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AgX Photography: Present and Future

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Abstract. *The analysis of the technologies for color films is followed by the comparisons in technology and performance between color films and digital still cameras. Since the image qualities of pictures taken by color films and digital still cameras are already good enough for amateur consumers, many people have come to use convenient digital still cameras. However, there are substantial differences in image quality and performance between them, which are based on the difference in technology, and provide the reason to predict that people will use color films in addition to digital still cameras in the future. Then, descriptions are made to indicate that various technologies cultivated in silver halide photography for many years are being extended to various new fields. © 2007 Society for Imaging Science and Technology.*
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INTRODUCTION

Silver halide photography was born in 1839 when Daguerre invented the daguerreotype with thin silver iodide layer as a photosensitive material.[1] Since then, silver halide photography has made such remarkable progresses as the achievements of huge speed increase by as large as four hundreds thousands times[2] and full color photography. At AgX 2004, the International Symposium on Silver Halide Imaging, Takada classified silver halide photographic materials into two groups in relation to digital imaging as shown in Table I.[3] Among the materials in competition with digital photography, the sales of color negative films are decreasing significantly, while those of motion picture films are maintaining. Among the materials in coexistence with digital photography, color papers for digital printing and dry imager films for medical diagnosis are maintaining or even increasing.

In this article, the present author analyzed the present state of the technologies used for color films, which are representatives of silver halide photographic materials, compared in technology and performance between color films and digital still cameras, and then discuss some examples of the extension of silver halide technologies to new fields, which are being carried out at the present.

TECHNOLOGIES IN COLOR FILMS

Figure 1 shows the scanning electron micrograph of the section of a color negative film having a photosensitive layer with about 20 μm thick on a triacetylcellulose (TAC) film base with about 100 μm thick. In addition to photosensitive layers, TAC film bases have ever been refined for many years.[4] Figure 2 shows the scanning electron micrograph of the section of the photosensitive layer in the above-stated color negative film. White lines are the sections of thin tabular silver halide grains. As seen in this figure, a color film is a three-dimensional sensor with many functional layers in pile. There are three major layers, which are sensitive to three primary colors, i.e., blue, green, and red. In each major layer, there are two or three sublayers with high, medium, and low sensitivities. A color film is thus designed to capture an image with full color and large dynamic range by taking advantage of its three-dimensional structure.

However, it has been theoretically predicted that the red-sensitive layer should have considerable negative sensi-

Table I. Trends of silver halide (AgX) photographic materials in digital imaging atmosphere (see Ref. 2).

Relation with digital imaging		AgX photographic materials	Trend
Competition	Image-capturing	Color negative films	Decreasing
		Color reversal films for high-end amateur	Maintaining
		Motion picture films	Maintaining
Co-existence	Printing	Color papers for digital printing	Increasing
		Photothermographic films for medical diagnosis	Increasing

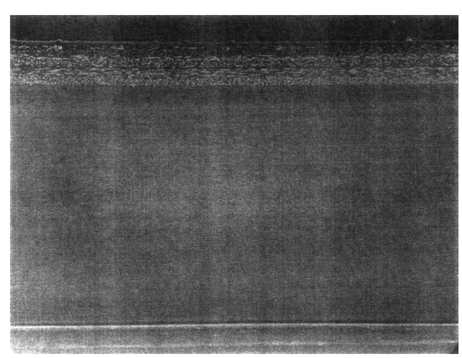

Figure 1. Scanning electron micrograph of the section of a color negative film composed of a photosensitive layer (~20 μm thick) with silver halide grains as white lines and spots suspended in gelatin on a TAC film base (~100 μm thick).

