TiO_2 Photocatalytic Oxidation R & D in Japan

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Overview

- Several historical events, 1972 to present
- Some science and interesting research results
- Some product photos
- Demonstration experiments

Splitting water with light

- A. Fujishima, K. Honda, *Nature* (1972)
- TiO_2 crystal produces O_2
- Pt counter electrode produces H_2

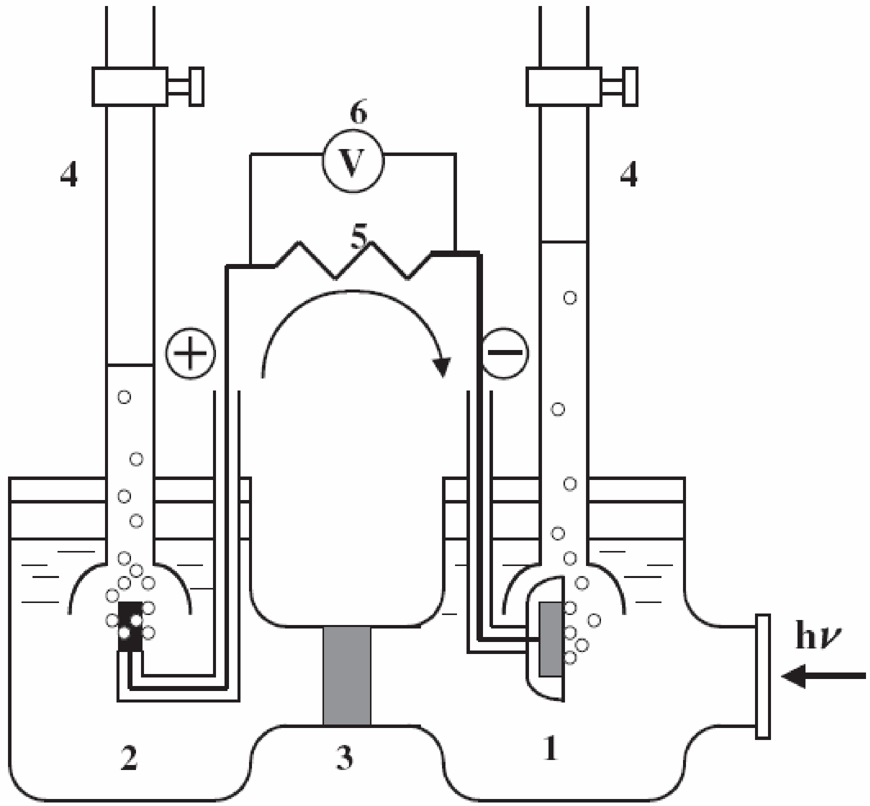


Fig. 1. Schematic diagram of electrochemical photocell. (1) n-type TiO_2 electrode; (2) platinum black counter electrode; (3) ionically conducting separator; (4) gas buret; (5) load resistance; and (6) voltmeter.

Natural UV too diffuse for energy production, cleanup of intense pollution (1990, TOTO, Inc. & Japanese researchers)

- Sunlight a diffuse resource
- UV is only 3 – 5 % of solar energy
- Even efficient processes not practical

- Strategy: small amounts of compounds adsorbed on TiO_2 surfaces can easily be decomposed, even in the shade

1995 serendipitous discovery of superhydrophilic effect by TOTO, Inc.

- Water wets TiO_2 surface; forms sheets, not droplets
- Distinct phenomenon from photocatalytic oxidation of organics

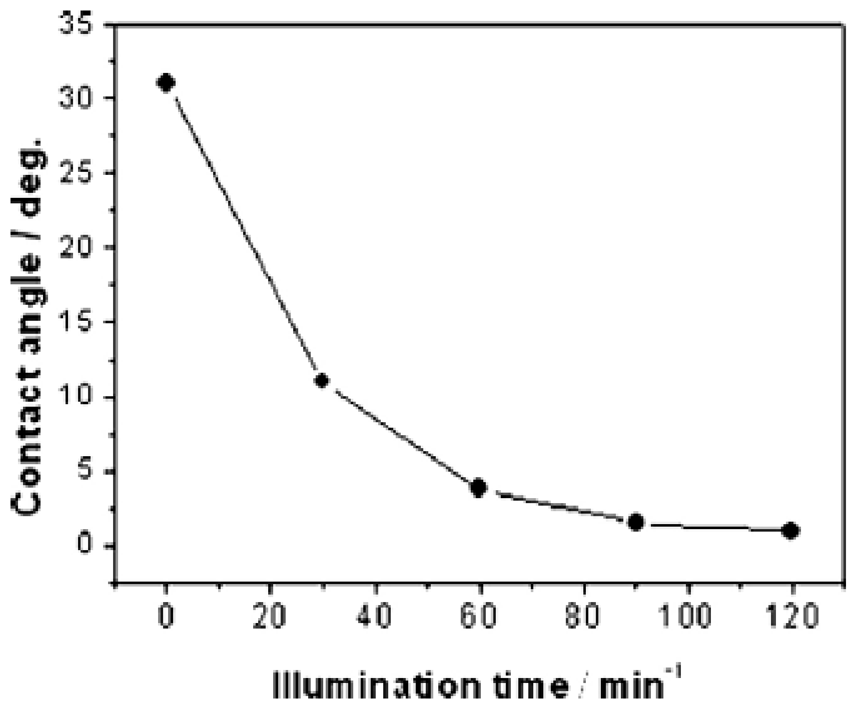


Fig. 5. Water contact angle as a function of time under UV illumination (1.1 mW cm^{-2}) for a polycrystalline TiO_2 film on glass.

