New Insights into the Fundamental Principle of Semiconductor Photocatalysis

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ABSTRACT: Although photocatalysis has been studied for many years as an attractive way to resolve energy and environmental problems, its principle still remains unclear. Some confusions and misunderstandings exist in photocatalytic studies. This research aims to elaborate some new thoughts on the fundamental principle of semiconductor photocatalysis. Starting from the basic laws of thermodynamics, we first defined the thermodynamic potential of photocatalysis. A concept, the Gibbs potential landscape, was thus then proposed to describe the kinetics of photocatalysis. Photocatalysis is therefore defined as a light-driven chemical reaction that still needs heat activation, in that light and heat play their different roles and interact with each other. Photocatalysis should feature an activation energy functioning with both light and heat. The roles of light and heat are correlative and mutually inhibit at both levels of thermodynamics and kinetics, so it is impossible for an intrinsic light−heat synergism to happen. Two criteria were further proposed to determine an intrinsic light−heat synergism in photocatalysis. Experiments were also carried out to calculate the thermodynamic potential and can agree well with the theory. Experimental results proved that there is no intrinsic light−heat synergism, in accordance with our theoretical prediction. This research clarified some misunderstandings and gained some new insights into the nature of photocatalysis; this is important for the discipline of semiconductor photocatalysis.

1. INTRODUCTION

Photocatalysis helps address environmental and energy issues by using sunlight and has drawn much attention in the world over the last 50 years.[1−5] Different from classical thermocatalysis, its scientific nature depends on both light and heat.[6−8] Although many efforts have been taken to study photocatalysis over decades,[9−13] there still remain some confusions and misunderstandings on its principle, which must be clarified at deep and general levels.[14−19]

The kinetic processes involved in semiconductor photocatalysis are elaborated in Figure 1.[3,4,8] Light illumination excites the electronic transition from the valence band (VB) o the conduction band (CB) of a semiconductor; the generated electrons and holes then experience subsequent recombination and transfer to their acceptors. Figure 1B illustrates the band potentials, reduction potential of electron acceptors, and oxidation potential of hole acceptors. The more negative CB potential and more positive hole potential let the electrons and holes be capable of causing reduction and an oxidation effect,[19] such as hydrogen and oxygen evolution from water.[20] Figure 1 is the viewpoint that is popularly used to explain photocatalysis in literature.

Except for light excitation, the other processes are all dependent on temperature (T) to some extent; for example, it has been revealed that the electron−hole recombination in TiO$_2$ materials increases with temperatures because of the trapping effect;[1,21,22] the transfer (processes 3 and 4 in Figure 1A) of electrons and holes to their acceptors, such as O$_2$ and
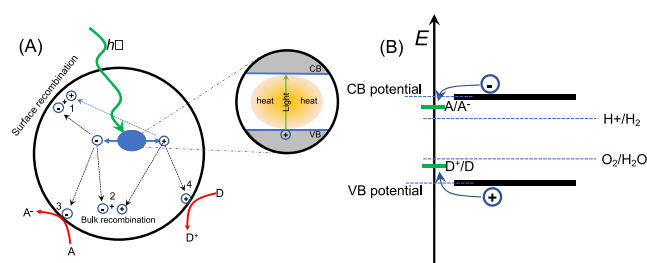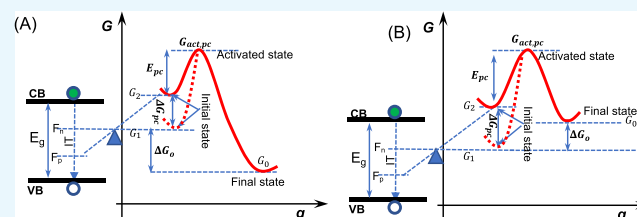

Figure 1. (A) Schematic of the kinetic processes of the charge carriers (holes and electrons) generated from the electronic transition from the valence band to the conduction band under light illumination. (1. Surface recombination; 2. Bulk recombination; 3. Electron transfer; 4. Hole transfer). The electron transfer and hole transfer are in direct connection with the photocatalytic effect. (B) Diagrammatic comparison between the band potentials (the conduction band potential and the valence band potential) and the reduction potential of an electron acceptor (A/A$^-$) and the oxidative potential of a hole acceptor (D/D$^+$). The electric potentials of hydrogen evolution and oxygen evolution are also shown. The electrons and holes can be generated by light-induced electronic excitation; they can also be generated by heat via the lattice−electron interaction in a statistic way.[3,4,8]
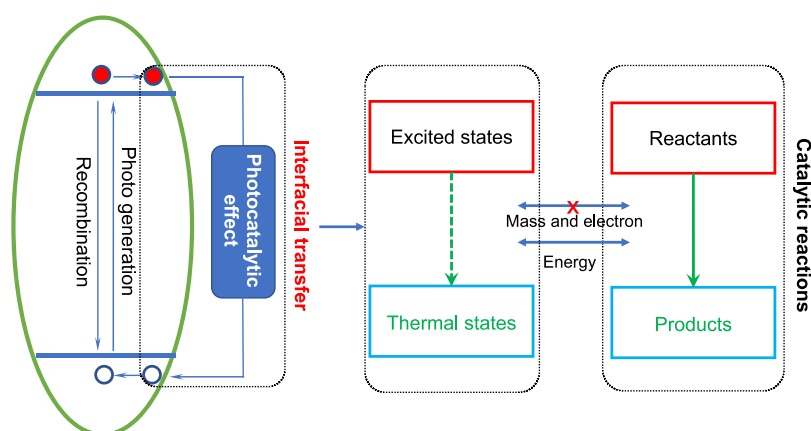
Figure 2. Relation between the interfacial transfer of electrons from the CB to the VB of a semiconductor and the induced photocatalytic effect.

water, was also found to be T-dependent.[23−27] A number of studies have observed that the apparent kinetics of photocatalysis, including organic photocatalytic oxidations (PCO) and water photocatalytic splitting, feature heat activation.[28,29] As the occurrence of photocatalysis needs heat assistance, photocatalysis has a thermodynamic potential.