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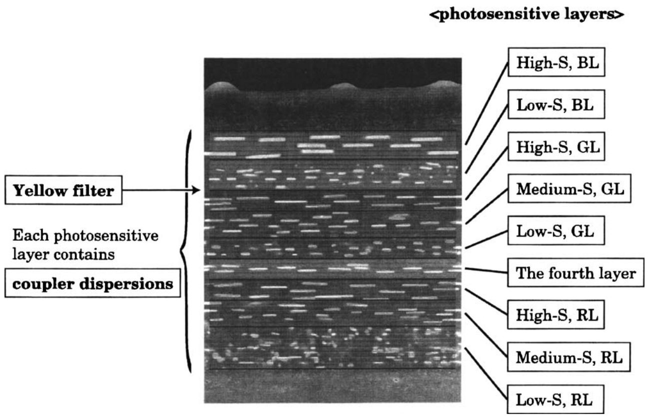

Figure 2. Scanning electron micrograph of a photosensitive layer of a color negative film with three major layers sensitive to blue, green, and red lights (BL, GL, and RL, respectively), and sublayers with high, medium, and low sensitivities (high-S, medium-S, and low-S, respectively).

tivity in blue-green region in order to achieve faithful color reproduction by a color film with layers sensitive to three primary colors only. In order to achieve this prediction, the fourth layer is introduced into color films, as seen in Fig. 2, to depress the development in the red-sensitive layer according the exposure to blue-green light.[5]

A light image is captured by silver halide grains, recorded by forming on the grains latent image centers composed of silver clusters, and displayed through photographic development, by which the grains with latent image centers on the surfaces are reduced. It is generally accepted that the smallest latent image center is composed of four silver atoms.[6] There are 20 billion silver ions in a cubic AgBr grain with edge length of 1 μm. Among them, only four silver ions are needed to be reduced to form a latent image center, which initiates the reduction of all the remaining silver ions in the grain by development. In this case, the degree of the amplification by development is at most as large as 5 billion times, contributing to achieve such a high sensitivity by a silver halide photographic material.

Since silver halide grains used for color films are now very thin, they can absorb blue light only weakly. In blue-, green-, and red-sensitive layers, silver halide grains are covered with monomolecular layers of J-aggregated sensitizing dye molecules, which absorb blue, green, and red light, respectively, and then inject electrons into the conduction band of silver halide grains.

The factors influencing photographic sensitivity are therefore the light absorption, efficiency of latent image formation, and size of the smallest latent image center.[7] As summarized in Table II, it is judged that room for improvement in light absorption is a factor of 2, and that the room for the improvement in the efficiency of latent image formation is more than threefold. The size of the smallest latent image centers will not be changed soon. In total, it is judged that the room for speed increase in the future should be several-fold.[7]

According to Marchant, the replacement of conventional silver halide grains by thin tabular ones developed at that time[8] could increase the light absorbance of a color film up to about one half.[9] At the present, thin tabular silver halide grains covered with mono-molecular layer of J-aggregated sensitizing dyes are used in color films. It is expected that the light absorbance of a color film is increased by two times through the improvement of tabular silver halide grains and the achievement of multimolecular layer of sensitizing dyes on each grain. Electron micrographs in Fig. 3 show recent improvements in tabular silver halide grains in color films, indicating the decrease in their thickness with time.

Table II. Factors influencing photographic sensitivity and technologies to improve them.

Factors	Present state	Limit	Room for improvement
Light absorption	~1/2	1	2 times
			Thin tabular grains
			Antenna dye sensitization
Efficiency of latent image formation	~1/3	1	3 times
(1) Yield of electrons			Two electron sensitization
(2) Site for latent image formation			Chalcogen sensitization (S $\rightarrow$ Se, Te)
(3) prevention of recombination			Dislocations to localize electrons
			Two electron sensitization
The smallest latent image centers	3 atoms	3 atoms	1 time

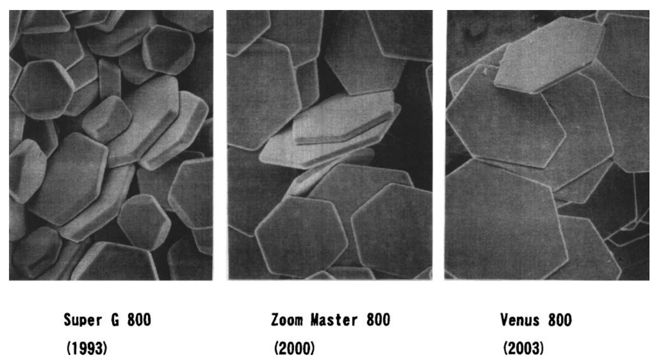

Figure 3. Scanning electron micrographs of tabular silver halide grains used in recently developed color negative films.

