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# A New Family of Photocatalysts Based on $Bi_2O_3$*

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Solid solutions of $Bi_2O_3$ and $Nb_2O_5$ crystallize in several distinct structures, each related to defective fluorite, and since each specific structure exhibits a particular band gap, scope exists for some tuning of the photoelectrochemical properties of the ternary oxides. A solid of composition $31Bi_2O_3 \cdot Nb_2O_5$ is capable of photooxidizing propan-2-ol and of photodecomposing chlorinated hydrocarbons.

Recently it has been shown (*1*) that a vast compositional range of $a\mathrm{Bi_2O_3} \cdot bMO_x$ ($a:b$ from 61 : 1 to 1 : 3, $M$ = Nb, Ta, Mo, W, V, Si, etc., $x$ = 2 to 3) exists, many members of which crystallize into structures which are related to defective fluorite (anion vacancy). The $Bi_2O_3 \cdot Nb_2O_5$ system, for example, takes up four distinct, but related phases, in the range 61 : 1 to 5 : 3, all of these being superstructural variants of the high-temperature defect fluorite structure taken up by the $\delta$-$Bi_2O_3$. The structures of these solids, which were made by solid state synthesis (*1a*) at temperatures around 820°C, have been elucidated by a combination of high-resolution electron microscopy, X-ray emission microanalysis, and image simulations (*2*). The wide range of superstructural variants found to exist within this $Bi_2O_3 \cdot Nb_2O_5$ system (e.g., $2 \times 2 \times 2$ for $20Bi_2O_3 \cdot Nb_2O_5$ and $8 \times 8 \times 8$ for $5Bi_2O_3 \cdot Nb_2O_5$) permits exploration of structural effects upon photoelectrochemical properties. Such effects have not been well studied (*3*) for a single well-defined system; and in this communication we present preliminary results describing the photoelectrochemical properties of the $Bi_2O_3 \cdot Nb_2O_5$ system, which constitutes a promising system for fine tuning of band gaps and flat-band potentials using the techniques of solid-state chemistry.

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* John Goodenough's appearance as Professor of Inorganic Chemistry at the University of Oxford in the mid-1970s added much stimulus to work in solid state chemistry in the United Kingdom. During the course of his tenure at Oxford, many new directions of research were opened up at the Inorganic Chemistry Laboratory. For most of his time there he was involved in photoelectrochemical studies and in the design and synthesis of new solids. The authors acknowledge their debt to John Goodenough and offer this short contribution as a token of their esteem for his qualities as a human being and as a scientist.

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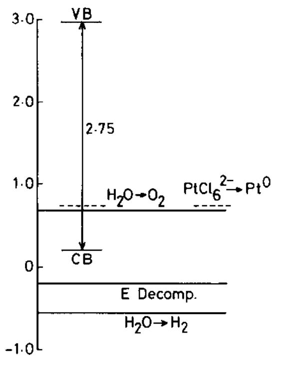

FIG. 1. Energy level diagram for *n*-type $Bi_2O_3$ at pH 9.2 showing its ability to oxidize water and reduce chloroplatinate.

$Bi_2O_3$ possesses (*4*) amphoteric character, functioning as both *n*- and *p*-type semiconductors under specific conditions. For samples of $Bi_2O_3$ prepared by both anodic and thermal oxidation of Bi, the optical band gaps ($E_{bg}$) measured by reflectance spectroscopy and by photoconductivity were 2.78 ± 0.05 eV, a value which compares well with previous measurements (*4*) which place $E_{bg}$ in the range 2.8 ± 0.1 eV. Flat-band potentials were determined by current–potential curves and by capacitance (*5*) measurements in aqueous solution at pH 9.2 (borate buffer). Under white-light illumination, *n*-type flat-band potentials ($E_{fb}$) of −0.33 and −0.12 V vs SCE, respectively, were derived for the anodically and thermally prepared samples. The flat-band potentials measured by Mott–Schottky plots were in good agreement with those obtained from current–potential curves. Normally, the flat-band potential derived from the capacitance measurements was about 50 mV more negative than that derived from the corresponding current–potential curves. Since linear Mott–Schottky plots were observed over a range of frequencies, these measurements were considered to be the more reliable estimates of the flat-band potential and were used in subsequent calculations. They were in very good agreement with literature values (*4*). The flat-band potential was found to decrease by 54 mV per unit increase in pH, consistent with surface protonation. The *n*-type decomposition level of $Bi_2O_3$ at pH 9.2 lies (*6*) at −0.37 V vs SCE, giving rise to the energy-level diagram shown in Fig. 1.

