

Regular Paper**VOC in Printers and its Elimination by Means of Thermally Activated Oxide Semiconductors (TASC)**

Yuichiro TSUKADA*, Yusuke SUZUKI*, Hiroo TAKAHASHI*, and Jin MIZUGUCHI*

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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. In this paper, we will present our novel VOC elimination system based upon thermally activated semiconductors (TASC) characterized by compact, lightweight, and low costs. Because of these appealing features, this system can easily be integrated into office printers or wet POD systems. The TASC technology dates back to our accidental finding that the semiconductor exhibits significant oxidative effects when heated at 350–500°C; whereas quite inactive at room temperature. The present phenomenon has been applied to the complete decomposition of VOCs. The destruction mechanism is composed of the following three steps: 1. oxidation, i.e. creation of radicals, 2. radical splitting, i.e. fragmentation of the giant molecule, and 3. reaction with oxygen, i.e. complete combustion into H₂O and CO₂.

Keywords : Volatile organic compound, Removal of VOC, Thermal activation of semiconductors, printer

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) can also cause 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 activated holes in oxide semiconductors such as TiO₂,⁴⁻¹³⁾ NiO,^{14,15)} Cr₂O₃,¹⁵⁻¹⁷⁾ and α -Fe₂O₃.^{18,19)} 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; whereas ours is

the application that utilizes semiconductive properties at high temperatures.

The purpose of the present investigation is to introduce our TASC technology to the imaging areas in an attempt to solve VOC problems in printers. The VOC elimination apparatus introduced here is characterized by heater-embedded and catalyst-coated honeycomb system, and has greatly been improved as compared with our previous model based on fluidized bed systems using semiconductor powders.¹³⁻¹⁸⁾

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. Since the VOC decomposition is carried out in air (*i.e.* in an oxygen atmosphere) at high temperatures, oxide semiconductors such as TiO₂, ZnO, Cr₂O₃, Fe₂O₃ etc. are the semiconductor of choice. Among these, we are particularly interested in Cr₂O₃ because of its high stability (melting point: about 2200°C). In addition, its safety is ensured as shown by the fact that Cr₂O₃ is widely used in our daily life as the green colorant for glass dyeing of whisky or wine bottles etc.

We explain first the optical excitation together with its subsequent photoconducting phenomenon [Fig. 1 (a)] and then discuss the oxidative property of 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

* Fiber Innovation Incubator, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan

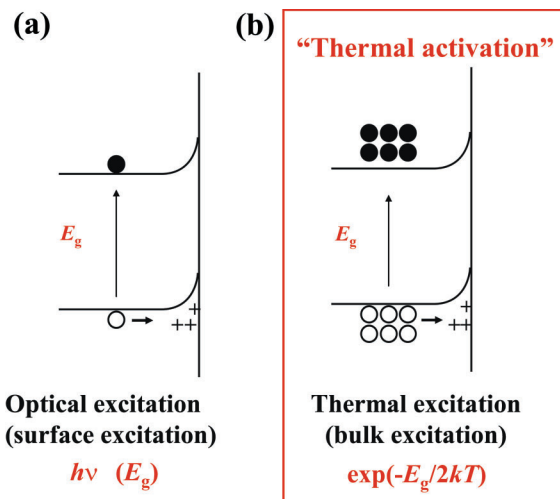


Fig. 1 Band diagram of semiconductors composed of the valence band and the conduction band: (a) optical excitation (i.e. surface excitation) and (b) thermal excitation (i.e. bulk excitation). E_g , k , and T designate the band gap of the semiconductor, Boltzmann constant, and temperature, respectively.

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 thus contribute to the increase in electrical conductivity. This is known as the photoconducting phenomenon. We focus here on the property of holes. The hole is known to strongly attract an electron from the conduction band or from organic compounds adsorbed on the surface in order to bring back the semiconductor to the original stable state. In other words, the hole has strong oxidation ability. These oxidative holes are utilized 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. We simply believed first that we could achieve it by creating a vast number of holes in the valence band by exciting the semiconductor 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 increases in accordance with an exponential function of temperature according to the semiconductor theory.²⁰⁾ In fact, our experiment using a single crystal of TiO_2 showed that the resistivity is about $10^{11} \Omega\text{cm}$ at RT. However, the resistivity is remarkably reduced to only $15 \Omega\text{cm}$ at 500°C .⁶⁾