In order to use sensitizing dyes, whose amount is larger that that for their mono-molecular layer on the grain surface, several proposals have been made in the past, including dye multilayer by Gilman et al.,[10] dye/silver halide junction by House,[11] and antenna dye system with energy transfer among dye molecules by Bird et al.[12] At AgX 2004, Muenter and others described an antenna dye sensitization with bimolecular layers of sensitizing dyes on the grain surface, which could be used to color films.[13]

It is predicted that the efficiency of latent image formation will be increased by three times owing to the enhancement of the yield of free electron, the optimization of the sites for latent image formation, and the prevention of recombination between electrons and positive holes.[7] The quantum yield of free electrons will be improved by the refinement of the two electron sensitization, according to which one absorbed photon creates two free electrons, as is already achieved in part by reduction sensitization.[6,14] This has led to the proposals of new types of the two electron sensitization with formate[15] and fragmentable electron donors.[16] In the latter case, an excited dye injects an electron to the conduction band of silver halide and leaves a dye positive hole. The oxidation of a fragmentable electron donor by a dye positive hole gives a radical with an activated electron, whose electronic energy level is higher than the bottom of the conduction band of silver halide.

Among the sites for latent image formation, a sulfur sensitization center is the most popular and has been used since it was discovered by Sheppard in 1925.[17] According to our recent investigation, a sulfur sensitization center is composed of a dimer of two substitutional sulfur ions associated with two interstitial silver ions for the compensation of excess negative charges on the sulfur ions.[6,18] Each interstitial silver ion has a hydrogen-like orbital, to which an electron is loosely bound. An electron is captured at the bonding orbital formed owing to the interaction between the two hydrogen-like orbitals associated with the interstitial silver ions in a sensitization center.

Hailstone has theoretically estimated the quantum sensitivity in terms of the number of absorbed photons per grain for latent image formation as functions of the depth and number of sites for latent image formation, showing the tendency that the sensitivity increases with decreasing the trap depth.[19]

According to the above-stated structure of a sulfur sensitization center, it is expected that the decrease in its trap depth should be achieved by increasing the sizes of ions in the center in order to decrease the degree of the interaction between two hydrogen-like orbitals associated with two interstitial silver ions in the center. One of the ways for that is the replacement of one of an interstitial silver ion by an interstitial gold ion to give a sulfur-plus-gold sensitization center.[6] In accord with this prediction, it has been already confirmed that the trap depth of a sulfur-plus-gold sensitization center is shallower than that of a sulfur sensitization center.[20] Sulfur sensitization and sulfur-plus-gold sensitization have been put to practical use for many years.

The other way to decrease the trap depth of a sulfur sensitization center is to expand it to chalcogen sensitization by replacing sulfur ions in a sulfur sensitization center by selenium and tellurium ions for the formation of selenium and tellurium sensitization centers, respectively. Morimura and others have comparatively characterized all the possible chalcogen sensitizations and found that the trap depths were 0.28 eV (sulfur sensitization center), 0.17 eV (selenium one), and 0.12 eV (tellurium one).[21] The increase in amount of a sulfur-sensitizer brought about significant decrease in sensitivity on exposure to high intensity light. This phenomenon is known as high-intensity reciprocity law failure owing to the difficulty for the growth of image centers bringing about the dispersion of latent image formation.[6] Selenium sensitization is superior to sulfur sensitization in that the degree of the high-intensity reciprocity law failure was smaller in selenium-sensitized emulsions than that in sulfur-sensitized ones. Tellurium sensitization is superior to sulfur and selenium sensitizations in that the high-intensity reciprocity law failure was nearly absent. On the other hand, the ability to enhance nucleation of latent image formation and depress low-intensity reciprocity law failure was found to increase in the order of sulfur sensitization, selenium sensitization, and tellurium sensitization. While tellurium sensitization has been realized recently,[21] all the chalcogen sensitizations have been studied for practical use in order to meet the necessary condition for new products.