Hydrophilic mirror reflects clear images

Current emphasis in Japan

- TiO_2 photocatalysis in transition from research and development into the marketplace
- Committee work on performance standards

- Search for modifications of anatase TiO_2 that
  - May be more effective
  - May utilize some of the visible spectrum

Hydroxyl radicals are key

- Water is on TiO_2 surface (r.h. > 0)
- $H_2O \rightarrow H^+ + OH^-$
- UV photon $\rightarrow e^- + h^+$
- $OH^- + h^+ \rightarrow OH\bullet$
- $OH\bullet$ has seven valence electrons and "wants" another; hence a strong oxidizer

PCO of NO

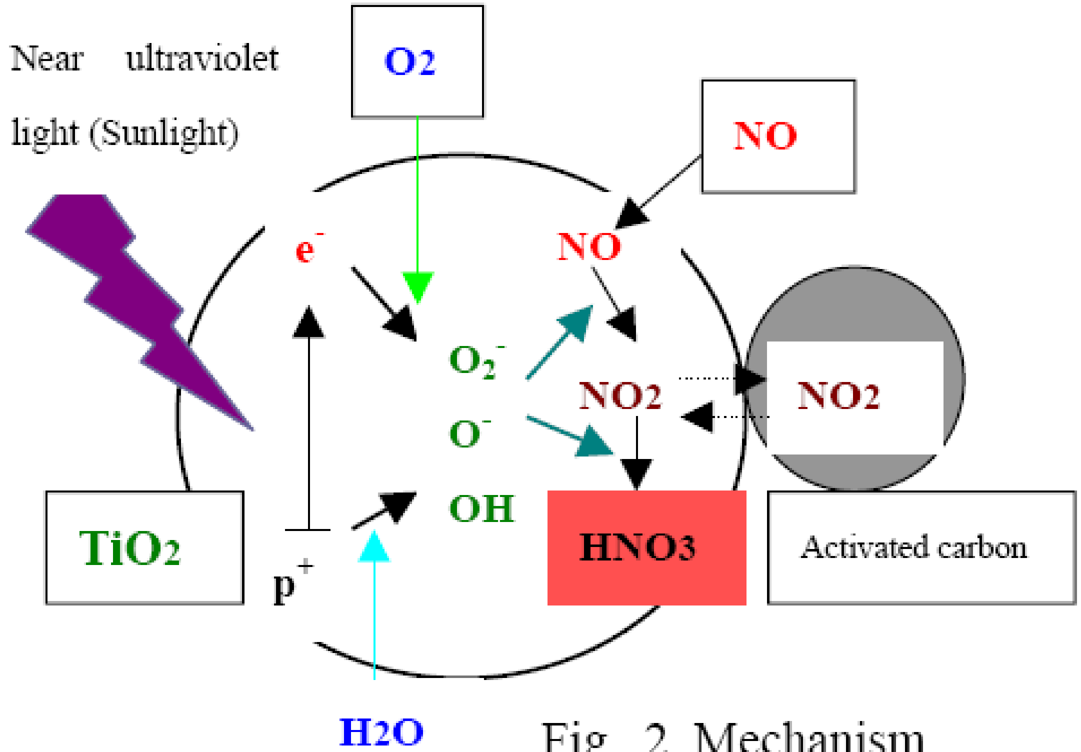


Fig. 2 Mechanism of photocatalysts

High reaction rates with OH suggest compounds that are readily photo-oxidized

Table 1 Reaction speed constants of air pollutants and OH (25°C) (k: 10^{-13} cm^3 $molecule^{-1}$ s^{-1})

Pollutant	k	Pollutant	k	Pollutant	k	Pollutant	k
CO	1.3	H2S	48	CH3COOH	8.0	C3H6	300
NO2	670	HCHO	92	CH4	0.06	CH3CCl3	0.1
NH3	1.6	CH3CHO	200	C2H6	2.5	CHCl=CCl2	21
SO2	20	CH3OH	7.9	C3H8	11	C6H6	10
CH3SH	330	C2H5OH	1.6	C2H4	90	Toluene	61

Sunada *et al.*, 2003: Quantum efficiencies > 25%

- Propanol oxidizes to acetone
- In low light each photon has a 30% chance to make an acetone molecule
- At 1 ppmv, photons are used less efficiently