The thermodynamic potential should be the most intrinsic thermodynamic problem for photocatalysis. Based on our understanding, the standpoint of Figure 1 might lead us to take the energy difference between the CB and VB potentials as the thermodynamic potential of photocatalysis.[30,31] Heat can generate holes and electrons in a statistical way.[32] As there is no difference in the absolute internal energies (U) of the light- and heat-induced charge carriers, Figure 1B also means that heat can drive the reactions happening in a photocatalytic way. For example, it has been thought that formaldehyde can be oxidized by heat-induced charge carriers in the dark;[33] this however cannot agree with the second law of thermodynamics in that the U cannot be the thermodynamic potential in an isothermal and isobaric system like photocatalysis. Therefore, what is the thermodynamic potential remains unclear and needs a clear elaboration.

Because of insufficient recognition of the thermodynamic potential, the intrinsic role of heat in photocatalysis is not well understood. Some common viewpoints might mistake the role of light with that of heat. Many publications said that light activates photocatalysis; it seems that photocatalysis does not need the assistance of heat; this is however in contrast to the experimental results that reported the existence of heat barriers in photocatalysis.[27−29] There are also some inconsistent studies on the role of heat. Some studies reported that heat can have a synergism with light in photocatalytic reactions. For example, Li et al. reported that heat can couple with light to increase the PCO of benzene over TiO_2 at elevated temperatures.[34] In addition to TiO_2, such synergism was also proposed in the PCOs over other materials, such as ZnO, WO_3, and titanate.[35−38] Many studies also attributed the increase of PCO rates at elevated temperatures to the normal activation of heat and did not claim a synergism.[27−29,39] Whether and how heat can correlate with light in photocatalysis were not well elaborated in literature. The role of heat thus needs a fundamental clarification on a general level.

Starting from the laws of thermodynamics, the present research first defined the thermodynamic potential of semiconductor photocatalysis and elaborated the roles of heat and light in thermodynamics. A Gibbs free energy potential (G-

potential) landscape was then proposed to illustrate the roles of light and heat as well as their correlation in kinetics. Based on the G-potential landscape, a heat activation model was advanced to describe the kinetics of photocatalysis. Photocatalysis is then defined as a light-driven chemical reaction activated by heat. It was clarified that it is impossible for light and heat to have a synergism because they are correlatively inhibited. Experiments were carried out to obtain the thermodynamic potential and compared with the theory. The effects of temperature and light intensity (I) on photocatalysis were studied by experiments; this also showed good consistence with the theory. After ruling out a thermocatalytic contribution, some research studies meant that a light−heat synergism can be defined if the photocatalytic rates at elevated temperatures are higher than those at low temperatures.[35−39] As photocatalysis contains heat processes that are dependent on temperatures in a Boltzmann statistical way, their definition to a light−heat synergism is inappropriate and will lead to misunderstandings. Two criteria were thus proposed to determine an intrinsic light−heat synergism in photocatalysis. The PCOs of acetone and formaldehyde over TiO_2 were re-examined with the proposed criteria; this showed that the photocatalytic reactions do not involve a light−heat synergism, reconciling our theory with the studies that claimed the synergism.

The G-potential landscape in form unifies the thermodynamics and kinetics of photocatalysis to that of classical thermocatalysis. This allows us to think of photocatalysis in reference to thermal activation theory. It is thus hopeful that our ideas can deepen and widen the knowledge of photocatalytic science and help develop photocatalysis discipline.

2. THEORETICAL ILLUSTRATION

2.1. Roles of Light and Heat in Thermodynamics. Could heat drive photocatalysis? This question associates with the thermodynamic nature of photocatalysis. The standpoint of Figure 1 indicates that heat can also cause a catalytic effect similar to photocatalysis; this however conflicts with the second law of thermodynamics. The second law of thermodynamics requires that the S (or the U) of an isolated system increases (decreases) to a maximum (or a minimum) until it reaches a thermodynamic equilibrium state in an irreversible process. Photocatalysis happens irreversibly under isothermal and isobaric conditions, so instead of the S and U, the G is its thermodynamic potential and tends to reduce itself
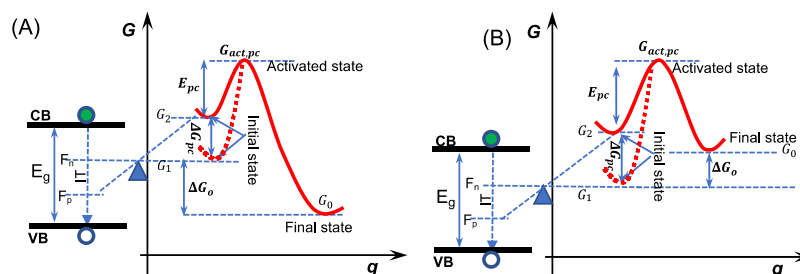
Figure 3. (A) Gibbs free energy landscape (G-potential landscape) of downhill photocatalytic reactions via the IT, such as PCOs; (B) G-potential landscape (G-potential landscape) of uphill photocatalytic reactions via the IT, such as the water splitting and the CO_2 reduction.

until it reaches minimum at the equilibrium state. We will elaborate what is the G and how it determines the principle of photocatalysis.