One of the ways to depress the recombination between electrons and positive holes is obviously the two electron sensitization. Another way to depress the recombination is to introduce dislocations along the edges of a thin tabular silver halide grain. Electrons are thus localized by dislocations along the edges, and separated from positive holes trapped by sensitizing dyes on the main surfaces of the grain.[22]

COMPARISON BETWEEN COLOR FILMS AND DIGITAL STILL CAMERAS

A digital still camera is equipped with a charge coupled device (CCD) or complementary metal-oxide-semiconductor (CMOS), in which pixels are placed side by side to form a two-dimensional image-capturing device. In a recently produced CCD, microlenses in each pixel focus incident photons on a diode, where absorbed photons generate electrons, the number of which is proportional to that of absorbed photons. It is therefore necessary to put in each pixel a filter which transmits one of three primary colors and absorbs the other two. Namely, it is noted that two thirds of incident photons are absorbed by a filter in each pixel and are not used for image formation.[23] Electrons generated in a diode are accumulated in a potential well in each pixel, and transferred to give a signal composed of the number of electrons in each pixel in series. A CCD thus operates with the generation, accumulation, transfer, and detection of carriers.

Figure 4 shows the characteristic curves of a CCD and silver halide grains. A CCD is a linear sensor in that the number of the generated electrons is proportional to the number of absorbed photons and is therefore suitable for an emissive display. The dynamic range for taking pictures is generally narrow, being limited by the number of electrons at the fog level and the number of electrons to fill the potential well in each pixel. A photographic material with silver halide grains is a nonlinear sensor in that the fraction of developable grains is linear in its most region with the logarithm of exposure and is therefore suitable for a nonemissive display, in which the Lambert–Beer law is important for the behavior of light. A pixel which is a photosensitive element in a CCD for a digital still camera is analog in the way of its

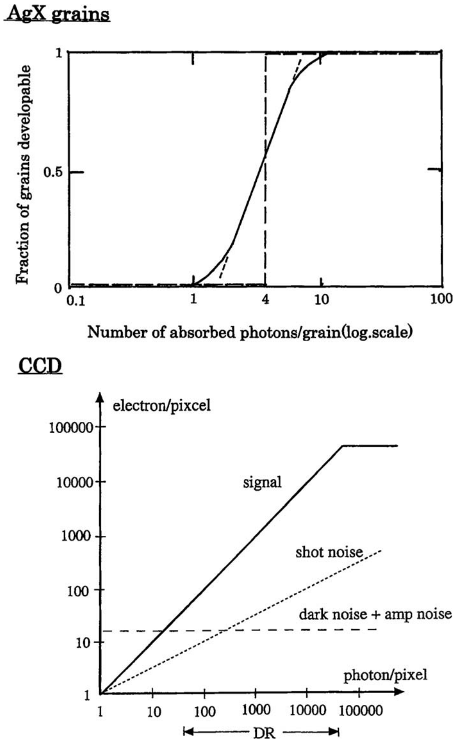

Figure 4. Characteristic curves of silver halide grains (solid curve) and a silver halide grain (dashed line) in terms of the fraction of developable grains as functions of the logarithm of the number of photons per grain, and of a CCD in terms of the number of electrons per pixel as a function of the number of absorbed photons per pixel.

operation. A silver halide grain is a photosensitive element in a color film and is digital in the way of its operation, insofar as a grain is either developable or not developable.