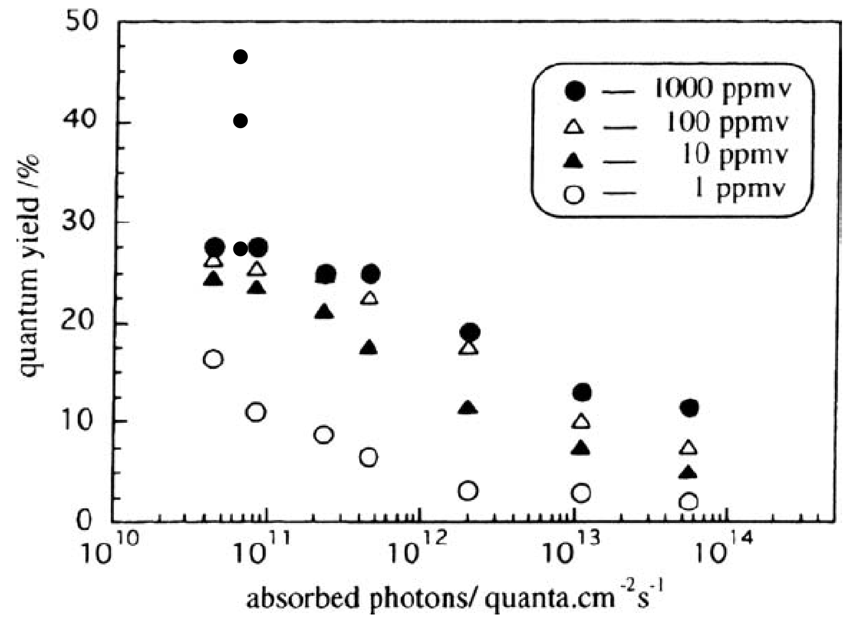
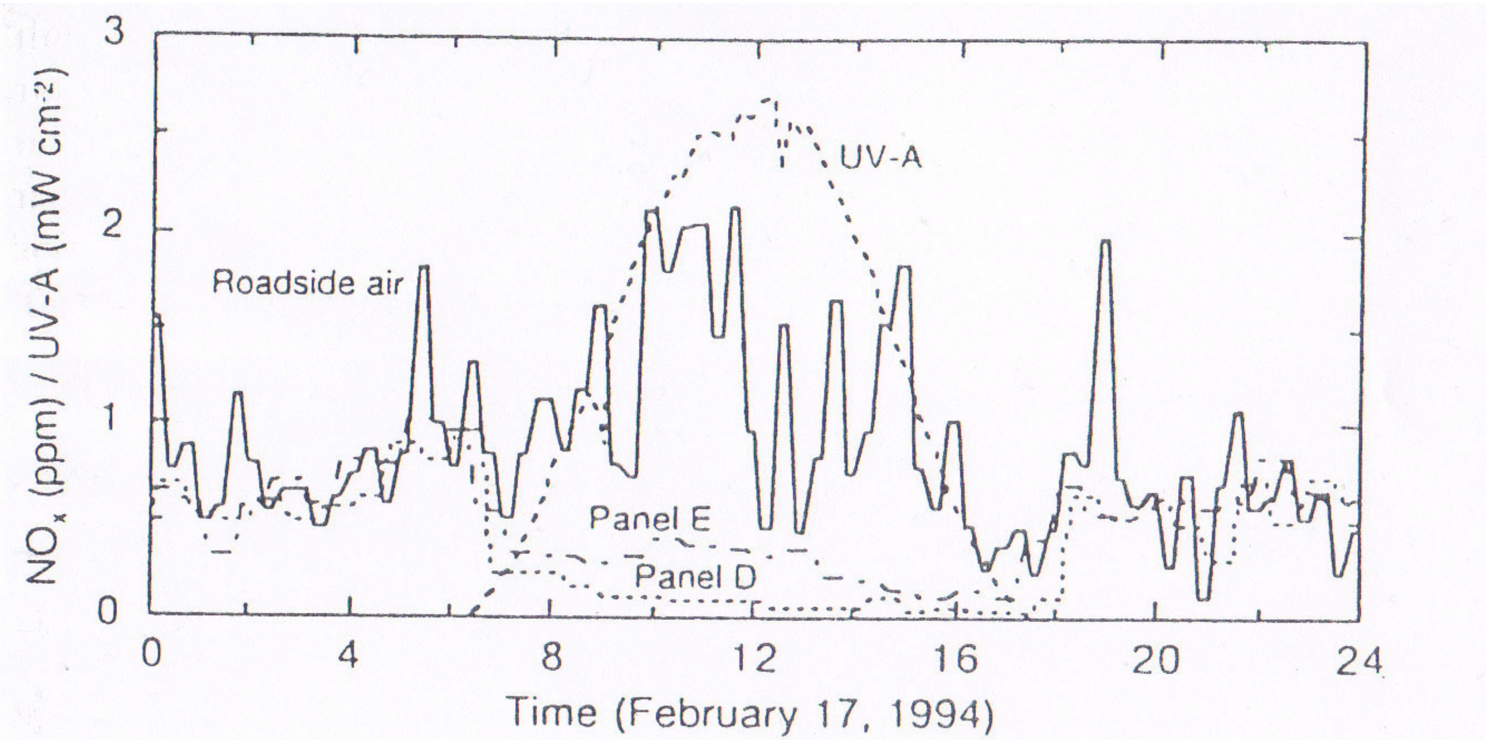


Fig. 3. Quantum-yield dependence on absorbed photons at various initial 2-propanol concentrations [17].