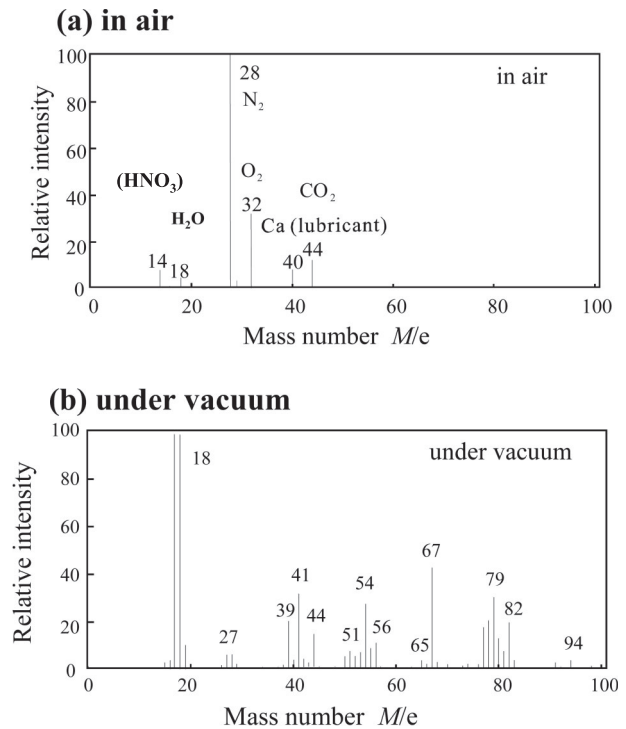


Fig. 2 Gas analysis of decomposition products of PC (i.e. a substrate for compact discs) by Q-mass: (a) in air, and (b) under vacuum.

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⁾ In this way, we finally achieved a very strong oxidation system with thermal activation of semiconductors.

We will show below an example of the instantaneous, complete decomposition of polycarbonate (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 . Gas analysis of the decomposition product was made by mass spectrometer and the result is 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 PC. 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

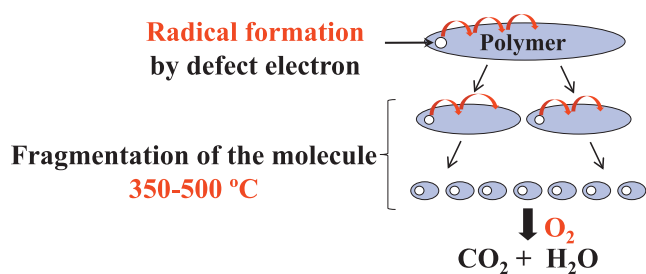


Fig. 3 Three destruction processes of PC by means of thermally generated holes in TiO₂: (a) thermal excitation, (b) radical splitting, and (c) complete combustion.

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 H₂O and CO₂. 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 schematically shown in Fig. 3.⁷⁾ The first process of the decomposition reaction is the capture of bonded electrons from polymers by defect electrons, 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 polymer chain unstable and induces “radical splitting”. This results in the fragmentation of the giant molecule, in a fashion, just “the reverse of radical polymerization”. The fragmented molecules then react with oxygen in air to give just H₂O and CO₂. To summarize the destruction mechanism, the process is composed of the three steps: 1. oxidation, i.e. creation of radicals, 2. radical splitting, i.e. fragmentation of the giant molecule, and 3. reaction with oxygen, i.e. complete combustion.

Up to now, we have achieved complete elimination of various VOCs by TASC: toluene & benzene,⁸⁾ chloro-based organic solvents²¹⁾, formaldehyde.²²⁾ The TASC technology has also been applied to the FRP (fiber-reinforced plastics) decomposition and the recycling of reclaimed reinforcing fibers.^{23,24)} Furthermore, metals recovered from mold motors²⁴⁾ as well as a novel repair method of carbon fiber FRP with reinforcing fibers intact has been also reported.²⁵⁾

3. Experiment

3.1 Materials and equipment

Cr₂O₃ powders (purity: 99%; specific surface: 3 m²/g) were obtained from Junsei Chemical Co., Ltd. Ceramic foam filters (#013) called “honeycombs in the present paper were purchased from Bridgestone Chemicals. The composition of the ceramic foam is similar to that of the cordierite which is a solid solution of 2MgO, 2Al₂O₃, and 5SiO₂. Isopar L fluid is characterized as a synthetic isoparaffinic hydrocarbon solvent

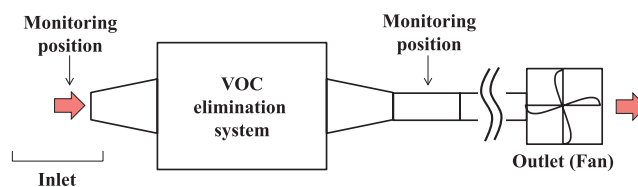


Fig. 4 Experimental setup for measurements of VOC concentrations.

