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A kinetic/thermodynamic study of transparent co-adsorbents and colored dye molecules in visible light based on microgravimetric quartz-crystal microbalance on porous TiO$_2$ films for dye-sensitized solar cells

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In this study, a quartz crystal microbalance (QCM) *in situ* method is used to study the kinetic and thermodynamic processes of the adsorption of ruthenium-based dyes (N719, N3, N749), and the co-adsorbent chenodeoxycholic acid (CDCA) on the TiO$_2$ film surface. The results of the kinetic studies show that the adsorption rate of N749 is slightly higher than the other two dyes, and the adsorption rate of CDCA is more sensitive to temperature change. The adsorption mechanism of the dye and CDCA on the surface of TiO$_2$ can be reasonably inferred based on the result of the activation energy. The isotherm adsorption model studies show that the ratio of the number of surface molecules (296 K) is $n_{(N719)} : n_{(N3)} : n_{(N749)} : n_{(CDCA)}$ = 0.69 : 1.48 : 0.50 : 1. The K_{eq} value of CDCA is about two orders of magnitude smaller than that of all the dye molecules, which indicates that the adsorption strength of CDCA is much weaker than that of the dye molecules. Thermodynamic studies show that the adsorption reaction is an endothermic reaction. The ΔS is ΔS(N3 = 143.11 J mol^{-1}) > ΔS(N719 = 112.72 J mol^{-1}) > ΔS(N749 = 109.43 J mol^{-1}) > ΔS(CDCA = 96.14 J mol^{-1}). The Gibbs free energy ΔG is negative, and indicates that the adsorption reaction of the four molecules on the surface of the TiO$_2$ film is spontaneous. The results of this paper show that the tedious and lengthy experimental process of the traditional method can be simplified by QCM. In addition, the development of this study provides a certain theoretical and experimental basis for future studies on the interaction mechanism between dyes and co-adsorbents.

1. Introduction

Studies were performed from the initial solar cells (containing only physical processes with monocrystalline silicon and polycrystalline silicon as the main materials) to new types of solar cells, which now contain both physical and chemical processes. Through the studies on these new types of solar cells, the understanding of the photovoltaic mechanism on the physical, chemical and molecular level has taken a step forward. The dye-sensitized solar cell (abbreviated as "DSC") is a photoelectrochemical system that uses a porous oxide semiconductor film as a framework layer for electron transport, and dye molecules and electrolyte as energy conversion media.[1] The framework layer materials commonly used in DSC are TiO$_2$, SnO$_2$, ZnO and other semiconductor materials.[2,3] The sensitizing materials are mainly classical and high-conversion efficiency ruthenium dyes, such as N719, N3 and N749.[4,5] The electrolyte used is an organic solution containing I$^-$/I$_3^-$, Co$^{(II)}$/Co$^{(III)}$ and other redox couples.[6]

After the dye molecules adsorbed on the surface of the porous semiconductor film directly capture sunlight, electrons are injected into the semiconductor film to complete a photoelectric conversion process. After the electrons are injected, the dye molecules are converted into an oxidized state. The oxidized dye molecules are converted into a reduced state through the redox couple in the electrolyte in contact with them, thus preparing for the next capture of sunlight. The activity described above is the energy conversion process of DSC. In such a complex energy conversion process, the dye

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loading amount and structure are important factors that determine the photoelectric conversion.[7] The semiconductor film that adsorbs the dye is called a dye-sensitized film, and this kind of functionalized film is formed when the dye is adsorbed by the film in solution. In the early stage, flat semiconductor film structures were used. Because the surface area was too small, the dye loading amount was insufficient, and it was difficult to obtain high conversion efficiency. In the later stage, Professor Grätzel from Switzerland introduced the nanoporous semiconductor film structure. The surface area was greatly increased, the dye loading amount increased geometrically, and the photoelectric conversion efficiency of DSC was significantly improved.[1] Studies have shown that when the dye forms a monolayer structure on the film surface, the photoelectric conversion efficiency is optimal.[5] However, the actual situation is very complicated. The commonly used dyes contain groups, such as COOH, which easily cause agglomeration on the surface of the film and form multilayer adsorption.[4] This multilayer adsorption brings additional energy loss, resulting in a decrease in the photoelectric conversion efficiency of the device. Different small molecules that are introduced can inhibit the agglomeration of dyes on the surface of the TiO$_2$ film, reduce the internal dark current in the DSC, and improve the photoelectric conversion efficiency of the cells. Such small molecules can be called co-adsorbents. Commonly used co-adsorbents include GBA, PPA, SA, DCA, and DINHOP.[8–10] The chenodeoxycholic acid organic molecule (CDCA) is the most widely used co-adsorbent in DSC. Many works of literature have reported the interaction between the CDCA molecules and various dyes, like ruthenium-based N719, anthracene-based TY6 and organic dyes.[10–12] However, the mechanism of CDCA in the cell is still unclear, and there are currently different opinions on many issues.

