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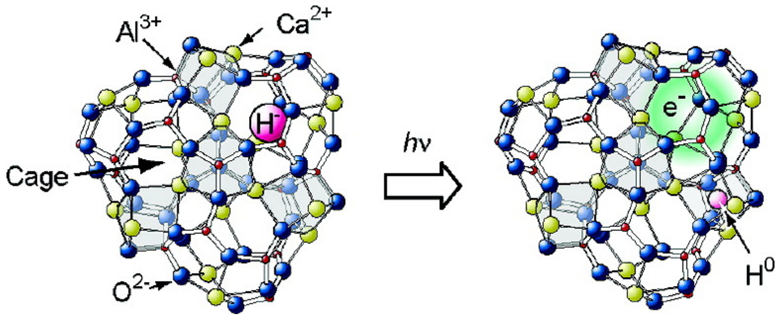

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Hydride Ion as Photoelectron Donor in Microporous Crystal

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Hydrogen is the lightest and most abundant element and is a common impurity in solids. Hydrogen as an impurity has attracted much attention for many years now because it works both as an electron donor and acceptor due to its medium electronegativity.[1] In other words, the valence state of hydrogen can change from positive to negative as expressed by H^+, H^0, and H^-, corresponding to different filling states of the 1s orbital. The hydride ion, H^-, that occupies halide ion sites in alkali−halide crystals has been known as the *U* center since the 1930s. UV illumination ($\lambda \sim 300$ nm) dissociates the H^- to an H^0 and an electron.[2] However, the resulting electron is localized at a halogen vacancy (*F* center) and does not yield significant electrical conductivity. In this report, we demonstrate that H^- in microporous crystal works as an electron donor on UV illumination, causing persistent conductivity, in contrast to that in nonporous crystals, such as alkali−halides.

We reported in the previous paper that the transparent insulating oxide crystal $12CaO{\cdot}7Al_2O_3$ (C12A7) heated in a hydrogen atmosphere at 1300 °C (C12A7:H) is converted to a persistent electrical conductor having moderate conductivity ($\sim$0.3 $S{\cdot}cm^{-1}$ at 300 K, conduction occurs via variable-range hopping) upon UV illumination ($\lambda \leq \sim 300$ nm).[3] Although the UV-illuminated C12A7:H shows optical absorption in the visible region due to two absorption bands centered at 0.4 and 2.8 eV, transmission loss in the visible range remains at only a few % for the 200 nm thick films.[4] Furthermore, the conductivity is eliminated by annealing at $\sim$600 K, and this cycle of emergence of UV-induced conductivity and thermal restoring is reversible unless the sample is heated to $\sim$800 K. Therefore, C12A7:H thin film may be used for the direct optical writing of rewritable conducting patterns in this insulating transparent media.

On the basis of the anion encaging nature of C12A7, it was suggested that the conductivity arising in C12A7:H is due to carrier electron generation by photoexcitation of H^- captured in the subnanometer-sized cage of C12A7.[5] The chemical formula of a unit cell of C12A7 is represented by $[Ca_{24}Al_{28}O_{64}]^{4+}(O^{2-})_2$. $[Ca_{24}Al_{28}O_{64}]^{4+}$ denotes 12 densely packed cages sharing planes to form a three-dimensional structure, and O^{2-} denotes an oxygen ion entrapped in 1 out of 6 cages, referred to as "free oxygen" (see Figure 1). The free oxygen can be replaced by two monovalent anions ($O^{2-} \rightarrow 2X^-$). If H^- substitutes for the O^{2-}, we may expect that UV illumination dissociates an H^- to an H^0 and electron pair, resulting in conductivity. Formation of the resulting unpaired electron was confirmed by electron paramagnetic resonance (EPR). An isotropic signal centered at $g = 1.994$ with a line width of 2 mT was observed after UV illumination. The line shape and negative *g*-shift ($\Delta g = g - g_e$; g_e is the *g* value of a free electron) are characteristic of an electron trapped in the cage, which is similar to the F^+ center in CaO (O^{2-} vacancy trapping an electron) because the center of the cage is octahedrally coordinated by six Ca^{2+} ions forming the cage skeleton.[6]

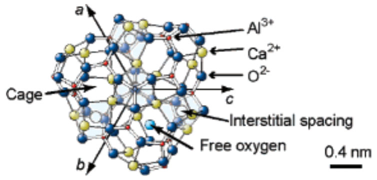

Figure 1. Part of the crystal structure of the microporous crystal C12A7 viewed from the ⟨111⟩ direction. The lattice is composed of subnanometer-sized cages and small cubes (shaded parts) filling the interstitial spacing among the cages. The H^- ion is expected to be accommodated in the cage in place of the free oxygen ion O^{2-}.

