Photoinduced Colour Transformation in WO_3 Particles

Masatoshi Fujii, Tomoji Kawai,* Hirohide Nakamatsu, and Shichio Kawai

The Institute of Scientific and Industrial Research, Osaka University, 8–1 Mihogaoka, Ibaraki, Osaka 567, Japan

Xe-Lamp irradiation of platinized WO_3 particles in the presence of water and an organic substance leads to a drastic colour change of the particles without application of a bias voltage, indicating photoelectrochemical-chromism.

Tungsten trioxide, WO_3, is a well known material which changes its colour on formation of a hydrogen bronze, (H_xWO_3),[1] colour centre[2] or by the extraction of oxygen.[3] This characteristic has made WO_3 of potential use as an electrochromic device.

We found that the colour transformation in a WO_3 particle is driven particularly by radiation with the band-gap energy in the presence of water and organic substances, such as alcohol or formic acid. This phenomenon was found to be based on a photoelectrochemical process of the semiconductor particle, in which a redox reaction occurs due to electrons and holes produced by the irradiation.

When WO_3 powder (1.0 g, Wako Chemical Co., extra-pure grade) in a deaerated mixture of H_2O (10 ml) and HCO_2H (10 ml) in a 280 ml Pyrex glass bulb, was irradiated by a Xe-lamp, the white-yellow colour of the WO_3 gradually changed to dark green, with the evolution of CO_2 gas. The colour change was observed neither in the dark even after a prolonged time (24—48 h) at room temperature nor in the absence of HCO_2H under irradiation.

By depositing a small amount of platinum (less than 0.1 wt %) on the WO_3 surface, the colour change was enhanced greatly; the colour changed to green even in the dark. Under irradiation, it changed to dark green and then deep blue, and the CO_2 production rate was greatly accelerated (× 13). The quantum yield of the CO_2 production on WO_3/Pt for light of λ 400 nm was of the order of 1%.

The irradiation of a semiconductor particle with light of energy greater than the band-gap leads to the formation of an electron and a hole in the conduction and the valence band, respectively. In the presence of water and an organic substance, the organic molecule can be oxidised by the hole if its redox potential is more negative than the valence band edge. Simultaneously, hydrogen production is possible using the electron at the conduction band if the conduction band edge is more negative than the redox potential of hydrogen and a catalyst, such as Pt, is present on the particle surface.[4,5] In the case of WO_3, the conduction band edge is too positive to produce hydrogen gas (0.3 V *vs.* normal hydrogen electrode).[6] Since CO_2 gas was observed without H_2 gas evolution (*i.e.* ratio $H_2 : CO_2 < 1\%$) accompanying the colour transformation, it is reasonable to conclude that the hole is used for the oxidation of formic acid,[4] and the electron is consumed by the bronze (H_xWO_3) formation changing the colour of the particle.

According to an *X*-ray diffraction analysis of coloured WO_3, the diffraction pattern of the dark green material is proved to be the same as WO_3 (monoclinic system),[7] while the pattern of the deep blue form is consistent with that of H_xWO_3 (tetragonal system, $0.15 < x < 0.23$).[8] Photoacoustic spectra of the dark green and deep blue forms have a broad absorption band (λ_{max} 1000 nm), which is similar to that of hydrogen tungsten bronze.[9] The amounts of hydrogen absorbed by the deep blue and dark green forms are at most 0.169 ± 0.001 mol % and 0.012 ± 0.001 mol %, respectively (found by estimation from the quantity of evolved CO_2 after subtraction of the small amount of H_2 gas produced). The deep blue colour of WO_3/Pt gradually turns to light green in air, and this change is promoted considerably by washing the coloured WO_3/Pt with water which contains dissolved oxygen. The dark green and the deep blue colours fade on heating the coloured samples in air above 70 °C.

These experimental results indicate that on using WO_3 alone, hydrogen penetrates into the WO_3, leaving its structure unchanged, whereas in the case of WO_3/Pt, more hydrogen can penetrate into the WO_3, causing changes to its structure. The effect is enhanced by depositing Pt owing to the 'spillover' effect, in which hydrogen is effectively transported into the WO_3 particle.[10]

Table 1. The colour change of WO_3 in the presence of various organic substances. 500 W Xe-Lamp irradiation.

Particle	Solution	Irradiation	Colour
WO_3	H_2O	—[a]	—[b]
WO_3	H_2O	$h\nu$	—[b]
WO_3	aq. $MeCO_2H$	$h\nu$	—[b]
WO_3	aq. EtOH	—[a]	—[b]
WO_3	aq. EtOH	$h\nu$	Dark green
WO_3	aq. HCO_2H	—[a]	—[b]
WO_3	aq. HCO_2H	$h\nu$	Dark green
WO_3/Pt	aq. HCO_2H	—[a]	Green
WO_3/Pt	aq. HCO_2H	$h\nu$	Deep blue

[a] Dark. [b] No colour transformation.

In the electrochromism of WO_3, an electron is injected by applying a bias voltage to change the colour of WO_3.[2] In the phenomenon we have described the electron which changes the colour is produced by the photoelectrochemical process instead of electric power. Therefore this phenomenon may be called photoelectrochromism.

The colour change was also observed using ethanol as the organic moiety (Table 1). The dependence of colour change on the organic substances shows that the molecule of more positive oxidation potential is more difficult to oxidize.

It should be noted that, utilizing this phenomenon, hydrogen can be stored in WO_3 powder: the irradiation of WO_3/TiO_2/Pt, WO_3/CdS/Pt, or WO_3/WS_2/Pt in the presence of water–ethanol leads to such storage since TiO_2/Pt, CdS/Pt, and WS_2/Pt are well known as photocatalysts for the evolution of hydrogen from water and organic substances. This may be interesting since it extends the function of the powdered photocatalyst. Furthermore, this phenomenon could have applications in information storage using light signals on a panel painted with WO_3/Pt powder.

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