The most commonly used method to measure the dye-loading amount on the film surface is the "lye desorption" method. This method involves placing the dye-sensitized film in lye for rinsing, collecting the eluted liquid, measuring the absorbance with the help of the ultraviolet-visible absorption spectrum, and finally obtaining the dye-loading amount indirectly by comparison with the standard curve. This method is an *ex situ* measurement method, where only one sample concentration can be measured at a time. In addition, the operation steps are cumbersome and time-consuming, frequent elution may change the surface structure of the film, and the strong lye may destroy the molecular structure. Besides, this method has an important flaw: it cannot measure molecules that do not absorb in the visible light range. Since the CDCA molecule is almost transparent in the visible light region, the corresponding loading amount cannot be obtained by measuring its absorbance. In addition, because the infrared absorption fingerprint area of CDCA overlaps with the dye molecular fingerprint area, the dyes and co-adsorbents cannot be distinguished by infrared spectroscopy.[13] Other methods, such as neutral impact collision ion scattering spectroscopy (NICISS), can accurately measure the dye molecules. However, because they contain the same elements as the dye molecules and have similar element ratios, the CDCA molecules cannot be detected. Compared with

other co-adsorbents, CDCA is more difficult to measure.[5] Marimamdo *et al.* use photoelectron spectroscopy to measure various co-adsorbents, and found that DINHOP, DPA, and others responded, but the CDCA response results cannot be obtained.[10]

The kinetic and thermodynamic mechanisms involved in the adsorption process of dye transferring from the liquid phase to the film surface are also more complicated. A two-step reaction may occur after the dye molecules are adsorbed on the surface of the film.[14] The isotherm adsorption process may need a modified Langmuir model to describe it better.[13] To study the kinetic and thermodynamic processes of dyes, it is necessary to obtain data on multiple dye-loading amounts of samples under multivariable conditions, such as different times, concentrations, and temperatures. When the traditional "lye desorption" method is used to study the thermodynamic and kinetic processes of dyes, the experimental process is complicated and lengthy with certain errors. In addition, because the CDCA loading amount is difficult to measure by the "lye desorption" method, as far as we know, there is no study report on the thermodynamic process of CDCA in the field of DSC, which made it impossible to analyze the CDCA adsorption process in detail.

Quartz crystal microbalance (QCM) is an *in situ* detection technique that can accurately detect small variations in the surface mass, and can theoretically detect variations in the mass on the order of nanograms. QCM is less used in the field of DSC, mainly focusing on dye adsorption kinetics.[15,16] As far as we know, in terms of thermodynamic study, the application of QCM to study the performance of dyes and co-adsorbents has not been reported.

Based on the above considerations, in this paper, utilizing QCM, the adsorption reaction of three ruthenium-based dyes (N719, N3, N749) and co-adsorbent (CDCA) on the surface of TiO$_2$ film was studied. In particular, the adsorption kinetics and thermodynamic characteristics were studied in detail. The results show that QCM can simplify the tedious and lengthy experimental process of the traditional method, and directly obtain important surface mass variation. The more valuable result is that upon changing the ambient temperature, the mass variation of the visible light transparent CDCA molecule on the film surface is measured *in situ*, and the adsorption kinetics and thermodynamic parameters can be obtained. The development of this study provides a theoretical and experimental basis for future study on the mechanism of interaction between dyes and co-adsorbents. It has certain theoretical significance for understanding the mechanism of the co-adsorbent, the adsorption process of the dye molecules, synthesizing new adsorbents, and improving the cell efficiency.

2. Experiment

The semiconductor paste used in the experiment is commercial TiO$_2$ paste (Dyesol-18NR-T) and N719, N3 and N749 dyes, which were purchased from Dyesol. CDCA was purchased from

Shanghai Aladdin Biochemical Technology Co., Ltd, and absolute ethanol was purchased from Sinopharm Chemical Reagent Co., Ltd.

The quartz crystal microbalance (QCM-200) was produced by Stanford Research Systems, USA, and the quartz wafer (5 MHz) was provided by JJK Electronic Co., Ltd. The surface of the wafer was treated with concentrated sulfuric acid, then cleaned with deionized water, dried with nitrogen, and cleaned in a UV cleaner for 10 min before use. TiO$_2$ paste was printed on the surface of the quartz crystal wafer, and sintered in a muffle furnace at 480 °C for 30 min to obtain a nanoporous TiO$_2$ semiconductor film. 1 mM N719 ethanol solution, 1 mM N3 ethanol solution, 1 mM N749 ethanol solution and 20 mM CDCA ethanol solution were prepared.

The quartz crystal oscillator was placed with the TiO$_2$ film in the electrolytic cell under a constant temperature water bath system in a pure ethanol solution until the frequency was stable. The dye or co-adsorbent solution was then injected into the electrolytic cell by static injection. 1 mM dye/CDCA solution was then injected into the system. After the dye/CDCA adsorption reached equilibrium, 1 mM dye/CDCA solution was injected again. The above steps were repeated to obtain the concentration–frequency variation curve of the dye/CDCA at different temperature measurement points

(280 K, 296 K and 308 K for dyes, and 280 K, 288 K and 296 K for CDCA). The actual concentration can be obtained by calculating the molecular weight and volume after injection.

3. Results and discussion

The four ethanol solutions of N719, N3, N749 and CDCA underwent the adsorption reaction with the TiO$_2$ film in the electrolytic cell. The microscopic molecular mass variations on the surface of TiO$_2$ are presented by the frequency variation of the QCM. Fig. 1 shows the frequency variation curves of the adsorption of the dyes N719, N3 and N749, and the co-adsorbent CDCA on the surface of the TiO$_2$ film under the conditions of temperature and concentration changes.