(number of carbons: C11–13) produced from petroleum-based raw material, and the flash point is about 62°C. This is used as a solvent for liquid toners in Indigo Press from Hewlett Packard, was obtained from ExxonMobil Chemical. Canon black toners for LBP3300 were purchased from Canon Inc.

A hydrocarbon meter of a TVA-1000B from Thermo Fischer Scientific Inc. was used for measurements of VOC concentrations. A quadrupole mass spectrometer called Q-mass (model: RG-102 from ULVAC) was employed for gas analysis.

The suspension used for the coating of powdered Cr₂O₃ onto the honeycomb substrate is composed of 100 ml of acetone, 10 g of powdered Cr₂O₃, 0.3 g of nitrocellulose as dispersant or surface active agent. The suspension was conditioned in the presence of zirconia balls (0.6 mm in diameter) by a paint shaker for 30 min.

VOC concentrations were measured at the front and the rear of the VOC elimination system, as shown in Fig. 4.

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3.2 Fabrication of heater-embedded honeycombs coated with powdered Cr₂O₃

Fig. 5 shows the Cr₂O₃-coated honeycomb unit with a 300 W heater-embedded in a groove of the substrate. The dimension of the heater-embedded honeycomb is 130 × 200 × 30 mm. Eight pieces of the catalyst unit were stacked in pile and arranged vertically to constitute a catalyst system as schematically shown in Fig. 6 (a). Fig. 6 (b) is the external appearance of the apparatus. VOC is then made to flow from the inlet through a series of the catalyst units, and the temperature was controlled with two thermocouples placed at the middle and the end of the honeycomb system near the outlet. This apparatus was used for decomposition experiments for Isopar L as well as for dry toners.

The above equipment was designed for the flue-gas whose temperature is about 250–300°C. The maximum operation volume is about 1 m³/min when combined with a heat exchanger; 0.3 m³/min for the flue-gas of room temperature.

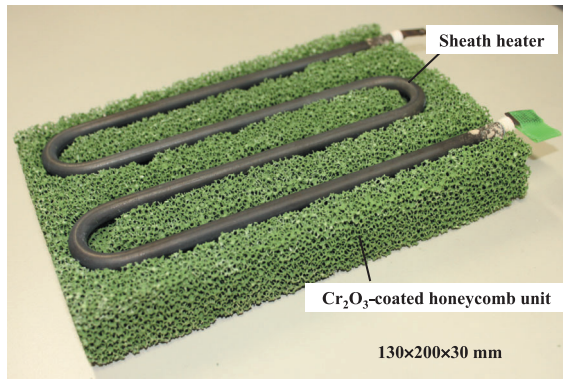


Fig. 5 Heater-embedded honeycomb unit coated with powdered Cr_2O_3 : $130 \times 200 \times 30$ mm.

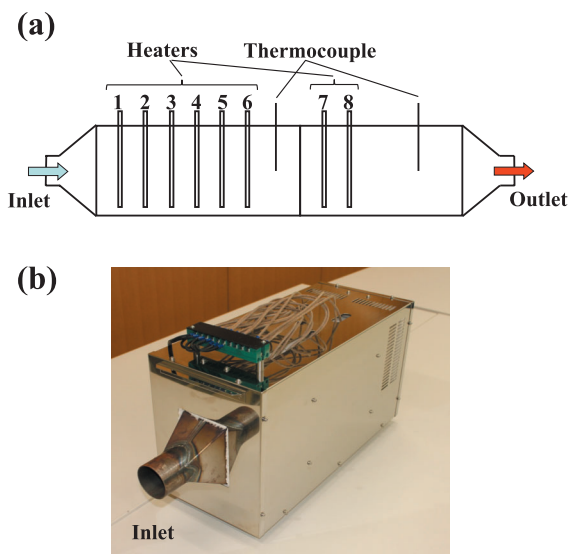


Fig. 6 VOC elimination system: (a) schematic representation and (b) external appearance ($240 \times 300 \times 560$ mm; 20 kg).

4. Results and Discussion

4.1 Complete decomposition of vaporized Isopar L

Isopar L was heated at 90°C for vaporization and the vaporized Isopar L (concentration: about 250 ppm) was then introduced into the VOC decomposition equipment (Fig. 6). Decomposition yield was evaluated by means of hydrocarbon meter for Isopar L, before and after VOC-elimination treatment. Fig. 7 (a) shows the decomposition characteristics of vaporized Isopar L as a function of temperature in the presence of Cr_2O_3 . The decomposition is about 90% at 400°C and almost 100% above 450°C . As a reference, the decomposition experiment was also carried out in the absence of Cr_2O_3 . The result is also shown in Fig. 7 (a). The decomposition remains at about 10% in the absence of Cr_2O_3 even at 500°C . This reflects the effectiveness of thermally activated Cr_2O_3 .