We discuss this topic by taking a semiconductor as a thermodynamic system. The photoinduced electronic transition lets a semiconductor change from thermodynamic equilibrium to nonequilibrium excited states. The excited state has a high G position than the ground state because of the presence of the photoinduced charge carriers. The difference of their G positions (ΔG_{IT}) corresponds the quasi-Fermi level (quasi-E_F) splitting[32,40]

$$\Delta G_{IT} = -N_A \, |F_n - F_p| = -N_A E_g + RT \, \ln \frac{N_C N_V}{np} \qquad (1)$$

where F_n and F_p are the quasi-Fermi levels of the electrons and holes, E_g is the band gap, T is the absolute temperature, R is the idea gas constant, n and p are the densities of the electrons and holes, N_C and N_V are the effective densities of states at the CB and VB edges, R is the ideal gas constant, and N_A is the Avogadro constant.

The ΔG_{IT} becomes negative under light illumination; this drives the flow of the electrons from the CB to VB via the interfacial transfer (IT) that simultaneously induces a photocatalytic effect, as shown in Figure 2. It means that the ΔG_{IT} is the thermodynamic driving force of photocatalysis, and the G of the excited state of a semiconductor is the thermodynamic potential of photocatalysis. Therefore, it can be known that, although organic oxidations are downhill in thermodynamics, their occurrence in a photocatalytic way is not spontaneously allowed but needs a thermodynamic potential; this is different from thermocatalysis. Under an equilibrium state, ΔG_{IT} becomes 0 according to the mass action law. The IT of electrons thus cannot happen in this case, as is photocatalysis. Therefore, heat cannot drive a reaction to happen in a photocatalytic way no matter how high the temperature is. The large difference between heat and light in their energy is not the intrinsic reason to distinguish their roles in photocatalysis, so the number of charge carriers do not determine the thermodynamics of photocatalysis. The attribution of dark catalysis to the heat-induced charge carriers is incorrect.[24]

Then, could heat affect the role of light in thermodynamics? We start from the first law of thermodynamics to discuss this question. The absolute inner energy (ΔU) of the electrons and holes can be transferred as a chemical work and heat dissipation to the environment according to eq 2.

$$\Delta U = \Delta A + \Delta Q \qquad (2)$$

We first discuss the reversible case; the first law of thermodynamics can be replaced with the Gibbs equation (the eq 3), which shows that the ΔG_{IT} is less than the ΔU by

an entropy term, $T\Delta S$, representing the nonavailable energy (here, ΔU is the product of N_A and E_g of a semiconductor).[32,40]

$$\Delta U = \Delta G_{IT} + T\Delta S \qquad (3)$$

The comparison of eqs 1 and 3 shows that the $T\Delta S$ in the IT is[40]

$$T\Delta S = RT \, \ln \frac{N_C N_V}{np} \qquad (4)$$

The statistical population of electrons and holes at the CB and VB states leads to the $T\Delta S$ term because the densities of photoinduced states only represent a small fraction of the densities of ground states. The ΔU includes the ΔG_{IT} and the $T\Delta S$. The ΔG_{IT} is the effective chemical work, and the $T\Delta S$ is a spontaneous heat loss. The above description took an assumption of a reversible process. Because photocatalysis is irreversible, the real chemical work ($|\Delta G_{pc}|$) that drives the electron IT and the photocatalytic effect is smaller than the $|\Delta G_{IT}|$, and the real heat loss (ΔQ_{pc}) happening in the IT is higher than the $T\Delta S$. Therefore, the first law of thermodynamics in photocatalysis is described with

$$\Delta U = \Delta G_{pc} + \Delta Q_{pc} \qquad (5)$$

Because the n and p increase with the I, eq 4 shows that the T and I have opposite effects on the $T\Delta S$, so the ΔG_{IT}. It is reasonable to assume that the T and I have opposite effects on the ΔG_{pc} and the ΔQ_{pc}. Therefore, the universal entropy increase principle leads to a mutual inhibition between light and heat in their thermodynamic roles, and a light–heat synergism cannot be defined in thermodynamics.

Thus, photocatalysis can be described from an energetic viewpoint. Figure 2 shows that the transfer of a semiconductor from the excited to the thermal-equilibrium states does not release electrons or mass; therefore, this in fact means that photocatalysis results from an energy transfer.

2.2. Roles of Heat and Light in Kinetics. As stated above, photocatalysis involves the generation of the charge carriers and the subsequent electron IT. The charge carrier generation is temperature-independent, but the electron IT is dependent on temperatures. By taking the irreversible feature into account, Figure 3 proposes the G-potential landscape of photocatalysis. The ΔG_{pc} of eq 5 is transferred to the photocatalytic reactants and promotes their initial G position (from G_1 to G_2); this opens new pathways for both downhill (Figure 3A) and uphill (Figure 3B) photocatalytic reactions. In the uphill cases, such as the water splitting and the CO_2 reduction, when the G_2 is higher than the G of the final state (G_0), the uphill reactions become thermodynamically available,

with part of the ΔG_{pc} being stored in chemical bonds.[41−43] However, in the downhill cases, such as PCOs, the initial G position (G_1) is not needed to be promoted to generate the thermodynamic driving force. It is considered that the energy transfer changes the pathways of organic oxidations by altering the heat activation of reactant species via the electron IT. How the ΔG_{pc} is transferred to reactants relies on the detailed microscopic mechanism of electron IT; this is not the purpose of our study.