According to the Sauerbrey equation, the transformation relationship between the changing frequency and mass is that:

$$\Delta m = \frac{\Delta f}{(-C_f)} \qquad (1)$$

In eqn (1), C_f is the constant of the proportionality between the mass and frequency (56.6 Hz μg^{-1} cm^2), and the difference
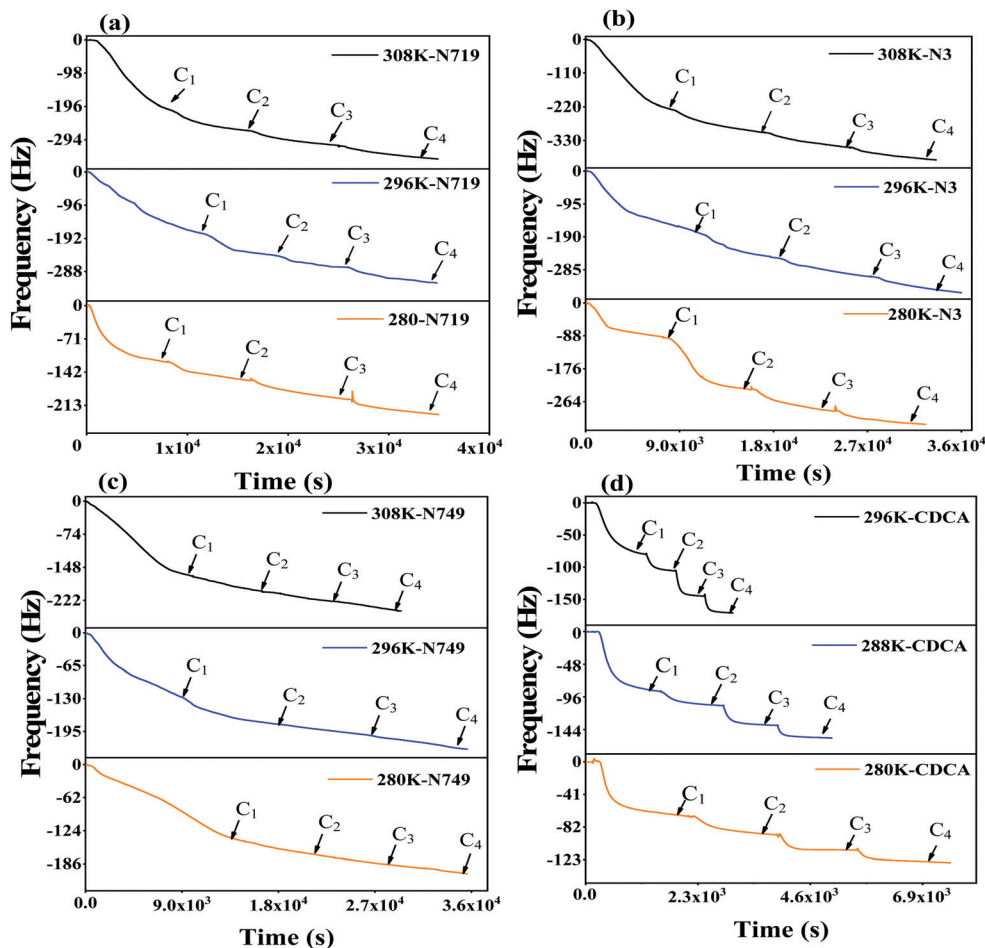

Fig. 1 The frequency variation plots of (a) N719, (b) N3, (c) N749 and (d) CDCA on the surface of the TiO$_2$ film under the conditions of temperature and concentration changes.

between the frequency and mass is a constant factor, so the variation rule of frequency in Fig. 1 is the variation rule of the film surface mass.

After the experimental temperature was set, the N719, N3, N749 and CDCA solutions at the initial concentrations were adsorbed for a period of time and reached the dynamic equilibrium of the first adsorption reaction on the TiO$_2$ film. After that, an appropriate amount of dye/CDCA was injected for the second time. As the concentration of dye/CDCA in the solution was increased, the initial adsorption equilibrium was disturbed. The adsorption rate then became greater than the desorption rate. The dye/CDCA molecules also began to undergo secondary adsorption on the TiO$_2$ film, and reached the adsorption equilibrium state again after a period of time. The dye/CDCA adsorption equilibrium was then reached under all experimentally set concentration and temperature conditions. The data needed for thermodynamic analysis of a molecule can be completed in three steps by QCM. Therefore, it is a simple and convenient method to study the adsorption mechanism of dyes or co-adsorbents by QCM under variable temperature conditions.

3.1 Adsorption kinetics

The proportion of the dye/CDCA occupying the film surface can be expressed by a coverage θ. The variation rule of the coverage rate θ over time is:[16]

$$\frac{d\theta}{dt} = k_a(1-\theta)c - k_d\theta \qquad (2)$$

In eqn (2), k_a represents the adsorption rate constant (M^{-1} s^{-1}), and k_d is the desorption rate constant (s^{-1}). By integrating in eqn (2), one can get:[17]

$$\theta(t) = \theta_{eq} + \left(\theta_i - \theta_{eq}\right)\exp(-k_0 t) \qquad (3)$$

In eqn (3), $k_0 = k_a c + k_d$ represents the attenuation constant, $\theta_{eq} = c/(c + k_d/k_a)$ represents the equilibrium coverage when the concentration is c, and θ_i represents the initial coverage. Eqn (3) shows that the coverage rate θ shows an exponential function rule, and is close to the equilibrium value over time.[17] Assuming that the adsorption mass on the film is proportional to the frequency shift of QCM (Sauerbrey equation), the frequency shift of the dye/CDCA adsorption follows eqn (3), namely $f(t) - f_{eq} \sim \Delta\theta = \theta(t) - \theta_{eq} \sim \exp(-k_0 t)$.