Benzene oxidation (Einaga *et al.*, 1999)

- Air must have moisture (to supply hydroxyl radicals, which are consumed)
- Products are 93% CO_2, 7% CO
- After a few hours of 80 ppm benzene, catalyst turns light brown
- Further photo-oxidation w/o benzene turns the catalyst white again
- Yield of CO can be reduced by adding some Pt to the catalyst

NO_x concentration *vs.* time



3.24 Variation of NO_x concentration at the test site (air pumping rate: panel D, 15,5; panel E, 24.21 min^{-1}).

NO_x removal *vs.* UV intensity

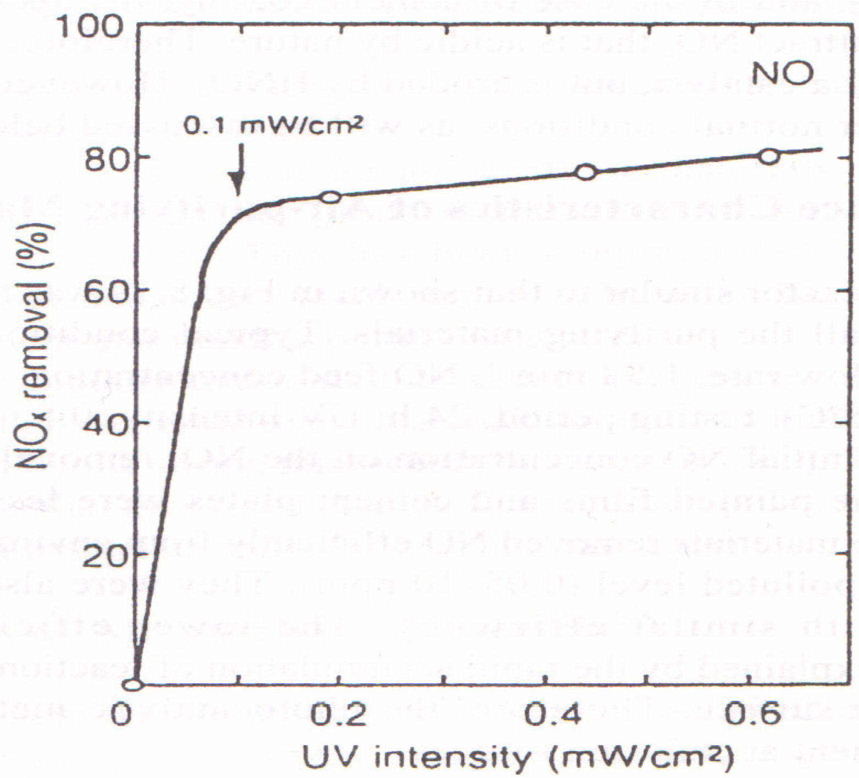


Fig. 8.23 Dependence of 24 h average NO_x removal on UV intensity. Material, cement plates (200 cm^2); [NO], 1.0 ppm, flow-rate, 1.5 l min^{-1}.

NO_x removal rates for different materials

- Efficient removal for low NO concentrations
- Comparable results for differing materials

