# VOC Elimination in Printers by Means of Thermally Activated Oxide Semiconductors (TASC)

***Y. Tsukada, Y. Suzuki, H. Takahashi, and J. Mizuguchi; Fiber Innovation Incubator, Faculty of Textile Science and Technology, Shinshu University; Ueda 386-8567, Japan***

## Abstract

*VOCs (volatile organic compounds) arising from fusers in printers, solvent inks in inkjet printers, or wet POD systems cause environmental problems at present. Therefore, efficient elimination technologies are in high demand. We will introduce our novel VOC elimination system utilizing thermally activated semiconductors (**TASC**). The TASC technology is characterized by the use of highly oxidative holes generated by thermal excitation of semiconductors. As is well known, the number of electrons and holes can be created in accordance with an exponential function of temperature according to the semiconductor theory. This clearly indicates the formation of a vast number of charge carriers when heated at about 350-500 °C. The first process of the decomposition reaction is the capture of bonded electrons (i.e. oxidation) from VOC molecules, even polymers, leaving behind free radicals. The free radical is unstable and can propagate throughout the molecule at 350-500 °C. This makes the whole molecule unstable and induces a radical splitting resulting in the fragmentation of the molecule. The fragmented molecules then react with oxygen in air to completely burn to give rise to $H_2O$ and $CO_2$. Our system is simple, small and low cost, and thus can easily be integrated into office printers or wet POD systems.*

## 1. Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere due to various human activities, for example, unburned fuel from power production, transportation, and solvents from painting or printing industries.[1] Particle emission from office printers (*i.e.*, emission of monomers from fusers) causes also an environmental problem.[2] Furthermore, in houses and buildings, VOC such as formaldehyde emitted from floor and furniture materials is harmful to human health.[3] Consequently, VOC causes serious environmental issues, such as photochemical smog, sick house syndrome etc.[1] In view of the present situation, we started our investigation on complete removal of VOC and organic wastes by means of thermally excited holes in oxide semiconductors such as $TiO_2$,[4-13] NiO,[14] $Cr_2O_3$,[15, 16] and $\alpha$-$Fe_2O_3$[17] at about 350–500 °C. The use of thermally generated holes for removal of VOC and organic wastes is an entirely new technology initiated by us in 2001.[4] The present technology dates back to our accidental finding that the catalytic effect suddenly appears when oxide semiconductors are heated at high temperatures of about 350–500 °C. This is due to the formation of a large number of highly oxidative holes caused by thermal excitation of semiconductors. Lasers, transistors, and diodes are the representative applications of semiconductors. However, ours is the application at high temperatures.

## 2. Outline of the TASC technology and an example of complete decomposition of polycarbonate (PC) by TASC

The TASC technology is characterized by the use of highly oxidative holes generated by thermal excitation of semiconductors. Oxide semiconductors such as $TiO_2$, ZnO, $Cr_2O_3$, $Fe_2O_3$ etc. are particularly preferred for this purpose, since the decomposition experiment is carried out in air at high temperatures. Among these, we are particularly interested in $Cr_2O_3$ because of its high stability (melting point: about 2200 °C). In addition, its safety is ensured as shown by the fact that $Cr_2O_3$ is widely used in our daily life as the colorant for glass dyeing of whisky or wine bottles etc.

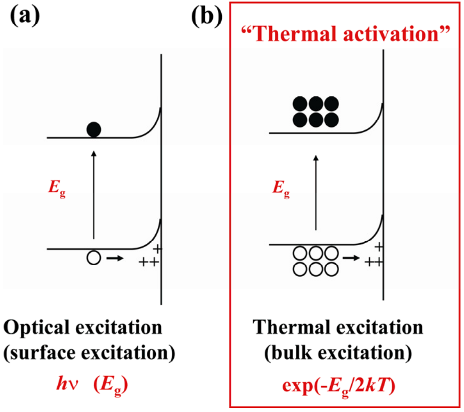


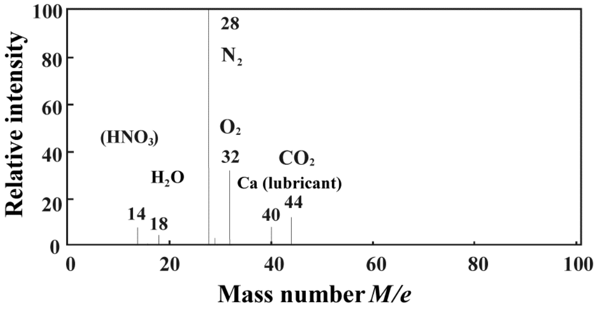
***Figure 1.*** *Band diagram of semiconductors composed of the valence band and the conduction band: (a) optical excitation (i.e. surface excitation) and (b) thermal excitation (i.e. bulk excitation). $E_g$, k, and T designate the intrinsic concentration of carriers, band gap of the semiconductor, Boltzmann constant, and temperature, respectively.*