Taking N719 as an example, eqn (3) is used to obtain the isothermal adsorption parameters. Fig. 2 shows the semi-logarithmic relationship of the frequency variation $f(t) - f_{eq}$ after the concentration of the N719 solution is changed at 296 K. It can be seen from Fig. 2 that $f(t) - f_{eq}$ follows an exponential function variation rule, and the attenuation constant k_0 increases with increasing concentration. It can be seen from $k_0 = k_a c + k_d$ that there is a linear relationship between the attenuation constant k_0 and c. The linear fitting of k_0 and c can get the adsorption rate k_a.

By fitting the frequency variation $f(t) - f_{eq}$ and time curves of the dye and co-adsorbent at different temperatures and concentrations, the relevant adsorption kinetic parameters can be obtained. The activation energies (E_a) of the dye and
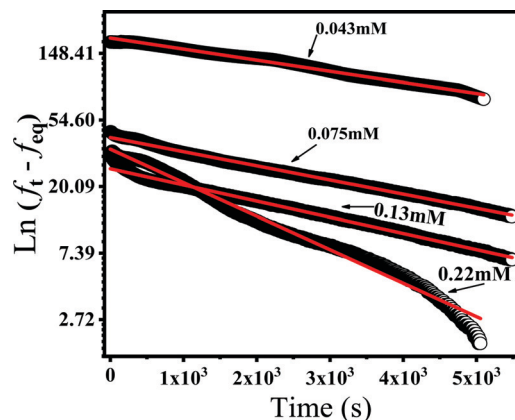

Fig. 2 Frequency variation $f(t) - f_{eq}$ and time function curve of dye N719 at 296 K.

co-adsorbent adsorbed on the film can be calculated by the Arrhenius equation:[18]

$$\ln(k_a) = \ln(A) - \frac{E_a}{RT} \qquad (4)$$

where k_a in eqn (4) represents the adsorption rate constant (M^{-1} s^{-1}), A is the frequency factor, R is the molar gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K).

Fig. 3 shows the Arrhenius plots for the adsorption of N719, N3, N749 and CDCA onto the TiO$_2$ surfaces. Table 1 shows the E_a for the adsorption of N719, N3, N749, and CDCA onto the TiO$_2$ surfaces.

The rapid adsorption reaction of the dye with the film is of great significance to the marketization of the device. Kim *et al.* showed that increasing the temperature can quickly complete the dye adsorption reaction.[19] Among the three dyes, the adsorption rate of N749 is slightly higher than the other two dyes. The adsorption of the dye molecules or co-adsorbent molecules on the surface of the film depends on the combination of the molecules on the surface of the semiconductor film, the diffusion and mass transfer in the solution and the
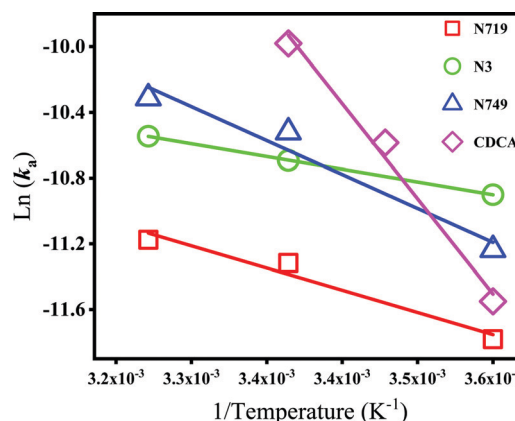

Fig. 3 Arrhenius plots for the adsorption of N719, N3, N749 and CDCA onto TiO$_2$ surfaces.

Table 1 Activation energy (E_a) for the Adsorption of N719, N3, N749, and CDCA onto the TiO_2 surfaces

Molecule	k_a ($\times 10^{-1}$ M^{-1} s^{-1})	E_a (kJ mol^{-1})
N719		
280 K	5.45	16.06
296 K	8.67	
308 K	9.98	
N3		
280 K	7.81	9.22
296 K	9.62	
308 K	11.14	
N749		
280 K	10.80	24.54
296 K	22.10	
308 K	27.20	
CDCA		
280 K	2.27	68.86
288 K	5.96	
296 K	10.90	

porous film, and other process factors.[20] The variation in temperature can change these factors.

The dye adsorption process may be related to the static electricity on the surface of the film. The surface of the film subjected to acid treatment has a positive charge, which can increase the adsorption rate of the dye.[19] The adsorption group of the N3 molecule is four COOH, the adsorption group of N719 molecule is two COOH and two COO–, and the adsorption group of N749 is three COO–. When the molecules are adsorbed, protons or TBA$^+$ ions are removed, resulting in different charge distributions of the molecules. The removed protons or TBA$^+$ ions will also be adsorbed on the surface of the film, resulting in different charged states of the TiO_2 surface.[21] The charge distribution of molecules and the surface charge state of TiO_2 also contribute differently to the adsorption rate. In this paper, N749 is a molecular structure with three TBA$^+$ ions. When the N749 dye is adsorbed, there is a situation in which the TBA$^+$ ions are adsorbed on the surface of the film, so that the N749 molecules with three negative charges may be attracted by static electricity.

