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The nature of hot electrons generated by exothermic catalytic reactions

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ABSTRACT

We review recent progress in studies of the nature of hot electrons generated in metal nanoparticles and thin films on oxide supports and their role in heterogeneous catalysis. We show that the creation of hot electrons and their transport across the metal–oxide interface is an inherent component of energy dissipation accompanying catalytic and photocatalytic surface reactions. The intensity of hot electron flow is well correlated with turnover rates of corresponding reactions. We also show that controlling the flow of hot electrons crossing the interface can lead to the control of chemical reaction rates. Finally, we discuss perspectives of hot-electron-mediated surface chemistry that promise the capability to drive catalytic reactions with enhanced efficiency and selectivity through electron-mediated, non-thermal processes.

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1. Introduction

Energy dissipation at surfaces and interfaces is mediated by excitation of elementary processes, including phonons and electronic excitation, once external energy is deposited to the surface during exothermic chemical processes [1–9]. Electron excitation in exothermic catalytic reactions or the incidence of photons on metal surfaces results in the flow of high-energy electrons with an energy of 1–3 eV, assuming that most of the chemical or photon energy is converted to electron flow on a short (femtosecond) time-scale before vibrations adiabatically dissipates the energy (in picoseconds). Energetic electrons not in thermal equilibrium with the metal atoms are called ‘hot electrons’. There have been a number of studies demonstrating the influence of hot electrons on atomic and molecular processes [8,10–12]. The detection of hot electron flow accompanying atomic or molecular processes and understanding its role in chemical reactions have been major topics in surface chemistry. In this Frontiers article, we outline recent research on the chemical nature of hot electrons generated during chemical processes. The chemicurrent, or hot electron flow, is well-correlated with the turnover rate of CO oxidation or hydrogen oxidation, as measured separately by gas chromatography,

suggesting an intrinsic relation between the catalytic reactions and hot electron generation. The influence of the flow of hot charge carriers on the chemistry at oxide–metal interfaces and the turnover rate for chemical reactions on metal–semiconductor hybrid nanocatalysts are discussed.

The basic mechanisms for energy dissipation may involve phonons, non-adiabatic electron–hole excitation processes, plasmons, exo-electron emission, and chemiluminescence, as shown in Figure 1a. Let us consider each of these processes in more detail.

Phonon or quantized lattice vibration: The energy of phonons is on the order of tens of meV, which is two orders of magnitude smaller than chemical energies. The direct transfer of energy into the phonon system of a metal requires multiple excitations of phonons during chemical processes.

Excitation of electron–hole pairs: The excitation of an electron–hole pair leads to a hot electron with energy above the Fermi level and to a hot hole with energy below the Fermi level. The excitation of an electron–hole pair takes place via a non-adiabatic process.

Emission of charged particles (exo-emission) [13] or light (chemiluminescence) [14] during gas adsorption or reaction is generally attributed to non-adiabatic charge transfer processes.

From a thermodynamic point of view, a solid body can be seen as a macroscopic system that consists of two coupled subsystems (i.e., electrons and atomic nuclei) that constitute the lattice of the solid body. Each subsystem may be characterized by means of

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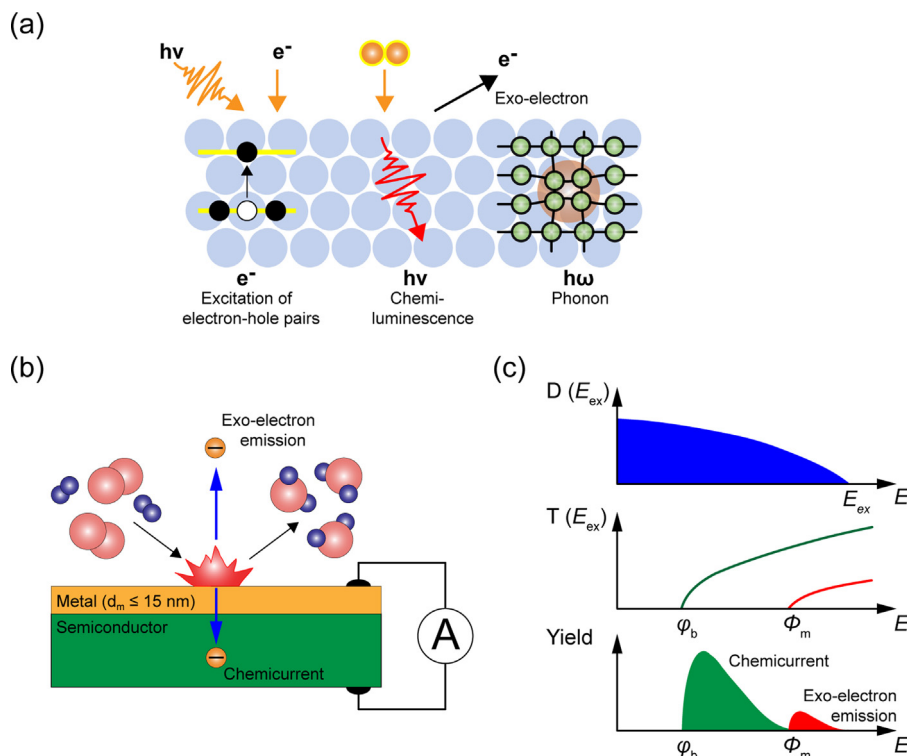