We start with the explanation of the optical excitation [Fig. 1(a)] and show how the thermal excitation [Fig. 1(b)] is, by far, advantageous to the optical excitation regarding the number of generated holes. When the semiconductor is excited by a photon whose energy is larger than the band gap, then an electron in the valence band is excited to the conduction band, leaving behind a positively-charged defect electron called hole in the valence band. Both electrons and holes are mobile and contribute to the increase in electrical conductivity. This is known as the photoconducting phenomenon. These holes are utilized, for example, in photocatalysts for decomposition of organic compounds adsorbed on the surface. However, the decomposition performance is known to be quite poor. Then, an important question arises how we can construct a strong oxidation system with semiconductors. The answer is very simple: that is, we should create a vast number of holes in the valence band. Then, we suppose that we can achieve it with higher light intensity. However, this is not the case. The electrons and holes are immediately recombined after excitation, because the light excitation occurs only on the surface of semiconductors, where there are a number of carrier recombination centers due to lattice defects. Therefore, the increase in electrical conductivity is limited to, at most, one order of magnitude. Instead, we then considered the thermal excitation [Fig. 1(b)] which is the bulk excitation rather than the surface one. The number of electrons and holes can be created in accordance with an exponential function of temperature according to the semiconductor theory.[18] In fact, our experiment using a single crystal of $TiO_2$ showed that the resistivity is about $10^{11}$ Ωcm at RT, however the resistivity is remarkably reduced to only 15 Ωcm at 500 °C.[6] That is, the resistivity is reduced by ten orders magnitude! This clearly indicates the formation of a vast number of charge carriers. This is actually the effect of the TASC that we found which leads to the appearance of significant catalytic effects. [4-7]

We will show below an example of the instantaneous, complete decomposition of PC by TASC together with its destruction mechanism.[6,7] We carried out an experiment using two glass tubes, each of which contains PC chips in the presence or absence of $TiO_2$ used as a semiconductor. These were heated in air at 500 °C for 30 min. The PC in the absence of $TiO_2$ melted at about 200 °C and then boiled, ending up with the carbonization. This is a typical result when a plastic is roasted in air. On the other hand, no trace of PC was recognized in the presence of $TiO_2$. Here remain just white powders of $TiO_2$. A gas analysis of the decomposition product was made by mass spectrometer and the result will be shown in Fig. 2(a).[7] Since the experiment was performed in air, we see peaks of $N_2$ (28) and $O_2$ (32) that are components of air, as well as peaks of $H_2O$ (18) and $CO_2$ (44). Furthermore, we observe a peak of Ca (40). This is due to a metallic soap of Ca used as a lubricant in optical discs. The present result indicates that PC (molecular weight: about 25,000) has entirely been decomposed into $H_2O$ and $CO_2$ in an instance. This is an amazing effect! On the other hand, when the experiment was carried out under vacuum, we see a number of small fragments as shown in Fig. 2(b). However, these peaks disappear in an oxygen atmosphere, leaving only two peaks of $H_2O$ and $CO_2$. This clearly indicates that oxygen is absolutely necessary for the disappearance of fragment peaks.

On the basis of the above experiments as well as those by electron spin resonance (ESR) for radicals, we proposed the destruction mechanism as shown in Fig. 3.[7] The interface drawn by the dotted circle is magnified as shown in the inset, where PC chains are adsorbed on the surface of $TiO_2$. The first process of the decomposition reaction is the capture of bonded electrons from PC chains, leaving behind cation free radicals. The free radical is unstable and can propagate throughout the polymer chain at 350-500 °C. This makes the whole chain unstable and induces a radical splitting resulting in the fragmentation of the giant molecule, just the reverse of radical polymerization. The fragmented molecules then react with oxygen in air to completely burn to give rise to $H_2O$ and $CO_2$.