The initial state of photocatalysis includes the excited semiconductor and the photocatalytic reactants; the final state contains the thermal semiconductor and the photocatalytic products. The change in energy states of a semiconductor shows that photocatalysis cannot be classified as a conventional catalysis.[44] A photocatalytic reaction via the electron IT (Figure 2) is written as

$$SC^{illuminated} + reactants \rightarrow SC^{Themal} + products \tag{6}$$

where $SC^{illuminated}$ and $SC^{Thermal}$ denote the semiconductors at the excited and the thermal equilibrium states, respectively. Based on the Euler equation, the total ΔG is the sum of chemical potentials (μ_i) and particle number (N_i) of all species. The G of the final state is constant, while that of the initial state changes with the G of the excited semiconductor.

The photocatalytic rate can be described by

$$\nu \approx k[reactants] \tag{7}$$

The roles of light and heat are enclosed in the apparent reaction rate constant (k). The k relates to temperatures in Arrhenius mode.

$$k = k_0 \exp\left(-\frac{E_{pc}}{RT}\right) \tag{8}$$

where E_{pc} is the real activation energy of photocatalysis. Statistically, k_0, the pre-exponential factor, is determined by thermal vibrations of reactants, which does not depend on light. Referring to the G-potential landscape, the G-difference between the $G_{act,pc}$ and the G_2 corresponds to the E_{pc}. If a photocatalytic reaction is assumed to proceed in a reversible way, eq 8 can be changed to eq 9. The real k of photocatalysis is smaller than eq 9 because of its irreversible feature.

$$k = k_0 \frac{np}{N_C N_V} \exp\frac{-(G_{act,pc} - G_1 - N_A E_g)}{RT} \tag{9}$$

Equation 9 shows that k is proportional to the n and p, in line with the prediction of Figure 1. Based on the G-potential landscape and eq 1, E_{pc} can be described as eq 10 in the reversible case. Although the real E_{pc} of a photocatalytic reaction is larger than eq 10 because of the irreversible feature, we can still use this formula to discuss the effects of T and I on the kinetics of photocatalysis.

$$E_{pc}(I, T) = G_{act,pc} - G_1 - N_A E_g + RT \ln\frac{N_C N_V}{np} \tag{10}$$

It can be seen that the above description on the photocatalytic kinetics is the same as that of thermocatalysis. It should be noted that the experimentally derived activation energy (E_{act}) is different from the E_{pc}, because the last term of eq 10 is proportional to temperatures. The kinetics of photocatalysis is different from that of thermocatalysis because the E_{pc} decreases with the I and increases with the T, so light and heat have inverse effects. An intrinsic light−heat synergism

thus cannot be defined in the kinetics of photocatalysis. The G-potential landscape shows that the photocatalytic activity can be increased by increasing the G_2 position and decreasing the $G_{act,pc}$ position (Figure 3). Inhibiting recombination or increasing light intensities increase the photocatalytic rates by upshifting the G_2 position;[45,46] this does not affect the E_{act}.[47] Surface decorations with cocatalysts or defects might change the photocatalytic rates by lowering the $G_{act,pc}$ position, so the E_{act} may be reduced. For example, we showed that Cu dopants can reduce the E_{act} of acetone PCO over TiO_2.[48] It is thus important to study the effect of surface decoration on the E_{act} so as to have a deep understanding of the nature of photocatalysis.

Based on the above discussion, we thought that the usual statement of light activating photocatalysis might be misunderstood as to the role of light compared with that of heat. The G-potential landscape indicates that this statement should be inappropriate as light solely cannot transfer reactants to activated states without heat assistance. This is in accordance with many experiments, as stated above. For example, the photocatalytic CO_2 reduction and ethylene epoxidation are dependent on temperature.[49,50] Our previous study and other first principle study further revealed that the electron IT to O_2 include heat activation.[27,47] It is thus considered by us that photocatalysis in principle is a reaction driven by light and activated by heat.

2.3. Rigorous Definition of a Light−Heat Synergism. The above illustration shows that light and heat are mutually inhibited. This is in contrast to some studies that reported a light−heat synergism at elevated temperatures.[34−39] In many cases, the intermediates and final products (sometimes including carbonate or soot deposition) block active sites. Elevated temperatures help clean surfaces and might lead to an apparently meaningful light−heat synergism. In our opinion, this however cannot be taken as the intrinsic light−heat synergism, which could be confused in these studies. Therefore, the light−heat synergism should be carefully re-examined at a more rigorous level. In addition, we thought that the way used in defining a light−heat synergism is inappropriate in some studies. They considered that, by taking the thermocatalytic contribution out, a light−heat synergism can be obtained if the photocatalytic rates at elevated temperatures are higher than that at ambient temperatures. This will lead to an unrealistic result that almost all photocatalytic reactions involve a light−heat synergism because photocatalysis itself is heat-activated in principle. In any case, we cannot attribute the intrinsic role of heat to a heat−light synergism.