Figure 1. (a) Scheme showing basic mechanisms for energy dissipation, which involves phonons, nonadiabatic electron-hole excitation processes, exo-electron emission, and chemiluminescence. (b) Detection of hot electrons during an exothermic reaction on a metal surface. Highly energetic hot electrons ($E_{ex} > \Phi_m$) can be detected due to exo-electron emission into the vacuum. Hot electrons with lower energy ($\phi_b < E_{ex} < \Phi_m$) can be detected due to their internal emission across the metal-semiconductor interface. (c) Different contributions to the hot electron yield for the cases of chemicurrent and exo-electron emission. Here, E_{ex} is the excess energy of a hot electron, Φ_m is the metal work function, ϕ_b is the Schottky barrier height at the metal-semiconductor interface, $D(E_{ex})$ is the distribution of hot electrons in the metal, and $T(E_{ex})$ is the probability of hot electron transport across the potential barrier at the metal-semiconductor (green curve) or metal-vacuum (red curve) interface.

temperature: T_e and T_I for electrons and atomic nuclei, respectively. Typically, it is assumed that when external energy is deposited onto the surface of a solid, the lighter electrons instantaneously adjust to the motion of the heavier (and therefore slower) atomic nuclei [5,15–22]. Thus, the whole system remains in a state of thermodynamic equilibrium at any time (i.e., $T_e = T_I$). In quantum chemistry, this assumption is well known as the adiabatic Born–Oppenheimer approximation (BOA) [23]. However, there is a growing number of experiments that provide trustworthy evidence that the BOA breaks down in many cases of chemical gas–surface interactions, giving rise to a variety of non-adiabatic effects. One well-known example is the case of highly exothermic chemical reactions catalyzed on a metal surface [10,15,21,24–35]. Here, chemical energy on the order of 1–3 eV can be liberated within several tens of femtoseconds. Considering the fact that the heat capacity of electronic subsystems in metals is 1–2 orders of magnitude smaller than the heat capacity of the lattice, this makes it possible to heat the electrons to temperatures much higher than the temperature of the nuclei subsystem (i.e., $T_e \gg T_I$), thereby driving the whole system far out of thermal equilibrium [15,17]. Another example is the case of the interaction of a metal surface with an incident photon flux of high energy density [18,36–39], which produces a similar effect as with exothermic chemical reactions.

Given the great practical importance of understanding the mechanisms of energy dissipation beyond the limits of BOA, several experimental techniques have been developed to detect hot electrons created in metals by exothermic chemical reactions. When exothermicity is so high that the excess energy of hot electrons $E_{ex} = |E - E_F|$ exceeds the metal work function (i.e., $E_{ex} > \Phi_m$), direct detection of the hot electrons is possible due to exo-electron

emission [16,20,40,41]. In this case, the chemically excited electrons overcome the potential barrier at the metal–vacuum interface to escape from the metal surface (see Fig. 1b). Otherwise, ($E_{ex} < \Phi_m$) the hot electrons can be detected as the chemicurrent [5,6,16,21,22,28,31,42]. For this reason, metal—in the form of an ultrathin film—must be deposited onto the surface of a semiconductor or insulator so as to form a potential (Schottky) barrier. As the height of the Schottky barrier is in the range of $\phi_b = 0.5 - 1.2$ eV for most materials [43], the chemicurrent approach allows for detection of hot electrons as a result of their internal emission across the metal–semiconductor or metal–insulator interface even when the electron energy is insufficient for emission into the vacuum [16–18,28,29,44]. This in turn allows a larger yield (i.e., number of hot electrons detected per molecule of reaction product formed on the surface), as compared with exo-electron emission into the vacuum, which is schematically shown in Figure 1c.

The aim of this Letter is to survey recent progress in the study of hot electron excitation via non-adiabatic chemical energy dissipation. We outline the aspects of hot electron detection as a chemicurrent using metal–semiconductor nanodiodes and review methods for separating hot electrons from other effects leading to charge transfer during catalytic reactions (e.g., thermoelectric effects, proton diffusion). We also address the relationship between chemicurrent and chemical kinetics for various types of metal–semiconductor nanodiodes and experimental conditions. The Letter is divided into two parts: (i) basic aspects of hot electron detection during catalytic reactions on metal–semiconductor nanodiodes (Section 2) and (ii) electronic control of catalytic activity using charge transfer across the metal–semiconductor interface using external biasing and light (Section 3).

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