The adsorption rate of CDCA is more sensitive to temperature change. When the temperature is higher than 296 K, the frequency signal is unstable (not shown), indicating that the adsorption of CDCA may be unstable at high temperature. This may be related to the fact that CDCA has only one adsorption group. In addition, the way that the molecules combine in the film may also cause changes in the adsorption rate. Due to the effect of steric hindrance, it is impossible for N3 or N719 to use four adsorption groups, but one or two of them can be used to anchor onto the TiO_2 surface. Literature study results show that there may be multiple bonding modes between ruthenium dye molecules and the TiO_2 surface.[22,23] CDCA can also be adsorbed on the surface of TiO_2 with the help of COOH groups. However, there are some complicated factors between the solution and the film, such as the mass transfer process of molecules in the solution, and the penetration of molecules in the film microstructure, which may affect the adsorption rate. Since the N749 molecule does not contain the COOH group, it can easily penetrate the porous interior.

According to the theory in the literature, an activation energy of between 0 and 40 kJ mol^{-1} represents physical adsorption, and an activation energy greater than 40 kJ mol^{-1} represents chemical adsorption.[18] The adsorption mechanism of N3, N719 and N749 on the surface of the film is still unclear, and there is still considerable controversy. However, there are some views that are supported by most study results: it is impossible for all of the adsorption groups contained in the dye to be adsorbed, and it is most likely that one or two of the groups are adsorbed.[8,14,22] When these two groups are adsorbed, there is the possibility of adsorption in two steps: during the reaction, one group adsorbs first, and then the other group adsorbs. Park *et al.* showed that the N719 dye molecule adsorption can be divided into two modes: strong adsorption and weak adsorption. The strong adsorption mode may be caused by the adsorption of two carboxylic acid groups, while the weak adsorption mode is the adsorption of one carboxylic acid group.[8] Lee *et al.* showed that N719 may be connected to the TiO_2 surface through two groups to form a hydrogen bond, and the other is a chemical bond.[22]

The results of this paper show that the activation energies of N3, N719 and N749 are all less than 40 kJ mol^{-1}, which implies that the adsorption processes at this time are all physical adsorption or form hydrogen bonds. The activation energy in this paper is obtained at the early stage in the adsorption process. Therefore, the results of this paper further support that physical adsorption is the first step to occur during the adsorption process of dye molecules. The dye adsorption mechanism can be reasonably inferred: when the dye molecule is adsorbed, the two groups undergo adsorption reaction on the film surface with two steps. The adsorption behavior of the first adsorbed group is physical adsorption, and the adsorption behavior of the other adsorbed group is chemical adsorption. Another possibility is that the two adsorption groups physically adsorb at the same time, and then convert to chemical adsorption. In addition, the molecular structure of N719 and N3 only differs in their adsorption groups, but the calculated adsorption energy values are indeed slightly different, so it can be inferred that the adsorption mechanisms of N719 and N3 are not the same.

The co-adsorbent CDCA can carry out the adsorption reaction on the film surface. However, it is still uncertain whether the CDCA performs physical adsorption, chemical adsorption, or performs both adsorptions on the film. The result obtained in this paper is that the activation energy of the co-adsorbent CDCA is greater than 40 kJ mol^{-1}, and it can be inferred that chemical adsorption is performed. Harms *et al.* showed that by washing the CDCA on the film surface, only a small part of the CDCA molecules can be permanently adsorbed on the film surface.[13] This result is similar to the result of our previous work.[24] The remaining part of the strongly adsorbed molecules on the film may be chemically adsorbed with the film. Because the CDCA molecule has OH or COOH groups, they tend to form hydrogen bonds.[25] Simply dividing the physical and chemical adsorption by the activation energy cannot fully explain the bonding of CDCA. The most likely mechanism involves both chemical adsorption and physical adsorption.

3.2 Isotherm adsorption study

For the adsorption reaction on the surface of the molecular film, the Langmuir and Freundlich isotherm adsorption models are commonly used to describe this process, which has been described in detail in many literatures.[26] Here is only a brief description.

The hypothetical conditions of the Langmuir isotherm adsorption model include: (1) the molecule is subjected to single-molecule adsorption on the solid surface; (2) the adsorption of the molecule on the solid surface is uniform; and (3) there is no interaction between the adsorbed molecules. The Langmuir isotherm adsorption model is:

$$q_t = q_{max} \times \frac{c \times K_{eq}}{1 + c \times K_{eq}} \qquad (5)$$

Since the relationship between the frequency and mass is a constant factor relationship, frequency still replaces mass here. In eqn (5), q_t represents the adsorption capacity (Hz) when the adsorption reaction equilibrium is reached, q_{max} represents the maximum adsorption capacity (Hz) achieved under ideal adsorption, c represents the solution concentration at equilibrium (mM), and K_{eq} represents the adsorption rate constant (M^{-1}) in the adsorption equilibrium state. The adsorption data obtained when the adsorption of the N719, N3, N749, and CDCA solutions reaches equilibrium under different temperatures and concentration experimental conditions are extracted, and eqn (5) is utilized to fit the data to obtain the q_{max} and K_{eq} parameters of N719, N3, N749 and CDCA, as shown in Table 2.

The characteristics of the Langmuir isotherm adsorption equation can also express its adsorption performance by its other dimensionless characteristic parameter R_L:[27,28]

$$R_L = \frac{1}{1 + K_{eq} C_0} \qquad (6)$$

In eqn (6), C_0 represents the highest initial solute concentration, and K_{eq} represents the equilibrium constant of the adsorption rate under the equilibrium state.