Comparison in technology between color films and digital still cameras is summarized in Table III. Each pixel in a color film with a three-dimensional structure captures the incident lights with three primary colors separately, while each pixel in a CCD with a two-dimensional structure captures the incident light of only one of the three primary colors. In addition, the frame area of a conventional color film with 135 format is about 30 times larger than that of a CCD with 1/2 in. format for a compact camera. In total, the number of pixels per frame of a color film should be about two orders of magnitude larger than that of a CCD for a compact digital still camera.

Here is an old tale. The productive yield of CCDs sharply decreased with increasing their frame area in 1986,[24] while that of color films was independent of it. Since pixels were electrically connected with each other in series in a CCD, only one defect or dust speck could deteriorate the whole function of a CCD. On the other hand, the function of a pixel in a color film is the accumulation of the responses from several hundreds independent silver halide grains and is hardly deteriorated by small numbers of defects and dusts. This was the reason why it was difficult at that time to increase the frame area of a CCD without deteriorating its productive yield.[25]

Table III. Comparison in technology between color films and digital still cameras.

	Color film	Digital still camera
Structure	Three-dimensional	Two-dimensional
Frame area	Larger (~30 times)	Smaller
	Easy to increase	Difficult to increase
Merit of image processing	Smaller	Larger (interpolation, etc.)

Table IV. Comparison in performance and capability between color films and digital still cameras.

	Color films	Digital still cameras	Reference
Image quality	Good enough	Good enough	
(Number of pixels)	Larger (4 times)		28
(granularity)		Better	
Expression	Details	Sharpness	T. Uchiyama *et al.*[a]
Sensitivity	Higher (2 stops)[b]		31
Dynamic range	Wider (6 stops)[b]		
Image permanence	Better		
Convenience		Better	

[a]Although the results were not presented independently, they were demonstrated in the references for the papers presented at recent several international meetings (Ref. 7(a)–7(d)) including at ICIS'06.

[b]One stop is 0.3 log *E*, where *E* is exposure.

Since then, this difference was significantly reduced by progress in the image processing technology, which made it possible to use CCD with deteriorated pixels for the production of digital still cameras by interpolating them with the responses of their surrounding pixels.[26] It is now possible to produce CCD with APS and 135 formats available for single lens reflex cameras and other purposes. It is considered that this is one of the most important causes for the fact that digital still cameras have recently made more extensive progress than the present author predicted previously.[7] However, it is still important to notice that color films are more suitable than digital still cameras to provide fine pictures with a large number of pixels, since the increase in the number of pixels per frame can be simply realized by increasing the frame area.[27]

Comparisons in performance and capability have been made between color films and digital still cameras according to Table IV. Although the image qualities of the pictures taken by color films and digital still cameras are good enough for amateur consumers, they are different from each other as analyzed by Noguchi and Ikoma in 1998.[28] When the image quality was judged to be the same, a color film was superior to a digital still camera in the number of pixels per frame by four times, while a digital still camera was superior to a color film in granularity.

In collaboration with Ueda, Uchiyama of Imaging Materials Research Laboratories in Fuji Film Co. has comparatively taken various pictures with the highest possible image quality using color films and digital still cameras. For this purpose, they used color reversal films including the recently developed one, to which latest technologies were applied as described in the paper presented by Ueda at ICIS'06.[22(b)] Along with this, they used a state-of-the-art single lens reflex digital still camera. Then, we analyzed and compared image quality, and found some substantial differences which could be ascribed to the differences in technology between them. The present author showed these pictures to the audience on the occasion of his keynote speech at ICIS'06, indicating the following points. First, he indicated the difference in the expression of the feel of a material by showing that color films could reproduce the details of the skin of a lady's face more precisely than digital still cameras. Then, he indicated the difference in the expression of the variety of colors by showing that the variety of colors in leaves of trees could be reproduced more widely by a color film than by a differential scanning calorimetry (DSC). Lastly, he indicated the difference in edge sharpness by showing that an airplane was reproduced more sharply by a digital still camera than by a color film.