As we do not predict an intrinsic light−heat synergism in photocatalysis, the reconciliation of these results with our theory is needed. The number of particles participating in photocatalysis depends on heat and light in different manners. Heat activates reactants in the statistical way, so the number of activated particles depends on reciprocal temperature exponentially. Light affects the number of charge carriers sublinearly and linearly, depending on recombination types. Therefore, if heat has a synergism with light, the photocatalytic rates must be higher than that predicted by the Arrhenius formula, so the T-dependence of photocatalytic rates should bend upward in Arrhenius plots (Figure 4A, blue line). The downward-bending (Figure 4A, red line) and normal linear line (Figure 4A, black line) do not mean an intrinsic light−heat synergism. Similarly, if light has a synergism with heat, the
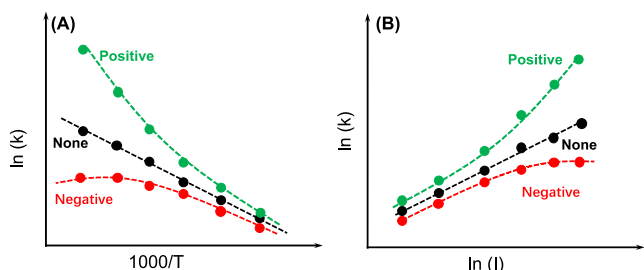
Figure 4. Kinetic diagram for determining the synergistic effect in semiconductor photocatalysis. (A) To determine the synergistic effect of heat on light; (B) to determine the synergistic effect of light on heat.

photocatalytic rates are higher than that predicted by a (sub-) linear mode in the log−log plot, so the *I*-dependence of photocatalytic rates will bend upward with the *I* (Figure 4B, blue line). Other cases (black line and red line) do not mean an intrinsic light−heat synergism.

3. EXPERIMENTAL VERIFICATION

3.1. Experimental Determination of the ΔG_{IT}.
The ΔG_{IT} is the thermodynamic driving force of photocatalysis. We will determine the ΔG_{IT} of the PCOs of acetone and discuss its connection to the *I* and the *T*. On-line electrical conductances were recorded to estimate the ΔG_{IT}. The electron transfer over PCOs is shown in Figure 5.[51] Upon UV light illumination,
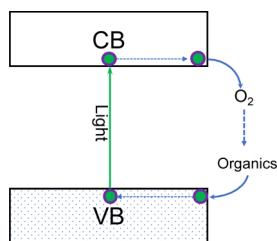

Figure 5. Schematic diagram of the electron IT pathway for organic PCO.

acetone molecules inject the electrons into the VB of TiO_2, which are then promoted to the CB and transfer to O_2. The kinetics of electron transfer to O_2 is slower than that of hole injection, so the electrons accumulate in the CB and contribute to the conductances. Because the holes are quickly consumed by acetone, the ΔG_{IT} is mainly contributed by the electrons according to eq 11.

$$\Delta G_{IT} = -N_A |F_n - F_{n_0}| = -RT \ln \frac{n}{n_0} \qquad (11)$$

where F_{n_0} denotes the dark Fermi level of electrons. As the conductances are proportional to the density of electrons, this can be written as

$$\Delta G_{IT} = -RT \ln \frac{\sigma(I)}{\sigma(0)} \qquad (12)$$

where $\sigma(I)$ and $\sigma(0)$ are the photoconductance and the dark conductance.

The effect of the light intensities and temperatures on the electric conductances and the acetone conversions (α) are shown in Figures S1−S4, respectively. Figure 6A shows the dependences of the ΔG_{IT} and the α on the light intensities, which show a correlation between them. Figure 6B shows the dependences of the ΔG_{IT} and the α with temperatures. This shows a different result that the decrease in the ΔG_{IT} accompanies an increase in the α. The increase of the ΔG_{IT} with the light intensities is attributed to the increased number of electrons; this can naturally increase the photocatalytic activity. Because the electron transfer to O_2 increases with temperatures,[52,53] so the density of electrons decreases with temperatures. The ΔG_{IT} accordingly decreases with temperatures according to eq 9. However, the decrease in the ΔG_{IT} does not mean a decrease in photocatalytic activity, because the increase in temperatures also increases heat activation. Therefore, it is seen that the increases of the light intensities and the temperatures have inverse effects on the ΔG_{IT}, so the E_{pc} changes inversely with respect to the light intensities and temperatures; this agrees well with our theoretical prediction.

3.2. Comparison between the Experimental Photocatalytic Rates and That Predicted from the Theory.
The relative change of the E_{pc} on the light intensities and the temperatures can be calculated from the electric conductances, based on which the relative changes in photocatalytic rates can be estimated from eq 6. By referring to the *G*-potential landscape, the photocatalytic rates at different light intensities are related to the photoconductances according to eq 13.