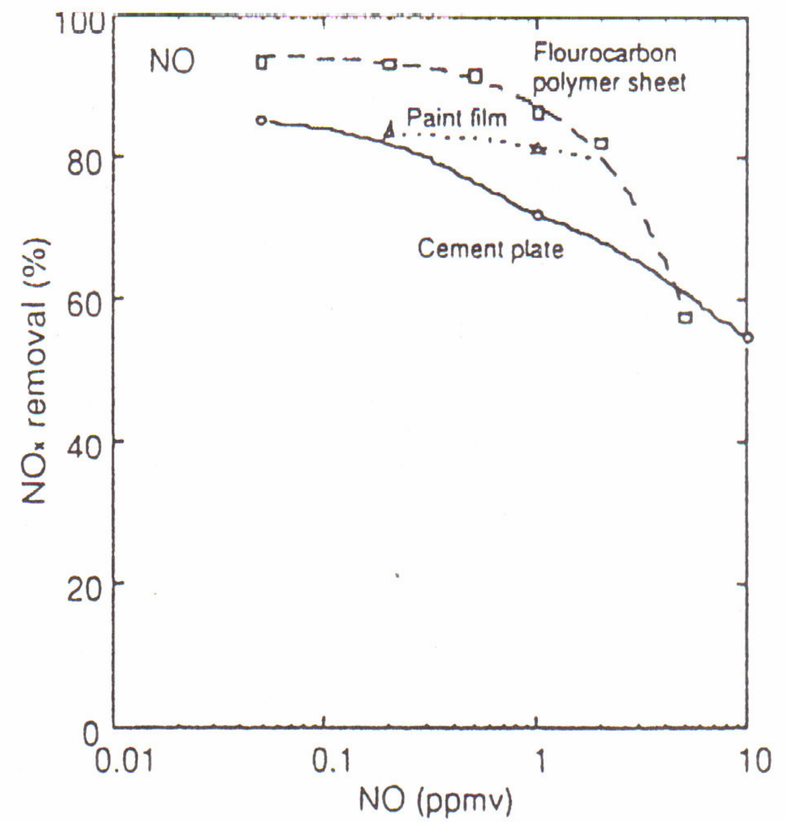
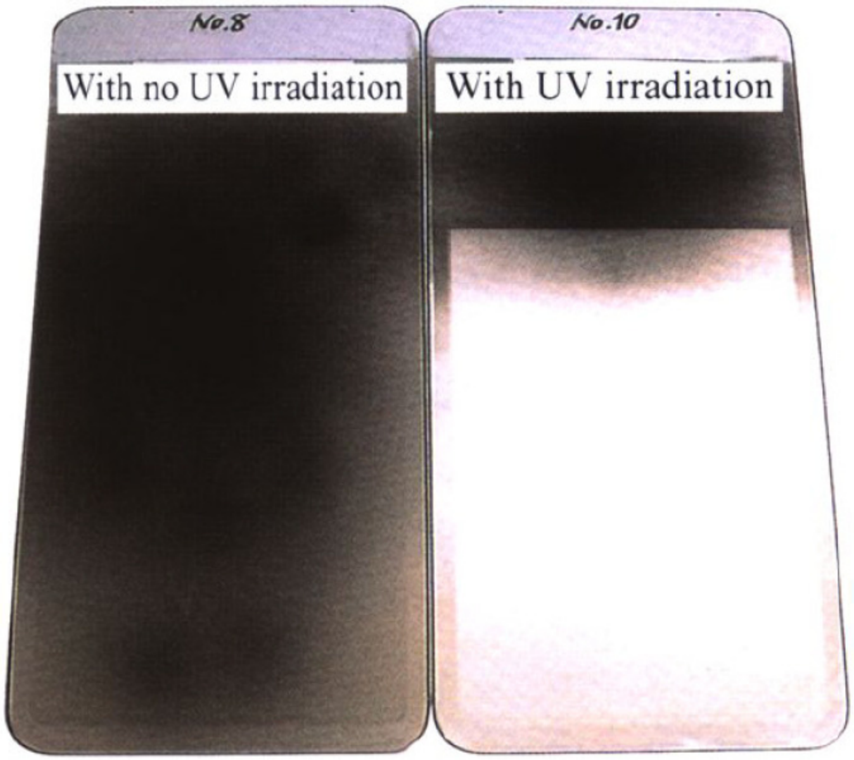


Fig. 8.22 Dependence of 24 h average NO_x removal on NO feed concentration. Air-purifying material, 200 Cm^2; flow-rate, 1.5 l min^{-1}; UV intensity, 0.5 mW cm^{-2}.

Photocatalytic oxidation of soot



Results of an accelerated test (using UV light) of the decomposition of an accumulated stain film composed of automobile exhaust residue.

Products in Japan (2005)

TiO_2-based photocatalytic products that have appeared on the market in Japan

Categories	Products	Properties
Exterior construction materials	Tiles, glass, tents, plastic films, aluminum panels, coatings,	Self-cleaning
Interior furnishing materials	Tiles, wallpaper, window blinds,	Self-cleaning, antibacterial
Road-construction materials	Soundproof walls, tunnel walls, road-blocks, coatings, traffic signs and reflectors, lamp covers	Self-cleaning, air-cleaning
Purification facilities	Air cleaners, air conditioners, purification system for wastewater and sewage, purification system for pools	Air-cleaning, water-cleaning, antibacterial
Household goods	Fibers, clothes, leathers, lightings, sprays	Self-cleaning, antibacterial
Others	Facilities for agricultural uses	Air-cleaning, antibacterial

Market share in Japan

Market share of the photocatalytic products by categories in 2 recent years

Year	2002 (%)	2003 (%)
Exterior construction materials	61	44
Interior furnishing materials	20	13
Road-construction materials	6	4
Purification facilities	9	33
Household goods	4	5
Others	–	1

Transparent stain-proof film

Stain-proof plastic film

This type of titanium dioxide-treated plastic film is being used now in many applications where ease of cleaning is important. For example, the "on" button of a rice cooker would normally become stained after month of usage; however, coated with this film, it can be wiped clean with a quick swipe.

(Courtesy of Nippon Soda Co., Ltd.)

Self-cleaning aluminum siding

Recent Applications of Photocatalysis in Japan

Self-cleaning aluminum siding

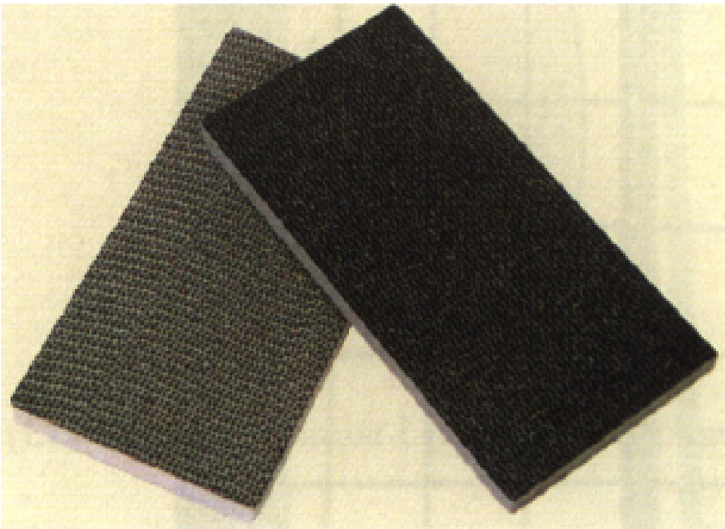
The aluminum siding on this building (Sendai YF Building of the YKK Corporation, in Sendai) is coated with titanium dioxide. Completed in April, 1999, it consists of 800 square meters of siding.

