad (4)$$

The tensor $\Delta\hat{\boldsymbol{\alpha}}$ in Eq. (1) is replaced in Eq. (3) by the scalar $\Delta\alpha$ with the meaning of the uniaxial polarizability whose axis makes an angle γ with the transition dipole moment, and δ in Eq. (4) is the angle between the vector $\Delta\boldsymbol{\mu}$ and the electronic transition moment. The angle χ between the electric vector of the light and the applied electric field is set experimentally by rotating the sample in polarized light beam. The least squares fit of ΔA expressed by Eq. (2) to experimental ΔA spectrum provides the coefficients a_0, a_1 and a_2, from which the values of $\Delta\mu$ and $\Delta\alpha$ are determined numerically. However, we neglected the term with a_0 since its contribution to the fits turned out to be irrelevant. Other details of experimental procedure were described previously [20]. The value of local field factor $f \approx 1.1$–1.3 is included in all values of $\Delta\mu$ and $\Delta\alpha$ presented in the next sections.

All chemicals were obtained from Sigma and used as received except for morin that was purified through recrystallization from methanol. Since the anhydrous ethanol was slightly basic, the undissociated form of morin was obtained by a small addition of acetic acid (≈0.01%), while the dissociated form of morin was obtained by titrating with aliquots of saturated NaOH in ethanol. Colloidal solution of TiO_2 nanoparticles in anhydrous ethanol was prepared by hydrolysis of titanium tetraisopropoxide [21] in the presence of 0.2% acetic acid. Adsorption of morin was performed by adding ethanolic solutions of the dye to the colloid and was controlled by UV–VIS absorption spectra. Samples used to measure the electroabsorption spectra were colloidal solutions between two conducting glass surfaces spaced by 0.08 mm, frozen in order to immobilize the molecules. Electroabsorption measurements were performed in the setup described previously [20]. The accuracy of the electrooptical parameters depends on relative amplitudes of the derivatives in the fit. It can be generally estimated as roughly 10% in $\Delta\mu$ and 15% in $\Delta\alpha$.

Semiempirical calculations were performed using the HyperChem v.8 [22]. The PM3 method was used as appropriate for transition metals. The TiO_2 structure was modeled by a single Ti atom bound to three OH^- groups with the Ti–O bond directions and distances mimicking those around a surface Ti atom in anatase.

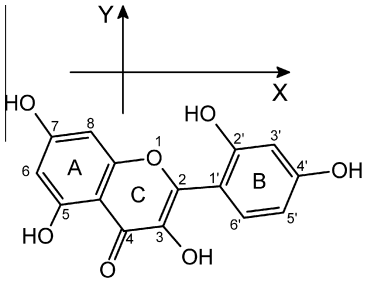

Fig. 1. The structure of the morin molecule and the orientation of the coordinate system used in semiempirical calculations. The X axis links the center of the chromone moiety (rings A, C) with that of catechol (B).

The whole structure was optimized in the ground state, and then the bond lengths and angles between Ti and OH^- oxygens were reset accordingly to the TiO_2 surface geometry, while the length of the bonds between Ti and oxygenic ligands of the flavone were left unchanged. The CI expansion in the electronic excited state calculations was gradually extended so as to obtain convergent energy values. CI expansion involving singly excited configurations between 16 occupied and 16 unoccupied orbitals was sufficient to fulfill this criterion.

3. Results

3.1. Free morin

The absorption maximum of neutral morin form in acidic ethanol (indicated by apparent pH 5.1 in ethanol) is at 360 nm (27,800 cm^{-1}) in room temperature. Dissociation causes significant red shift of 2500 cm^{-1} and morin anion in basic ethanol (pH 12.5) absorbs at 395 nm (25,300 cm^{-1}). Absorption spectra of both these forms at low temperature are shown in Fig. 2A. The tail at 24,000–22,000 cm^{-1} (400–450 nm) appears in concentrated solution used in Stark experiments and is the result of partial aggregation of morin. It is not an effect of impurities, since morin after recrystallization did not show any changes in the RT spectrum in this range. Absorption spectra of solutions ranging 250 times in morin concentration have shown that the weak tail extending from 400 to 450 nm comes from the interaction of dye molecules and is stronger at the millimolar concentrations used for electroabsorption measurements.

Fig. 2B shows electroabsorption spectra of morin in neutral and anionic forms frozen in ethanol at low temperature. The Stark spectra in Fig. 2B (shown with points) are approximated quite well

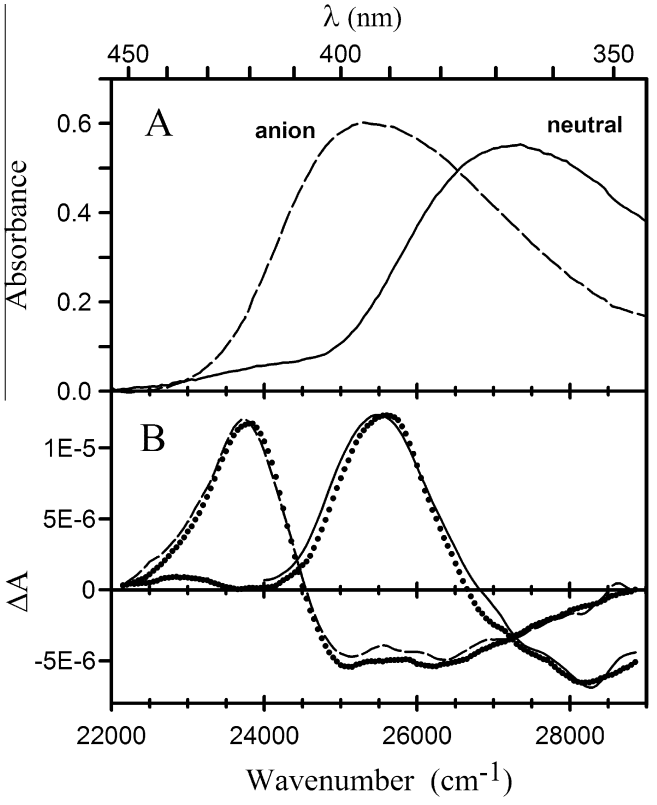

Fig. 2. Absorption (A) and electroabsorption (B) spectra of morin (6 mM) in ethanol. Neutral form – solid line; fully dissociated – dashed line. Electric field intensity: 1.5×10^5 V/cm (r.m.s.), temperature 80 K.