The resolution of a light sensor is usually evaluated by its modulation transfer function (MTF), which is given by the ratio of the amplitude of the corresponding output signal to that of an input light signal with a sine curve as a function of the frequency of the sine curve.[29] While the MTF of a color film gradually decreases with frequency, it still keeps a positive value well into the high frequency region. While the MTF of a CCD also decreases with frequency, it becomes zero at the Nyquist frequency, which is given by $1/2p$ when a pixel pitch is p, and even becomes negative on further increasing the frequency. This phenomenon is known as "aliasing" in a one-dimensional image and "moiré" in a two-dimensional one. An image taken by a CCD is thus processed by a low-pass filter in a digital still camera in order to eliminate its response in the region with frequencies, near and larger than the Nyquist frequency. This is responsible for the lack of the detailed reproduction of the skin of a lady's face. The enhancement of the response of a digital still camera in the middle frequency region is responsible for sharp reproduction of the airplane by a digital still camera. The above-stated image processing sometimes makes pictures taken by DSCs appear unrealistic.

Wide and rich reproduction of a variety of colors by a color film is caused by an inter-image effect taking place during development in the presence of DIR, development inhibitor releasing couplers.[30] Namely, a development inhibitor is released in a layer according to exposure, and depresses the development in its adjacent layer to enhance the difference among reproduced colors.

According to the analysis by Uchida and Takada reported at ICIS'02,[31] the International Congress of Imaging Science in Tokyo in 2002, the sensitivity of a color negative film was higher by two stops than a digital still camera, and the dynamic range of a color film was larger by six stops than a digital still camera. A similar situation was reported by Yamaryo for color films and DSCs for taking motion pictures.[22(a)] By combining a highly sensitive color negative film ISO 1600 with a compact camera having a bright lens $f/1.9$, it is possible to take pictures of almost all objects without aid of flash;[32] a picture taken without flash is more natural than that taken by use of flash.

One of the most important advantages of color films over DSCs is the image permanence for a long period. It is predicted that pictures taken by recently developed color films will exist for more than 100 years without noticeable deterioration in image quality.[22(b)] However, it is not certain at present if we can keep the pictures recorded in electronic media available for such a long period, taking into account of the fact that electronic recording media have been replaced rapidly by new ones with different technology and have often become unavailable.

While digital still cameras have become very popular owing to satisfactory image quality and overwhelming convenience, color films are characterized by several strong points as stated above, which provide us with the reason to believe that people will use color films along with digital still cameras in the future.

EXTENSION OF SILVER HALIDE TECHNOLOGIES TO NEW FIELDS

It is noted that silver halide technologies, which have been developed for many years, are being extended to new fields. They include new nuclear silver halide emulsions for detection of neutrinos,[33,34] silver iodide grains, which act as image-capturing elements and are fixed during thermal development in photothermographic materials as reported at ICIS'06,[35] application to liquid crystal displays of cellulose triacetate films, which have been extensively refined for color films,[36] application of technologies in color films to CCD and CMOS in digital still cameras,[37–39,23] the knowledge of the electronic structure of the interfaces between dye layers and silver halides as extended to that of the interfaces between organic layers and electrodes in electronic devices,[40–42] and influence of dye sensitization on dye-sensitized solar cells and photocatalysts.[43–47] Although thorough reviews on all the above topics exceed the capacity of this article and the capability of the present author, brief descriptions on some of them from the viewpoint of the present author might be still meaningful to recognize the importance of photographic science and technology.

The presence of the neutrino oscillation, which should be evidenced by observing the change of μ neutrinos to ν neutrinos during the travel of the former for a long distance, is one of the most exciting topics in nuclear physics. For this purpose, Super Kamiokande with huge amount of water and more than 10 000 photoelectron multipliers was successfully used by Koshiba and others to measure the decrease in the dose of μ neutrinos,[33] although it was not available to confirm the appearance of ν neutrinos owing to its poor at resolution. Now, a big project named OPERA is being planned to directly observe appearance of ν neutrinos during travel of μ neutrinos for a long distance, by use of a detector employing the newly developed nuclear emulsion films.[34] Each film has two nuclear emulsion layers 44 μm thick on both sides of a film base 200 μm thick. The emulsion tracking apparatus for this project is composed principally of lead plates and the above films. Silver halide emulsions of 100 tons in weight are needed to detect neutrinos, which are only weakly interactive with materials, and have to travel for distances as long as $>$700 km to carry out the oscillation.