(Courtesy of YKK Corporation)

Active PCO filters, aided by activated carbon

Photocatalytic air cleaners

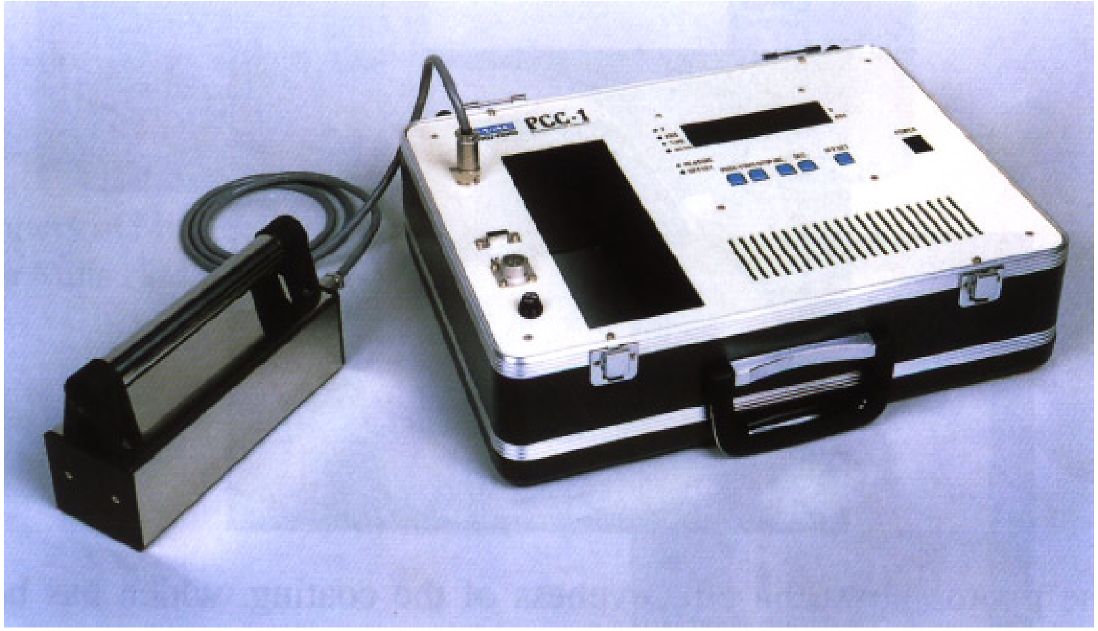
These photocatalytic filter elements for air cleaners. They contain titanium dioxide plus activated carbon, the latter trapping pollutants for subsequent destruction by the irradiated titanium dioxide. They feature a honeycomb-type construction for minimum pressure drop.



Evaluation system uses fading of methylene blue dye

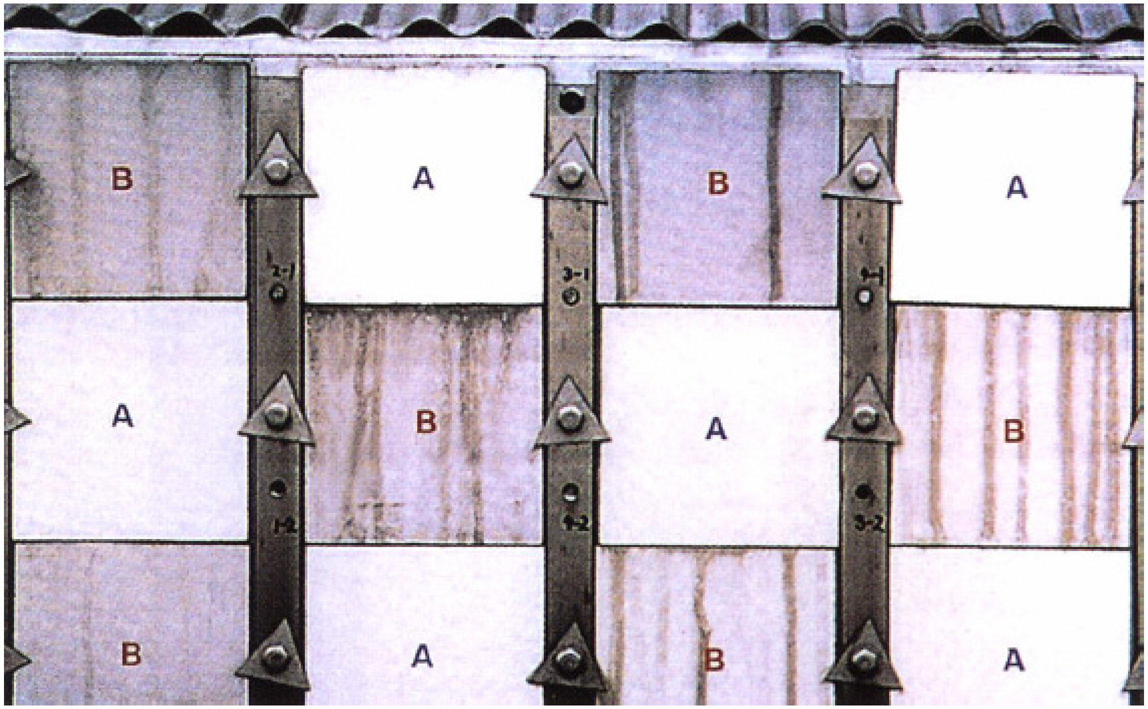
Photocatalysis evaluation system

This is a small portable evaluation system for testing photocatalytic coatings.