On the other hand, there was no direct evidence for the presence of H^- and H^0 in C12A7. No EPR signal due to H^0 ($1s^1$, $S = 1/2$) was observed at room temperature. For alkali−halides, the EPR signal due to photogenerated H^0 was observed below $\sim$100 K.[2] However, H^0 disappears when the temperature is increased above $\sim$100 K because H^0 becomes mobile and, thereby, recombines with an electron to form H^- or dimerizes to form an H_2 molecule. It is plausible that the same event takes place for C12A7:H. Thus, we examined the UV-induced signal of C12A7:H at low temperature.

The polycrystalline C12A7:H was synthesized and hydrogenated according to the method reported previously.[3] The sample containing deuterium (C12A7:D) was prepared by using D_2/N_2 gas. CW-EPR spectra were measured with a Bruker E580 X-Band spectrometer in dispersion mode to reduce the effect of microwave power saturation of H^0 with high *s*-character at low temperatures.[7] Samples were sealed in silica glass tubes and inserted into a microwave resonator installed in a helium cryostat with an optical window. The sample was then cooled to 4 K and illuminated with an ultrahigh-pressure Hg lamp (500 W) filtered by a glass filter transmitting $\sim$330 nm light for 1−16 min. At the end of the illumination, isochronal annealing was performed between 4 and 300 K. The samples were kept at each temperature for 15 min, quickly cooled to 4 K, and then the EPR spectra were measured.

Figure 2a shows EPR spectra of UV-illuminated C12A7:H and C12A7:D. The illumination and measurement were performed at 4 K without an intervening warm-up. In C12A7:H, a doublet signal centered at $g = 2.002$ due to H^0 (^1H, $I = 1/2$) was observed with the signal of an F^+-like center at $g = 1.994$. In C12A7:D, a triplet signal due to an atomic deuterium D^0 (^2D, $I = 1$) was observed. The values of the isotropic hyperfine coupling constant (A_{iso}) are 48.6 mT for H^0 and 14.9 mT for D^0, corresponding to 96% of those in the free space ($A_0^H = 50.6$ and $A_0^D = 15.6$ mT). Such a large reduction of −4% ($\Delta A = [A_{iso} - A_0]/A_0$) is rather unusual because ΔA of H^0 is smaller than about −1% in conventional cases.[9] However, H^0 trapped at the interstitial site in alkali−halides shows a large negative shift (−2 to 15%).[10] Spaeth et al. explained that the negative shift is induced by the van der Waals interaction between the H^0 and the neighboring halide ions, based on Adrian's theory.[11] Please note that H^0 at the halogen vacancy has A_{iso} equal to A_0.[12] The large negative shift observed in C12A7 implies a

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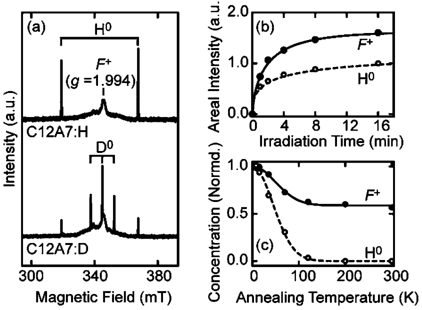

Figure 2. (a) EPR spectra of C12A7:H and C12A7:D observed at 4 K after UV illumination. In C12A7:H, a doublet centered at $g = 2.002$ due to an H^0 (^{1}H, $I = ^1/_2$) was observed with the signal of the F^+-like center (F^+) at $g = 1.994$ with a 0.2 mT line width. C12A7:D yielded a triplet signal due to D^0 (^{2}D, $I = 1$). (b) Areal signal intensities of H^0 and F^+ as a function of UV illumination time. Almost 1:1 generation indicates photodissociation of H$^-$: $H^- \rightarrow H^0 + e^-$. (c) Isochronal annealing of H^0 and F^+. No H^0 remained above ~200 K, while 60% of F^+ remained even at 300 K.

plausible model that UV-induced H^0 and D^0 are located at the interstitial site among the cages (see Figure 1).