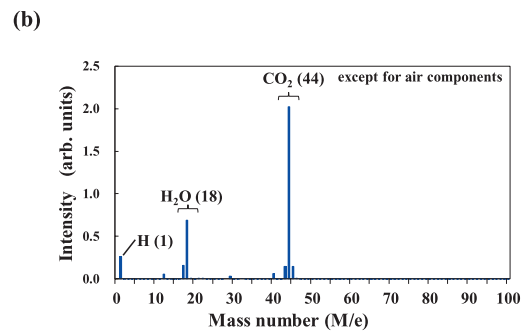
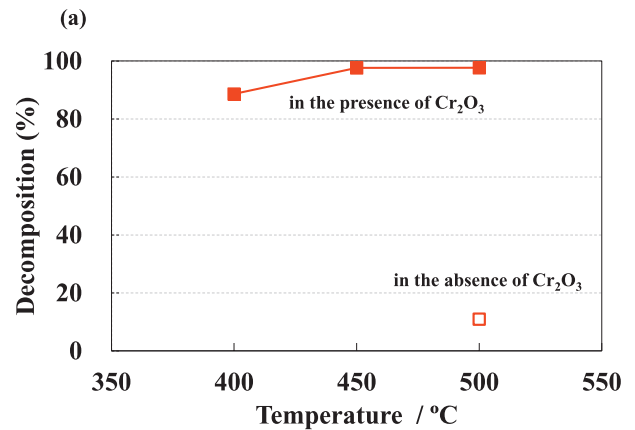


Fig. 7 (a) Decomposition characteristics of Isopar L as a function of temperature, and (b) decomposition products of Isopar L analyzed by Q-mass.

Fig. 7 (b) shows the gas analysis of the decomposition products of Isopar L after treatment at 500°C . We see peaks of CO_2 , H_2O , followed by H, showing the complete decomposition.

4.2 Decomposition of VOC arising from toner-fusing

In a similar way, dry toners were heated on a hot plate at 200°C and then the evolved VOCs were made flow into the mass spectrometer (Q-mass). Gas analysis revealed a number of fragments below mass number of 100, as shown in Fig. 8 (a). These are the decomposition products due to pigments, wax, polymers, charge control agents etc. contained in toner particles. On the other hand, when the VOC gas was treated with the VOC elimination apparatus (Fig. 6), the fragments mostly disappeared except for H_2O , N_2 , and CO_2 [Fig. 8 (b)], showing the complete elimination of the VOC.

4.3 Trial to lower the operation temperature

The operation temperature of 500°C appears to be a bit high for office printers. The trial to lower the operation temperature will be discussed below in view of the three reaction steps of the VOC decomposition described in section 2 (i.e. 1. oxidation, i.e. creation of radicals, 2. radical splitting, i.e. fragmentation of the giant molecule, and 3. reaction with oxygen, i.e. complete combustion). The temperature factor is variously involved in these steps. In step 1, the number of charge carriers is determined by the Fermi-Dirac distribution and increases

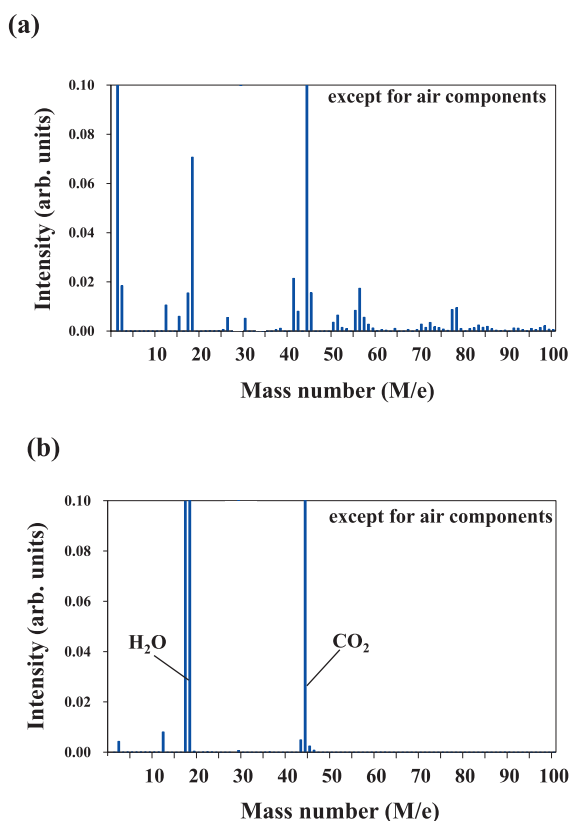


Fig. 8 Gas analysis of dry toners heated at 200°C : (a) as heated and (b) after treatment with TASC.