(Courtesy of Sinku-Riko, Inc.)

Self-cleaning tiles by TOTO, Inc.



A: Tiles with photocatalytic, superhydrophilic coating

B: ordinary painted wall tiles

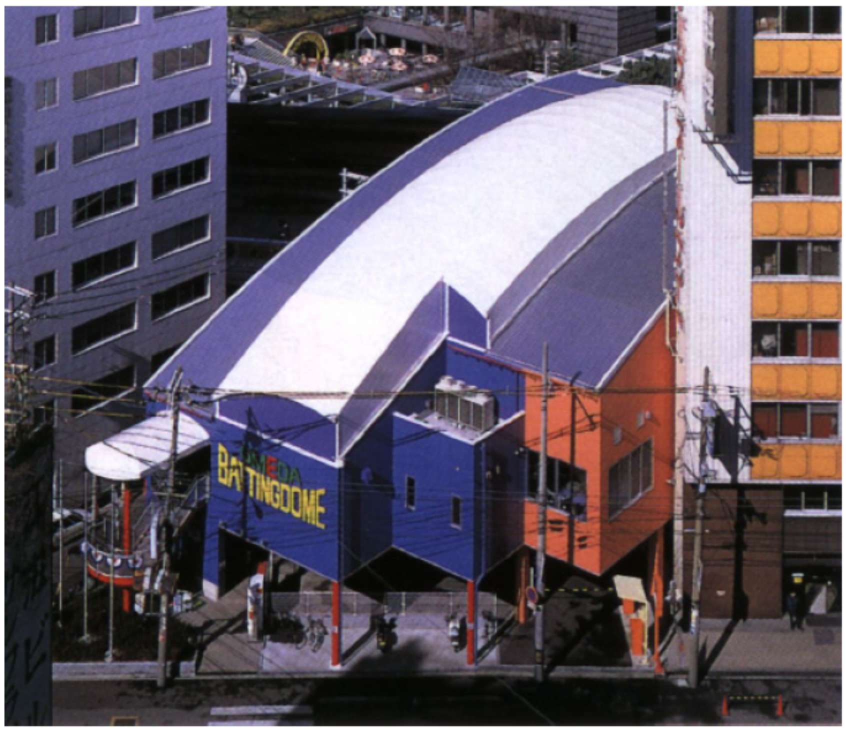
Self-cleaning tiles

- On 5,000 buildings in Japan in year 2003
- Buildings normally cleaned every 5 years
- New tiles: projection of cleaning after 20 years
- Self-cleaning tiles also decompose NO_x

Self-cleaning tarpaulin

Self-cleaning tent material

The tent for this batting practice center, located opposite the main railway station in Osaka, was made from tarpaulin material containing titanium dioxide.



(Courtesy of Taiyo Kogyo Corporation)

Self-cleaning tent

Self-cleaning tent material

These small test-size tents were located on the grounds of a factory in Saitama prefecture, north of Tokyo, where they were exposed to significant air pollution. After a three-month exposure, the conventional tent material, seen on the left, had become severely stained. On the right, the photocatalytic tent material has remained clean, having been washed off periodically by rainwater.

(Courtesy of
Taiyo Kogyo Corporation)

This tent, located in Tsukuba Science Center, is a full-size storage tent made from the photocatalytic tarpaulin material. Also having been washed by rainwater, it remains clean.