R_L has a different significance in the characterization of the adsorption curves in different numerical ranges. $R_L = 0$ for the irreversible case, $0 < R_L < 1$ for the favorable equilibrium, $R_L = 1$ for the linear case, $R_L > 1$ for unfavorable equilibrium.[27,29] The dimensionless parameter R_L is between 0.16 and 0.44, which is in accordance with the favorable equilibrium of $0 < R_L < 1$.

The Freundlich model is an empirical equation, without assumptions, the expression is:

$$q_e = K_f c_e^{1/n} \qquad (7)$$

In eqn (7), q_e is the adsorption capacity (Hz) when the adsorption reaction equilibrium is reached, c_e is the concentration of the solution at adsorption equilibrium, K_f is the adsorption rate equilibrium constant $(Hz\ M^{-1/n})$ under the Freundlich model, and n is the Freundlich constant, larger K_f and n values are signs of better adsorption performance. Fig. 4 shows the fitting curves of the Langmuir and Freundlich

Table 2 Parameters of the isotherm models used to fit the adsorption equilibrium data for N719, N3, N749 and CDCA onto the TiO_2 surfaces

Molecule	Langmuir isotherm				Freundlich isotherm		
N719	K_{eq} $(\times 10^4\ M^{-1})$	q_{max} (Hz)	R_L	R^2	K_f $(\times 10^3\ Hz\ M^{-1/n})$	n	R^2
280 K	1.54	300.99	0.23	0.99	4.01	2.60	0.98
296 K	1.89	377.52	0.19	0.99	4.50	3.10	0.94
308 K	2.20	422.81	0.16	0.99	4.90	3.20	0.96
N3							
280 K	1.10	457.44	0.44	0.99	6.57	2.27	0.95
296 K	1.30	480.65	0.26	0.98	6.87	2.37	0.94
308 K	2.30	489.31	0.17	0.99	7.13	3.22	0.97
N749							
280 K	1.76	291.35	0.30	0.99	2.28	2.28	0.96
296 K	2.08	311.11	0.30	0.99	2.70	2.70	0.99
308 K	2.40	346.00	0.27	0.99	2.90	2.90	0.98
CDCA							
280 K	0.037	144.38	0.17	0.89	0.53	2.98	0.99
288 K	0.048	164.18	0.16	0.90	0.54	3.36	0.98
296 K	0.050	180.09	0.16	0.82	0.58	3.39	0.99

isotherm models of adsorption of the N719, N3, N749, and CDCA solutions, respectively.

Table 2 shows the parameters obtained by fitting the Langmuir and Freundlich isothermal models. The fitting results show that the adsorption reaction of the three dyes on the film is more consistent with the Langmuir model, which is similar to the results reported in the literature.[30–32] The adsorption characteristics of the co-adsorbent CDCA are more consistent with the Freundlich model. This result is consistent with the previous experimental results of our group using the QCM flow cell.[24] It indicates that the adsorption reaction of the CDCA molecules on the surface of TiO_2 may not meet Langmuir's assumptions.

Whether a dye or co-adsorbent molecular adsorption process, as the experimental temperature changes from low to high, the q_{max} frequency increases correspondingly. During the preparation of the DSC devices, the sensitization process of the dye and semiconductor film is carried out at room temperature. The parameters at room temperature have practical guiding significance for the performance of DSC. When the temperature is close to room temperature (296 K), $q_{max}(N3) > q_{max}(N719) > q_{max}(N749) > q_{max}(CDCA)$. q_{max} is the theoretical maximum adsorption capacity obtained under the same film surface area in this paper. The order of the molar mass of several molecules is: $M_{(N749=1364.98\ g\ mol^{-1})} > M_{(N719=1187.7\ g\ mol^{-1})} > M_{(N3=705.64\ g\ mol^{-1})} > M_{(CDCA=392.57\ g\ mol^{-1})}$. The molecular molar mass does not correspond to q_{max}. The difference in q_{max} may be caused by the average area per molecule (APM).[21] The calculation results of the APM of the molecules are different in different works of literature due to different techniques being used. Cole et al. can roughly estimate the APM of the molecule by using the same technique.[21] For example, the APM of N719 is about 128.2 $Å^2$, and the APM of N3 is about 85 $Å^2$. Therefore, although the molar mass of the N719 molecules is larger than that of the N3 molecules, its surface concentration is lower. There is another
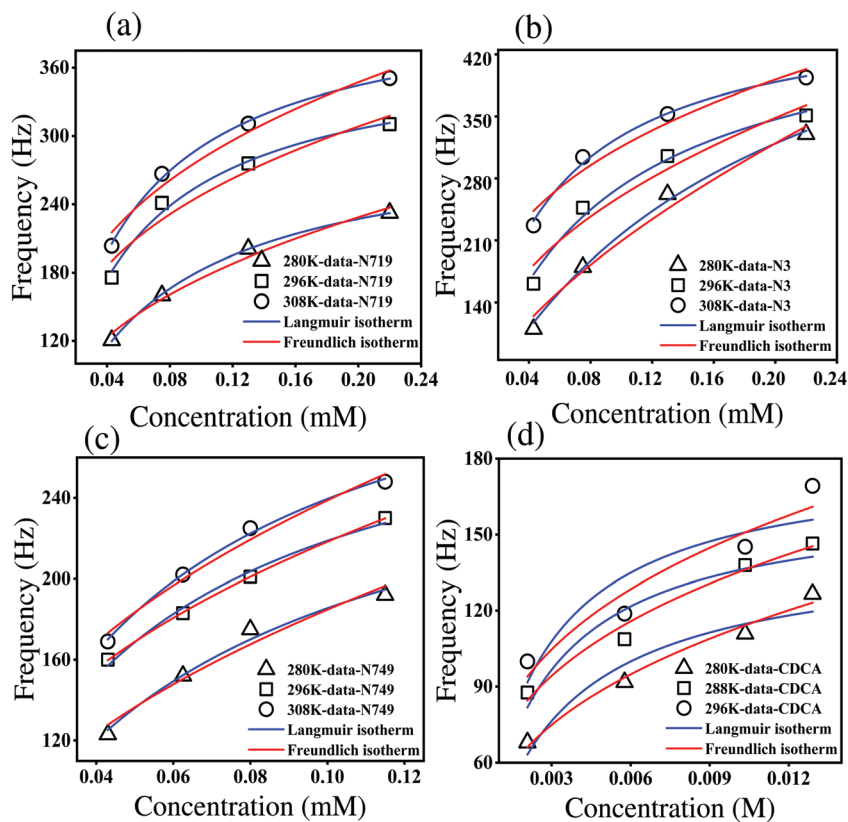
Fig. 4 Fitting of the Langmuir and Freundlich models: the adsorption process of (a) N719, (b) N3, (c) N749, and (d) CDCA.