$$r(I) = \frac{k(I)}{k(I_0)} = e^{G_2(I) - G_2(I_0)/RT} = \frac{\sigma(I)}{\sigma(I_0)} \qquad (13)$$

where $k(I)$, $k(I_0)$, $\sigma(I)$, and $\sigma(I_0)$ denote the photocatalytic rate constants and the on-line photoconductances at the light intensity of I and I_0, respectively. I_0 is set as the reference I. The photocatalytic rates at different temperatures depend on the on-line conductances according to eq 14.
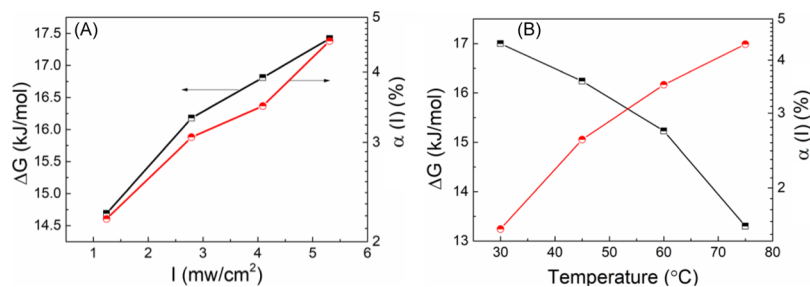

Figure 6. (A) Linear dependence of the ΔG_{IT} and semi-log dependence of the acetone conversions on the light intensities (A) and temperatures (B).
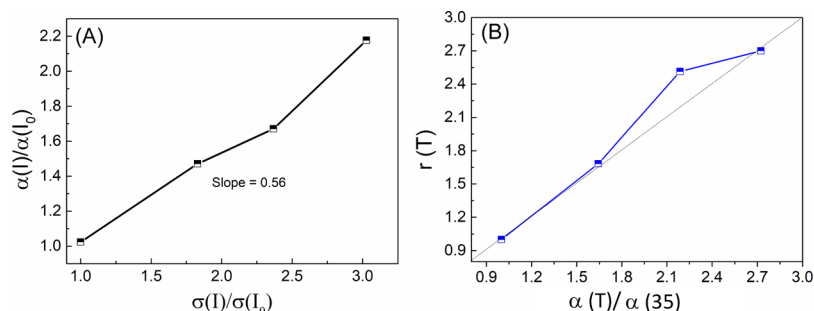
Figure 7. Correlation between the experimental-derived acetone photocatalytic conversions in the case of different light intensities (A) and temperatures (B).
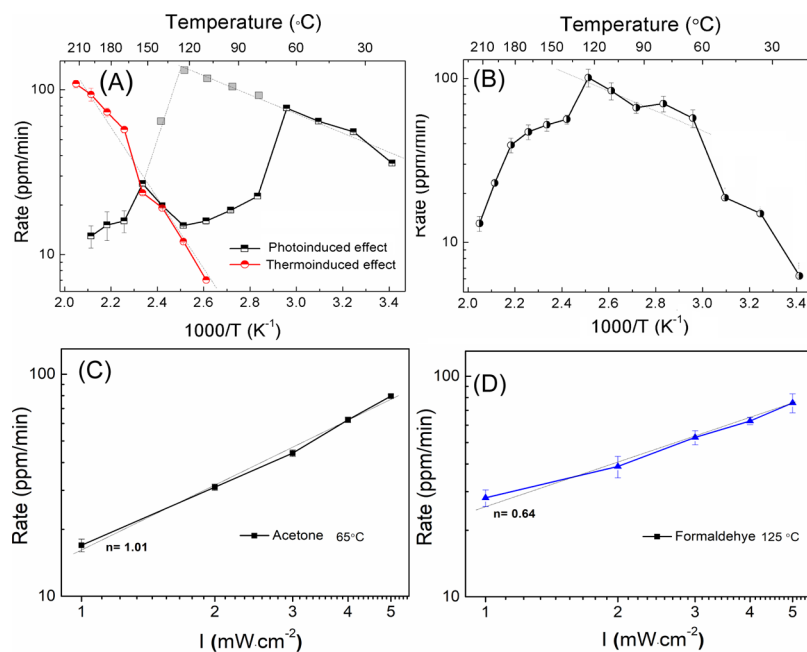

Figure 8. (A) Arrhenius plots of the PCOs and thermocatalytic oxidations of acetone by TiO$_2$ at different temperatures; (B) Arrhenius plot of the photocatalysis of the PCOs of formaldehyde over TiO$_2$ at different temperatures; (C) log−log dependence of the acetone PCO rates on light intensities (experiments were done at 65 °C); (D) log−log dependence of the formaldehyde PCO rates on light intensities (the experiments were done at 125 °C).

$$r(T) = \frac{k(T)}{k(T_0)} = e^{-E_0\left(\frac{1}{kT_1} - \frac{1}{kT_0}\right)} \frac{\sigma(T)}{\sigma(T_0)} \quad (14)$$

where $k(T)$, $k(T_0)$, $\sigma(T)$, and $\sigma(T_0)$ denote the photocatalytic rate constants and photoconductances at the temperatures of T and T_0, respectively. T_0 is set as the reference temperature, and E_0 is a constant.

The I_0 and the T_0 were set as 7.6 mW/cm^2 and 40 °C, respectively. We compared the correlations between the experimentally derived α and that estimated from eqs 13 and 14, as shown in Figure 7A,B, respectively. Figure 7A shows a close linear correlation that supports the role of light in increasing the photocatalytic activity by decreasing the E_{pc}. The line slope is 0.56, smaller than 1 as predicted in eq 13. The electrons first transfer to O$_2$ and then contribute to the PCO of acetone. Figure 7A means that the electron transfer to O$_2$ is faster than that contributing to photocatalysis. Our previous study showed that the electron transfer to O$_2$ contributes to the photoassisted O$_2$-sorption recombination.[44] This might lead to a fast change of photoconductances compared to the photocatalytic activity. In addition, the assumed kinetic model is based on the reversible case that cannot fully accord with the

real case. The photocatalytic rate predicted from a reversible model is naturally higher than the real irreversible case, in good accordance with the experimental results. It was reported that some intermediated products, including acetate and formate, can be formed during the PCOs of acetaldehyde.[13] We thought that similar products might also be formed in the course of acetone PCOs over TiO$_2$; this may block the active sites and lead to a decrease in photocatalytic rates as compared to the theoretical prediction, as shown in Figure 7A.