Self-cleaning cars

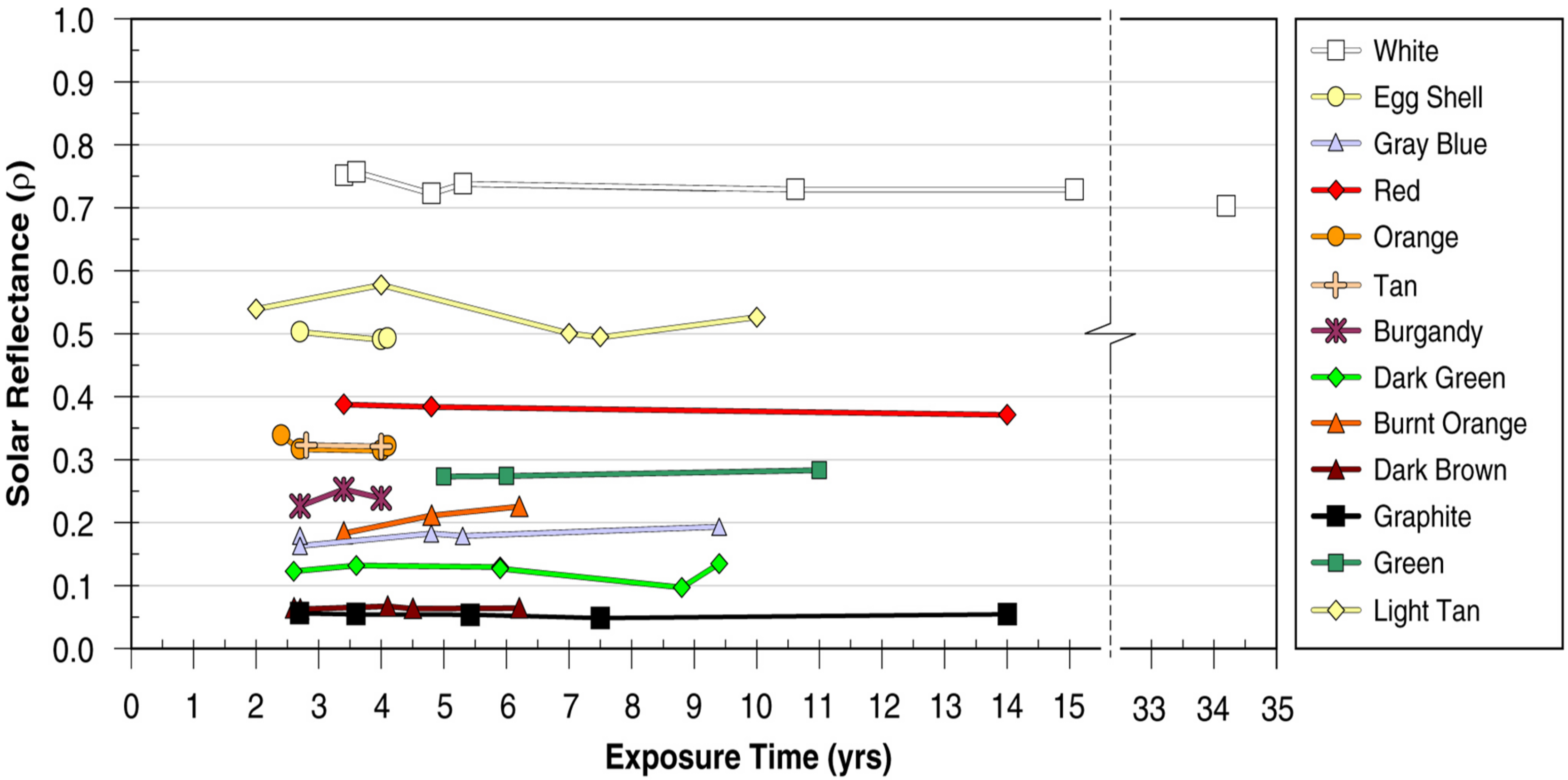
Car body spray coating

Thanks to the superhydrophilic effect of the "Hydrotect" coating, stains and grime caused by exhaust emissions, as well as rain droplets, are easily removed.

The photo shows the effectiveness of the coating, which has been applied only to the right side of the car. After one month´s exposure to polluted urban air, it remains clean while the left side has become dingy.

(Courtesy of TOTO Ltd.)

PVDF surfaces w/o PCO stay clean in Florida for many years



Roadway demonstrations in Japan (i)

- 1997 collaboration of six companies in Osaka
- Some deployed materials could maintain initial NOx purification performance ($20\ m^3$ of air per hour per m^2) after 12 months
- After further improvement a practical construction material appeared feasible

Roadway demonstrations in Japan (ii)

- Next, Osaka Prefecture installed new soundproof barrier using a photocatalyst
- 500m of roadway, 2m high, both sides of road
- Daily NO_x removal rate 0.5 to 1.5 mmol/m^2 (15 to 45 mg/m^2)
- Very little performance degradation over two years
- Surface remains clean even though it is porous

Roadway demonstrations in Japan (iii)

- Last year (2006) Fujita, Fujita Road, Taiheiyo Cement and Ishihara Sangyo/ Ishihara Techno announced installation tests of a “Photo Road Construction Method”
- Large areas are needed to demonstrate performance
- To clarify air cleaning performance of large-scale tests, numerical simulations of air flow are needed

References (i)

- A. Fujishima, X. Zhang, Titanium dioxide photocatalysis: present situation and future approaches, *C. R. Chimie* 9 (2006) 750–760
- K. Hashimoto, H. Irie and A. Fujishima, TiO_2 Photocatalysis: A Historical Overview and Future Prospects, *Japanese J. Appl. Phys*. 44, (2005), 8269–8285
- A. Fujishima, K. Hashimoto, T. Watanabe, *TiO_2 Photo-catalysis: Fundamentals and Applications*, BKC, Tokyo (1999)

References (ii)

- Takashi Ibusuki, Cleaning Atmospheric Environment, Chap. 8 in *Photocatalysis Science and Technology*, M. Kaneko & I. Okura, eds., Kodansha, Tokyo; Springer, Berlin (2002)
- Asian-Pacific Economic Cooperation (APEC) Virtual Center for Environmental Technology Exchange (http://www.apec-vc.or.jp)