**(a) in air**



**(b) under vacuum**

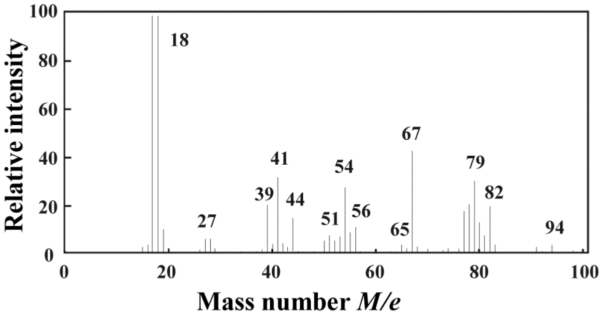


*Figure 2. Gas analysis of decomposition products of PC (i.e. a substrate for compact discs) by mass spectroscopy: (a) in air, and (b) under vacuum.*

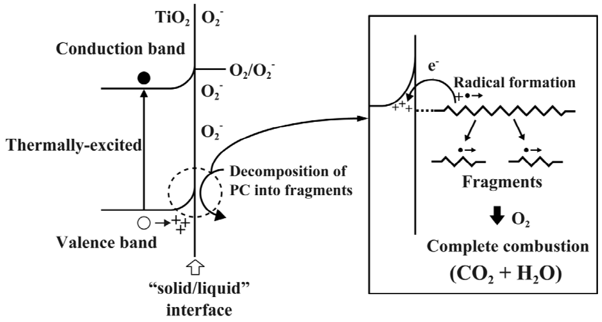


*Figure 3. Three elementary processes of PC decomposition by means of thermally generated holes in $TiO_2$: (a) thermal excitation, (b) radical splitting, and (c) complete combustion.*

## 3. Successful results achieved by TASC

Up to now, we have achieved complete elimination of various VOCs by the TASC technology: toluene & benzene,[8] chloro-based organic solvents[18], formaldehyde (FA).[19]

An example is shown in Fig. 4 for the elimination of formaldehyde with $Cr_2O_3$-coated honeycomb systems.[9] Fig. 4(a) shows the FA decomposition process as a function of temperature for a FA concentration of 1200 ppm. FA decomposition starts at about 100 °C and is completed at about 450 °C. Fig. 4(b) is the result of FA decomposition for concentrations of 100 and 1200 ppm carried out at 500 °C. In both experiments, the outlet concentration was entirely zero, showing the reading of the hydrocarbon meter for air. The outlet gas had no smell of FA at all.

In addition, we collected the outlet gas with a plastic bag and analyzed its component with a mass spectrometer. However, no FA component was detected.

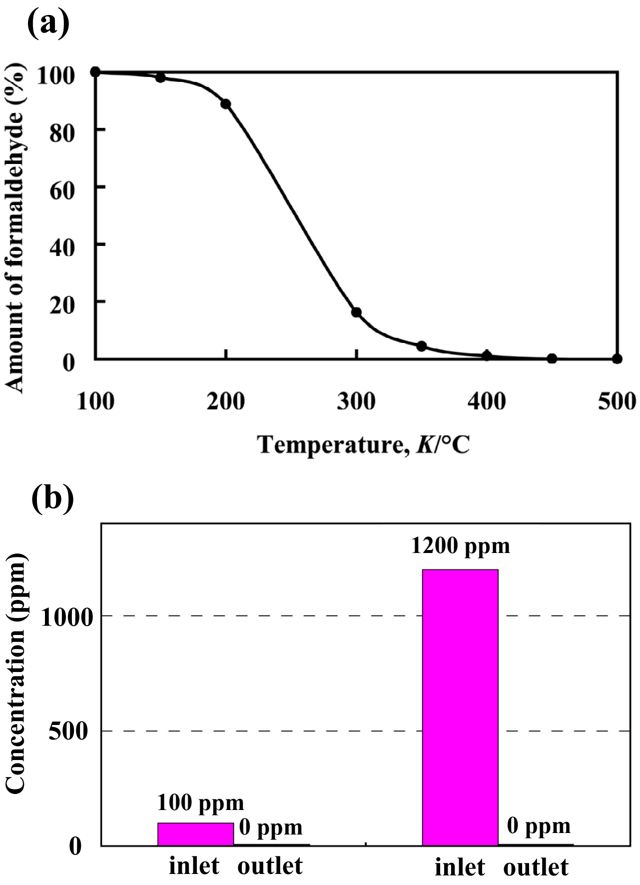


*Figure 4. (a) FA decomposition characteristics as a function of temperature for an FA concentration of 1200 ppm, using the VOC removal system with a heat exchanger, and (b) FA decomposition for concentrations of 100 and 1200 ppm carried out at 500 °C.*