reason: N719 molecules contain TBA$^+$ ions, which may be adsorbed on the surface, resulting in a larger APM.[21] The N749 molecule used in this paper contains three TBA$^+$ ions, so the APM is estimated to be larger.

Due to the same film structure, the ratio of the surface molecules in the maximum adsorption state of N719, N3, N749 and CDCA can be estimated. It is assumed that the number of adsorption sites on the TiO$_2$ surface is the same. The number of CDCA molecules is used for normalization, so the ratio of the number of surface molecules is $n_{(N719)}:n_{(N3)}:n_{(N749)}:n_{(CDCA)} = 0.69:1.48:0.50:1$. The molecular structure of N749 does not contain a proton. It may not completely cover the entire TiO$_2$ surface due to electrostatic repulsion, resulting in the lowest number of N749 surfaces. Literature studies show that the surface coverage of N749 is 30% lower than the full monolayer coverage.[33] Since N3 contains four COOH groups in its molecular structure, it is most prone to causing agglomeration and multi-layer adsorption.[4] The number of surface molecules of N719 is smaller than that of N3. Although N719 removed two protons and retained only two COOH groups, the agglomeration could not be completely eliminated. The number of CDCA molecules was only lower than that of N3. The competition mechanism between CDCA and the dyes was reported, which reduced the amount of dyes on the surface of TiO$_2$. The uncovered part of the TiO$_2$ surface is a way for electrons to undergo a composite reaction, which causes a decrease in the photoelectric conversion of the cell.[8] Theoretically, one dye

molecule leaves two adsorption sites on the surface of TiO$_2$, and then two CDCA molecules can be adsorbed. CDCA is co-adsorbed on the surface with dye molecules to form a physical barrier to inhibit the occurrence of dark current.

K_{eq} is an equilibrium constant obtained when the molecular adsorption rate and desorption rate reach dynamic equilibrium. K_{eq} is related to the combination strength of molecules on the TiO$_2$ surface.[34] The K_{eq} of the three dyes is not significantly different, but the K_{eq} value of CDCA is about two orders of magnitude smaller than that of the dye molecule. This indicates that the adsorption strength of CDCA is much weaker than that of all of the dye molecules. Our previous results also support this conclusion.[24] After CDCA is adsorbed to the TiO$_2$ film and washed with absolute ethanol, the amount of CDCA remaining on the surface of the film is very small.

In terms of the variation rule of Freundlich's adsorption rate constant K_f, the K_f variation of each molecule increases with the increase of temperature, which proves that the increase of temperature has a positive effect on the adsorption process of the three dyes. Another constant n of Freundlich can reflect the degree of non-linearity between the adsorbent concentration and adsorption capacity.[35] The fitting n values of the N719, N3, N749 and CDCA molecules are all greater than 1, and all increase with the increase of temperature, that is, the $1/n$ value decreases with the increase of temperature. This shows that the adsorbent has good adsorbability, and the ease of adsorbtion increases with decreasing $1/n$ value.[36]

3.3 Thermodynamic study

The thermodynamic principle is used to study the above four molecules, mainly for the following parameters: adsorption enthalpy ΔH, adsorption entropy ΔS, and Gibbs free energy ΔG. The van't Hoff equation is commonly used in the study of adsorption thermodynamics to calculate the above three thermodynamic parameters.[37] The van't Hoff equation is an equation used to calculate the equilibrium constant of a certain adsorption reaction at different temperatures:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{8}$$

Integrate in eqn (8):

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

$$\Delta G = -RT \ln K \tag{10}$$

From eqn (9) and (10), we can get:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

Therefore, a straight line is generally obtained by fitting the natural logarithm $\ln K$ of the rate equilibrium constant to the corresponding reciprocal $1/T$ of the temperature. The slope of this straight line is $\Delta H/R$, and the intercept of the straight line is $\Delta S/R$. The thermodynamic equilibrium constants of N719, N749, N3 and CDCA in this paper can be expressed by the parameter K_{eq} in the Langmuir isothermal adsorption model. The adsorption frequency data of the N719, N3 and

CDCA solutions obtained from QCM are fitted by the van't Hoff equation, as shown in Fig. 5.