Eq 14 shows that the relation between experimental-derived α and $r(T)$ is more complicated. The term $\exp(-E_0(1/kT - 1/kT_0))$ is the function of heat activation; the term $\sigma(T)/\sigma(T_0)$ is the effect of temperatures on the ΔG_{IT}. It is seen from Figure 6B that the ΔG_{IT} decreases with temperatures, so the increase of acetone conversion with temperature is due to the role of heat activation. Figure 7B shows the correlation between the $r(T)$ and $\sigma(T)/\sigma(T_0)$ by setting the E_0 at 55 kJ/mol. According to Figure 3, the E_0 corresponds to the difference between $G_{act,pc}$ and G_1. The prediction of eq 14 can accord with experiments to some extent. However, eq 14 does not predict a pure Arrhenius mode as the experimentally

derived $\sigma(T)/\sigma(T_0)$ varied with temperatures; this shows that the predicted photocatalytic rates tend to decrease at elevated temperatures. Because the electron transfer is dependent on the temperatures, the electron density (n) in TiO_2 is also affected by the temperatures in addition to light intensities. Our theory predicts the T-dependence of photocatalytic rates on the premise that n is independent of temperatures. However, it is inevitable for n to change with temperatures. The increase of electron transfer results in a decrease in n with temperatures. Therefore, the change of the ΔG_{IT} indicated from $\sigma(T)/\sigma(T_0)$ is larger than that predicted from our theory, which assumes that n does not change with temperatures. This finally leads to the result that the photocatalytic rates predicted from eq 14 deviate from the experimental results.

3.3. Reconciliation of the Reported Light−Heat Synergism to Our Theory.

Temperatures were first varied to show whether heat can have a synergism with light in the PCOs of acetone over TiO_2. The catalytic rates were obtained from CO_2 evolutions at different temperatures in the presence and absence of light illuminations (Figures S5 and S6). As acetone can also be oxidized in the dark, pure photocatalytic rates were obtained by subtracting the total rates with that in the dark. Figure 8A shows the Arrhenius plots of the thermocatalysis (red line) and the photocatalysis (black line). The thermocatalytic oxidations agree well with Arrhenius mode, and the apparent activation energy (E_{app}) is 42 kJ/mol. The PCOs also show an Arrhenius dependence on temperatures below 65 °C, with an E_{app} of 8.0 kJ/mol. At the temperatures ranging between 65 and 140 °C, the photocatalytic rates show a first-decrease-then-increase because of the carbonate deposit and the removal by thermocatalysis. The photocatalytic effect starts to decrease again and goes on to disappear when the temperatures are higher than 140 °C, possibly because of the inhibition of heat on the role of light. The fictitious photocatalytic rates were also plotted after excluding the effect of carbonate deposit. Despite the effect of carbonate deposit, the results still shows that the photocatalytic rates first increase and then decrease with temperatures. Figure 8A shows that the PCOs of acetone do not locate in the positive region of Figure 4A, and thus heat cannot have a synergism with light. Light intensities were also varied to determine whether light can have a synergism with heat. Figure 8B shows the log−log dependence of the photocatalytic rates on the light intensities. The index n is about 1 (rate $\propto I^n$), indicating that the PCOs of acetone should belong to a single-electron-driven process. The log−log plot does not locate in the positive region of Figure 4B, so light cannot produce a synergism with heat in the acetone photocatalysis.

Formaldehyde PCOs were also used to check an intrinsic light−heat synergism. CO_2 evolutions at different temperatures in the presence and absence of light illuminations are shown in Figures S7 and S8. Figure 8B,D shows the dependences of the photocatalytic rates on the temperatures and light intensities in Arrhenius and log−log modes, respectively. Formaldehyde was not subject to the thermocatalytic oxidations at all temperatures, and there is no carbonate that can deposit on the TiO_2 surfaces. The photocatalytic rates show a first-increase-then-decrease with temperatures, and depend on the light intensities in the sublinear mode ($n = 0.64$). The photocatalytic rates below 65 °C are lower than the Arrhenius predictions because of inadequate evaporation of formaldehyde aqueous solutions. The PCOs between 65 and 125 °C agree well with Arrhenius mode; the E_{app} is about 9.0 kJ/mol. The photocatalytic rates

show a continuous decrease and go on to disappear when the temperatures are higher than 125 °C, also possibly due to the light−heat coinhibited effect. The PCOs do not locate in the positive regions of Figure 4A,B. It has also been reported that formaldehyde PCOs over TiO_2 show a decrease in the n at high light intensities.[54] It is concluded that the formaldehyde PCOs should not include a light−heat synergism.

Some studies reported the location of PCOs in the positive region of Figure 4A.[55,56] We considered that the results are hardy to be believed because the observed superexponential behaviors are completely beyond the theory of statistical thermodynamics. We thought that other effects should be carefully taken out before confirming an intrinsic light−heat synergism. For example, if light-induced surface heating is underestimated, the measured photocatalytic rates can go to the "positive" region of Figure 4A. In recent studies, we found that the light-induced increase of surface temperatures is always underdetermined. Therefore, in a broad sense, although their results might be attributed to a "light−heat synergism", it does not mean the intrinsic one defined above.