with temperature. This indicates that a certain number of electrons and holes are surely produced even below 200°C, for example. This may appear to assure the formation of cation radicals at lower temperature in VOC molecules to be decomposed. However, it is important to note that the activation energy for the radical formation (that is, capture of bonded electrons) depends greatly on the type of molecule: aliphatic or aromatic compounds. In general, the aliphatic molecule can easily be more attacked by oxidative holes than the aromatic one.

The second activation step (i.e. "fragmentation") is related to the propagation ability of radicals throughout the entire molecule to induce a radical splitting, yielding fragmented molecules. Step 3 is a reaction of fragmented molecules such as ethylene or propane with oxygen in air. This is related to the flash point of each molecule in question.

To sum up the above discussion, it is worth while trying to experimentally lower the operation temperature in consideration of the temperature-involved destruction mechanism of VOCs.

4.4 Compact VOC elimination equipment of the built-in type

A compact VOC elimination equipment is shown Fig. 9 that can easily be integrated into office printers or wet POD systems. The present prototype is composed of a VOC collector

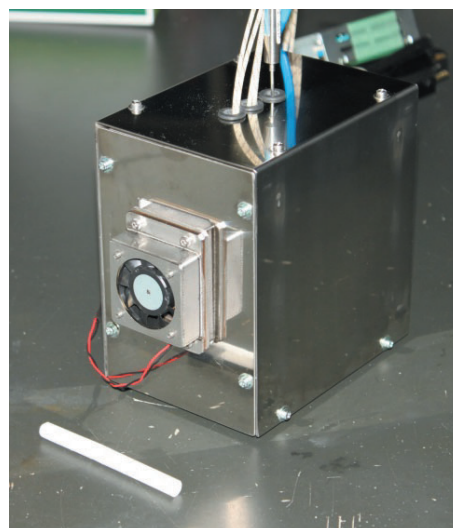


Fig. 9 Compact VOC-elimination system of the built-in type (100 × 130 × 140^H mm ; 1.5 kg).

at the front and the VOC elimination body. The apparatus should be placed as close as possible to a heat source such as the toner fuser.

5. Conclusions

The result of the present investigation can be summarized as follows :

1. TASC is characterized by the use of oxidative holes in semiconductors heated at high temperatures.
2. The TASC technology has been applied to the complete elimination of VOCs in printers.
3. Our VOC elimination system is simple and compact, so that it can easily be integrated into conventional printers.

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Yuichiro TSUKADA

He received his BS and MS degrees in physics from Yokohama National University in 2006 and 2008, respectively. He worked at Seiko Epson Corp. from 2008 to 2012. Since 2012, he has been working as a research scientist at Shinshu University. His current interest is VOC elimination by thermally activated semiconductors.



Yusuke SUZUKI

He received his BS from Shinshu University in 2012. He is currently master's student at the same university, majoring in applied chemistry. His interest includes materials science of the complete recovery of reinforcing fibers from fiber reinforced plastics by means of thermally activated oxide semiconductors.



Hiroo TAKAHASHI

Hiroo Takahashi received his Bachelor of Engineering from Waseda University in 1968 and Dr. of Engineering from Yokohama National University in 2005. He worked at Sony Corporation from 1968 to 2004. He was involved in R & D of Trinitron TV from 1968 to 1975 as a senior manager, as well as of optical discs from 1975 to 2004 as the general manager. He is currently a research professor at Shinshu Univ.

**Jin MIZUGUCHI**

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Sc. from the University of Tokyo in 1982 and Venia Docendi from the University of Bern in 1994. He worked at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. From 1995 to 2011, Prof. Mizuguchi was at Yokohama National University as professor of materials science. In 2011, he retired from Yokohama National University. Since 2011, he has been at Shinshu Univ. as a research professor. He is a recipient of the Fellowship Award and the Carlson Memorial Award of the Society of Imaging Science and Technology in U.S.A. in 2000 and 2008, respectively. He received three times the Journal Award of Imaging Society of Japan in 2001, 2005, and 2006. He was awarded in 2006 the Society Award of Imaging Society of Japan.