The ΔH of N719, N3, N749 and CDCA in Table 3 is more than 0, which indicates that the adsorption reaction of the three dyes and co-adsorbent solutions on the TiO$_2$ surface is endothermic.[29,38] The ΔS of N719, N3, N749 and CDCA is ΔS(N3 = 143.11 J mol^{-1}) > ΔS(N719 = 112.72 J mol^{-1}) > ΔS(N749 = 109.43 J mol^{-1}) > ΔS(CDCA = 96.14 J mol^{-1}). ΔS is more than 0, which indicates that as the temperature increases, the randomness of the adsorption reaction between molecules and the solid TiO$_2$ surface increases, that is, the degree of chaos increases.[29,38]

In Table 3, the Gibbs free energy ΔG of N719, N3, N749 and CDCA are all negative, and ΔG gradually decreases with the increase of temperature, which indicates that the adsorption reaction of the four solutions on the surface of the TiO$_2$ film is spontaneous. The driving force of the adsorption process increases with increasing negative value of ΔG.[29,38] What needs to be explained here is that there is a certain deviation caused by utilizing the Langmuir model to fit the CDCA adsorption process. When using the van't Hoff equation in this paper, we still use K_{eq} in the Langmuir model. Thus, there may be a certain error in the Gibbs free energy of the obtained CDCA.

4. Conclusion

In this paper, QCM is used to study the kinetic and thermodynamic processes of dyes (N719, N3, N749) and co-adsorbent CDCA on the surface of the film. Among the three dyes, the adsorption rate of N749 is slightly higher than the other two dyes. The adsorption rate of CDCA is more sensitive to temperature changes. The activation energies of N3, N719 and N749 are all less than 40 kJ mol^{-1}. The results of this paper can reasonably infer the dye adsorption mechanism: when the two groups of the dye molecule are adsorbed, it is divided into two steps: first, one adsorption group undergoes physical adsorption, and then the other adsorption group conducts chemical adsorption. Alternatively, both adsorption groups undergo physical adsorption first, and then convert to chemical adsorption. The activation energy of the co-adsorbent CDCA is greater than 40 kJ mol^{-1}, and it can be inferred that chemical adsorption is performed.

The study of the isotherm adsorption model in this paper shows that N719, N3 and N749 conform to the Langmuir model, while CDCA conforms to the Freundlich model. When the temperature is close to room temperature (296 K), q_{max}(N3) > q_{max}(N719) > q_{max}(N749) > q_{max}(CDCA). The ratio of the number of
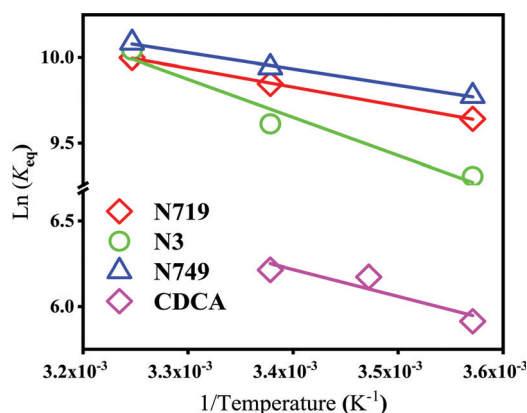

Fig. 5 Van't Hoff plots for the adsorption of N719, N3, N749 and CDCA onto the TiO$_2$ surfaces.

Table 3 Thermodynamic parameters for the adsorption of N719, N3, N749 and CDCA onto the TiO$_2$ surfaces at different temperatures

Molecule	ΔH (kJ mol^{-1})	ΔS (J mol^{-1})	ΔG (kJ mol^{-1}) 280 K	ΔG (kJ mol^{-1}) 296 K	ΔG (kJ mol^{-1}) 308 K
N719	9.12	112.72	−22.44	−24.24	−25.60
N3	18.49	143.11	−21.58	−23.87	−25.59
N749	7.89	109.43	−22.75	−24.50	−25.81
	ΔH (kJ mol^{-1})	ΔS (J mol^{-1})	ΔG (kJ mol^{-1}) 280 K	ΔG (kJ mol^{-1}) 288 K	ΔG (kJ mol^{-1}) 296 K
CDCA	13.07	96.14	−13.84	−14.61	−15.38

surface molecules is $n_{(N719)} : n_{(N3)} : n_{(N749)} : n_{(CDCA)} = 0.69:1.48: 0.50:1$. The K_{eq} values of the three dyes are not significantly different, but the K_{eq} value of CDCA is about two orders of magnitude smaller than that of the dye molecule, which indicates that the adsorption strength of CDCA is much weaker than that of the dye molecule.

Thermodynamic studies show that $\Delta H > 0$, which indicates that the adsorption reaction of the three dyes and co-adsorbent molecule on the TiO$_2$ surface is an endothermic reaction. The ΔS is $\Delta S(N3 = 143.11$ J mol$^{-1}) > \Delta S(N719 = 112.72$ J mol$^{-1}) > \Delta S(N749 = 109.43$ J mol$^{-1}) > \Delta S(CDCA = 96.14$ J mol$^{-1})$. The Gibbs free energy ΔG is negative, and ΔG gradually decreases with the increase of temperature. This indicates that the adsorption reaction between the four molecules and the surface of the TiO$_2$ film is a spontaneous reaction process.

The results of this paper show that the tedious and lengthy experimental process of the traditional method can be simplified by QCM. In addition, the mass variations of the visible light transparent CDCA molecules on the surface is measured *in situ* under the changing ambient temperature, and the adsorption kinetics and thermodynamic characteristics can be obtained.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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