The experimental results are in accordance with our theory, so an intrinsic light−heat synergism cannot exist in the PCOs over TiO_2, which is opposite to the conclusions obtained in some studies.[34,57,58] According to these works, if the pure photocatalytic rates at elevated temperatures are higher than that at ambient temperature, a light−heat synergism can be defined. Based on this rule, a similar conclusion can be obtained that the PCO of acetone at 65 °C and the PCO of formaldehyde at 125 °C should have a light−heat synergism because their rates are higher than that at ambient temperature. We think that these works might take the natural increase of photocatalytic rates with temperatures as a light−heat synergism. Because the photocatalysis itself contains heat-activated processes, we cannot attribute such results to a light−heat synergism essentially. The light−heat synergism is a concept that relates to the fundamentals of photocatalytic science, so great care must be taken to study light−heat synergism in photocatalysis so as to avoid misunderstandings. It is therefore better to use our proposed criteria to provide a rigorous definition.

4. CONCLUSIONS

A detailed elaboration was given on the fundamental principle of semiconductor photocatalysis on both thermodynamics and kinetics levels. The G of the charge carriers in semiconductors was defined as the thermodynamic potential of photocatalysis. Heat is incapable of driving catalysis happening in a photocatalytic way. A G-potential landscape of photocatalysis was also proposed. The role of light in kinetics is included in the apparent activation energy. In addition to the activation, heat can also affect the apparent activation energy. Photocatalysis was thus defined as the light-driven chemical reaction activated by heat, in that the roles of heat and light also correlate with each other. We obtained the conclusion that there is no intrinsic light−heat synergism in semiconductor photocatalysis as light and heat mutually inhibit at both the thermodynamic and kinetic levels. Rigorous criteria were further proposed to reconcile the light−heat synergism reported in some studies to our theory. Experimental results agree well with the theory. We clarified some confusions and misunderstandings on the fundamentals of semiconductor photocatalysis. The above proposed theory should be

important for photocatalytic discipline and open a door for thinking of photocatalysis from an energetic perspective.

5. EXPERIMENTAL DESCRIPTION

5.1. On-Line Electrical Conductances. On-line electric conductances over the acetone photocatalysis were measured in a self-designed flow bed quartz reactor system (refer to our recent publication[39]). Pure N_2 (5 N), pure O_2 (5 N), and acetone–N_2 mixture (500 ppm of acetone in pure N_2) were continuously let into the reactor under careful control by flow meters. The flow rates of N_2, O_2, and acetone-N_2 gases were set as 1, 0.05, and 0.01 L/min, respectively. The concentrations of acetone in the outlet of the reactor were monitored by a gas chromatograph equipped with a FIB detector (Shimadzu GC-2500). A thin TiO_2 coating was coated on a piece of quartz glass substrate by doctor-blading from p25 paste; this was then annealed at 450 °C for 1 h. Two gold electrodes were deposited on the TiO_2 coating, with a 0.2 mm gap being left for conductance measurements. Two larger area TiO_2-coated quartz glasses were also prepared for acetone oxidations. A heat plate was used to heat the reactor to the set temperature, which was monitored by a PT100 resistance temperature detector. A mercury lamp (USHIO SP-9) equipped with a 365 nm band-passed optical filter was used as the light source. The intensity of the light reaching the TiO_2 surface was determined by a Si diode photodetector. Photocatalytic activity was evaluated by acetone conversation (α), defined as the ratio of the difference between the acetone concentrations before and after UV light illumination. The on-line electron conductances were simultaneously monitored by an electric source meter (KEITHLEY 2450 Source meter).

5.2. Catalytic Experiments. Photocatalytic and thermo-catalytic experiments were done in a self-designed quartz closed-circulation cylindrical reactor (refer to our recent publication[43]). The reactor was linked with a photoacoustic IR multigas monitor (INNOVA Air Tech Instruments model 1412). The reactor was heated to the set temperature before catalytic experiments. The same light source was used, and the light intensity was checked by a Si diode photodetector. Infrared thermography (FLIR E60) was used to confirm that the light illumination had no effect on surface temperatures. As carbonate contaminations can also lead to CO_2 evolution, all samples were pretreated by UV light before photocatalysis reactions. Fresh air was then flowed through the reactor to purge out the old air until the residual CO_2 concentration was lower than 20 ppm.

Acetone and formaldehyde were used for the PCOs. Two experiments were designed for photocatalysis and thermoca-talysis. The reactor was kept in the dark for 60 min at the set temperature, and after that, 2 μL of liquid acetone or formaldehyde was injected into the reactor to see a pure thermocatalytic effect. The photocatalytic effect was measured according to the same procedure under simultaneous light illumination. The CO_2 evolution rates were used to evaluate photocatalytic activity. Pure photocatalytic effects were obtained by subtracting the CO_2 evolutions under light illumination from that in the dark.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02145.

Time dependences of on-line conductances and photo-catalytic effects in the courses of the PCOs of acetone and formaldehyde over TiO_2 materials at different temperatures and light intensities and time dependences of the CO evolutions during the PCOs acetone and formaldehyde over TiO2 at different temperatures (PDF)

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Notes

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