The technologies used for color films are being transferred to the design of CCD and CMOS. In the first place, the three-dimensional structure of a color film was applied to a CMOS by use of the fact that the images of three primary colors are captured by silicon at different depths owing the difference in the penetration depth of light among the three primary colors in silicon.[37] This system is free from the color moiré problem without aid of any low-pass filter. At ICIS'06, Takada and colleagues proposed a three-dimensional sensor with organic thin films as a photosensitive materials.[23]

Following the idea that the dynamic range of a color film is expanded by use of two or three emulsion layers with different sensitivity in a stack, the dynamic range of a CCD has been expanded by such a way that each pixel is equipped with two diodes with different sensitivities side by side.[38] The fourth layer technology for the improvement of color reproduction in color films was applied to the design of a CCD by using one of two green-sensitive pixels in the Bayer arrangement to reduce the response of the red-sensitive pixel according to exposure to blue-green light.[39]

There are many devices, which have in common the interface between an organic layer and a substrate. They include dye sensitization in photography, solar cells with thin organic layers, and organic electroluminescent devices. In collaboration with the present author, Seki and others have found by ultraviolet photoelectron spectroscopy that the vacuum levels of sensitizing dye layers are always considerably lower than that of a silver bromide layer when they are in contact with each other.[40] This result has driven Seki and others to study the electronic structure of the interface between an organic layer and a metal electrode. They have then revealed that the vacuum level of the former is considerably lower than that of the latter for almost all the combinations between organic materials and metal electrodes.[41] The above result indicates the formation of an electric double layer at the interface between an organic layer and a metal electrode, to which many scientists are now paying attention because of its importance in understanding and design of electronic devices with organic layers.[42,43]

It is also interesting to note the extension of dye sensitization originally developed in silver halide photography to new fields. Dagueere invented silver halide photography in 1839,[1] and Vogel invented dye sensitization for it in 1873.[44] While Kikuchi was studying photographic chemistry in his laboratory in 1940s–1960s, the present author began to study dye sensitization in his laboratory in 1963. He also studied photoelectrochemistry under the guidance of Honda and proposed a new model for the mechanism of dye sensitization on the basis of the photoelectrochemical study.[45] In 1965, Fujishima started to study dye sensitization with silver bromide as an electrode from photoelectrochemical viewpoint also under the guidance of Honda, and then used titanium oxide instead of silver bromide as an electrode to demonstrate the photolysis of water.[46] This discovery stimulated studies on titanium dioxide[47] and led Fujishima and Hashimoto to observe the marked change in the water wettability of its surface before and after UV irradiation in 1995, which then made it possible to put the photocatalytic phenomenon of titanium dioxide into practical use by providing self-cleaning surfaces.[48] It is, however, noted that the photocatalytic behavior of titanium dioxide had already been observed for the first time by Frank and Bard in 1977,[49] and studied by many scientists after that.[50] Although Fujishima and Hashimoto thought it difficult to use titanium dioxide for solar energy conversion owing to the lack of its ability to absorb visible light,[48] Graetzel developed a dye-sensitized solar cell with a sintered layer of fine titanium oxide grains, whose surfaces are covered by specially selected sensitizing dye molecules,[51] following many studies on dye sensitization of semiconductors.[52,6] Now, many scientists and engineers are optimistically trying to put dye-sensitized solar cells into practical use.

The above descriptions indicate the timelines of some of the aspects of the sciences and technologies, which have originated from silver halide photography and are developing new fields. It is expected that these activities will be highly successful in developing new sciences and technologies for the future.

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