Figure 2b shows the areal intensities of the signals of the F^+-like center (abbreviated as F^+ in the following) and of H^0 as a function of illumination time. The areal intensity ratio $I(F^+)/I(\mathrm{H}^0)$ is ~1.6 and is independent of illumination time, indicating the simultaneous generation of H^0 and F^+. Areal intensity is proportional to the concentration of paramagnetic species. However, the concentration of H^0 is not determined exactly from $I(\mathrm{H}^0)$ owing to the extremely easy saturation of the H^0 signal at low temperature.[7] Taking into account the power saturation, the concentration of H^0 is almost the same as that of F^+. This finding reveals that H$^-$ is accommodated in C12A7, and the conduction carrier is generated by the photodissociation of H$^-$.

Figure 2c shows the fractions of H^0 and F^+ remaining after thermal annealing. No H^0 was left after annealing above ~200 K, while ~60% of the F^+ remains even at 300 K. Therefore, it is implied that some H^0 recombines with the F^+ to form H$^-$ ($H^0 + e^- \rightarrow H^-$) and the rest was removed in a different way, without consuming the F^+. The reaction of H^0 with free oxygen to form OH$^-$, yielding additional F^+: $H^0 + O^{2-} \rightarrow OH^- + e^-$, is a plausible candidate for the latter.[13] A similar mechanism was proposed for MgO surfaces.[14] When ~70% of H^0 recombines with electrons and the remaining H^0 reacts with free oxygen to form OH$^-$, the fraction of remaining F^+ is evaluated to be ~60%, which was observed in the experiment. OH$^-$ is rather stable in the cage at room temperature and does not react with trapped electrons. Thus, when the C12A7:H is illuminated with UV quanta at room temperature, several tens of % of photoinduced electrons survive and yield hopping conductivity. At temperatures above ~600 K, the OH$^-$ is reduced by trapped electrons to form H$^-$ and O^{2-}, and thereby, the conductivity is eliminated. The reactions occurring after UV illumination are illustrated in Figure 3.

In conclusion, we succeeded in observing the EPR signal for H^0 in C12A7 after UV illumination at 4 K. The concentration of generated H^0 is almost equal to that of F^+. This observation demonstrates that H$^-$ is trapped in the cage of C12A7 in place of O^{2-} and is photodissociated to a pair of H^0 and F^+. According to the quantum-chemical calculation based on an embedded cluster model, the remaining electron is localized in the cage.[15] This calculation also shows that hopping of electrons between cages results in electrical conduction with a relatively small activation energy of ~0.1 eV. Although the resulting electron is localized in the cage, the densely packed structure of empty cages in C12A7 enables hopping conduction of electrons throughout the lattice. This situation originates from the unique network topology that is completely different from that of conventional ionic crystals, such as alkali−halides, which consist of densely packed ions.

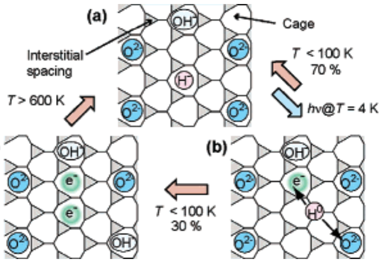

Figure 3. Scheme of photoinduced insulator−conductor conversion. (a) Before UV illumination, H$^-$ ions are incorporated in the cage of C12A7 in place of O^{2-}. (b) Upon UV illumination, H$^-$ ions are photodissociated to H^0 and electron pairs ($H^- \rightarrow H^0 + e^-$). (c) The resulting H^0 is rather mobile and recombines with electrons ($H^0 + e^- \rightarrow H^-$) or reacts with free O^{2-} to form OH$^-$ and e$^-$ ($H^0 + O^{2-} \rightarrow OH^- + e^-$). By annealing at ~600 K, OH$^-$ and electrons trapped in the cage return to the initial state via the reaction $OH^- + 2e^- \rightarrow O^{2-} + H^-$.

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