As described above, our system is simple in structure and quite small. Nevertheless, it exhibits a high performance for FA decomposition. $Cr_2O_3$ is quite stable and resistant even to halogen-based gases.[18]

### *Our newest model of the VOC-removal equipment - Heater-integrated honeycomb systems -*

Our newest model is characterized by the use of heater-integrated honeycombs (coated with powdered $Cr_2O_3$) as shown in Fig. 5(a), where a heater of the W shape is placed in a groove of the honeycomb. The present catalyst units are stacked in pile for the construction of the catalyst system. The entire system is composed of part 1 (24 cm in length) and part 2 (16 cm in length) which are connected in tandem [Fig. 5(b)]. Part 1 is an operating system; whereas part 2 is used as an auxiliary system. The external appearance looks like as shown in Fig. 5(c). The temperature distribution is controlled by a thermocouple. The present system has a performance of SV (space velocity) value of about 50000. Since the catalyst unit is simple and flexible, we can extend the catalyst system as long as possible by connecting the unit in series or can also arrange the units in parallel, depending on the VOC concentration and its flow rate.

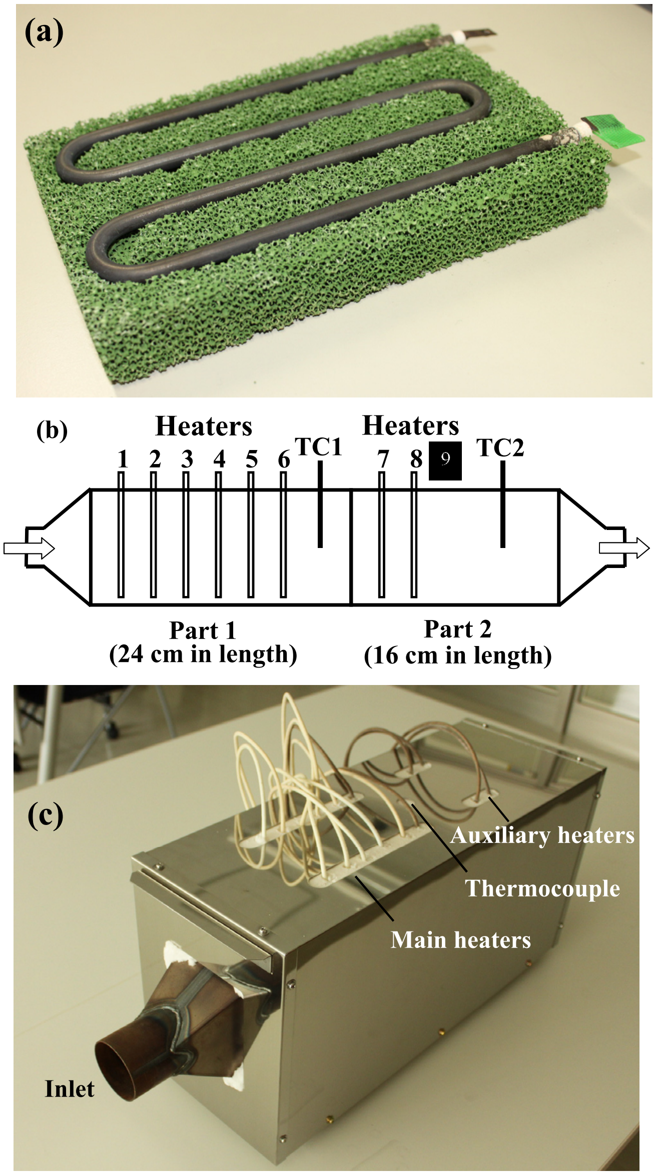


*Figure 5. (a) Heater-integrated honeycomb systems (130×200×30 mm), (b) Schematic structure of the stacked honeycombs with heaters, and (c) Appearance of the equipment.*

## 4. Conclusions

The TASC system has been surveyed with special attention to the application for VOC removal. A variety of systems can be customized with the TASC technology so as to meet the requirement of VOC elimination arising from printers and wet POD system. The TASC technology has also been applied to the FRP (fiber-reinforced plastics) decomposition and the recycling of reclaimed reinforcing fibers.[22,23] Furthermore, metals including rare earth elements have also been recovered from mold motors and bond magnets in 20-30 minutes at about 500 °C.[23]

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## Author Biography

*Yuichiro TSUKADA received his BS and MS degrees in applied physics from Yokohama National University in 2006 and 2008, respectively. He joined EPSON Corporation in 2008 and worked there for four years. Since 2012, he has been working as a research scientist for a government project on environmental problems at the Shinshu Univ.*