When illuminated with visible light ($\lambda >$ 320 nm), the observed photocurrent increased with increasing applied potential and the photostability was reasonably good. At 0.6 V vs SCE applied potential, the photocurrent density was ca. 2 mA $cm^{-2}$ and reasonably stable; under such conditions, bubbles of $O_2$ form at the photoelectrode.

Incorporation of $Nb_2O_5$ into $Bi_2O_3$ has a marked influence upon the band gap of the material. Surprisingly, low levels of $Nb_2O_5$ lower $E_{bg}$ from 2.78 to 2.26 eV, but further increase in the doping level raises $E_{bg}$ (Fig. 2). This effect is related to the detailed structure of the ternary oxide, and each particular phase appears to give a characteristic $E_{bg}$. Thus, subtle structural changes occur at $Nb_2O_5$ levels of <10, 10–20, 30, and >33%, and the corresponding phases show $E_{bg}$ values of 2.26, 2.52, 2.67, and ca. 3.0 eV, respectively. Samples having 2–6% $Nb_2O_5$ are clearly the most attractive in regard to their ability to harvest sunlight, especially since such materials absorb ap-

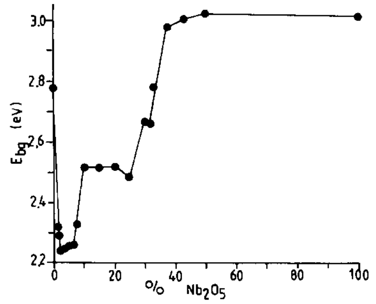

FIG. 2. Band-gaps measured by photoconduction and diffuse reflectance spectroscopy for the various $Bi_2O_3 \cdot Nb_2O_5$ solid solutions.

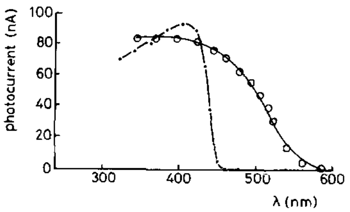

FIG. 3. Photocurrent spectra recorded at pH 9.2 for pure $Bi_2O_3$ (●) and 31 $Bi_2O_3 \cdot Nb_2O_5$ (○) electrodes.

preciably in the visible region. Current–potential plots show that the flat-band potentials of the mixed oxides decreased systematically upon increasing the level of $Nb_2O_5$. However, the decrease was slight (i.e., 1 : 1 $Bi_2O_3 \cdot Nb_2O_5$ gives $E_{fb} = -0.22$ V vs SCE), signifying that the valence band position changes for the various compositions of the solid solutions. Similar changes in the flat-band potentials were found from capacitance measurements made with a few of the mixed-oxide electrodes. Again, linear Mott–Schottky plots were obtained over a range of frequencies but the dopant appears to have only a minimal effect upon the flat-band potential.

In order to demonstrate that the observed band gaps correspond to photoelectrochemical activity, photocurrent action spectra were determined for some of the electrodes. For these measurements, the electrode was housed in a chamber containing electrolyte at pH 9.2 and equipped with a glass optical window. The electrode was illuminated with light from a 950-W xenon lamp passed through a high-radiance monochromator and focused onto the electrode via a fiber optic. A fraction of the incident light was monitored by a thermophile so that changes in intensity could be evaluated. The photolysis chamber was connected to a dark chamber via a salt bridge. This chamber contained a Pt foil electrode in contact with an aqueous solution of potassium ferricyanide (2 m*M*) at pH 9.2. A potential of 0.6 V vs SCE was applied to the photoelectrode, using a potentiostat, and a SCE reference electrode was positioned close to the photoelectrode, but out of the light beam.

With pure $Bi_2O_3$, photocurrents can be detected upon illumination with light of $\lambda <$ 450 nm (Fig. 3). This corresponds to band-gap excitation and there is a good correspondence between the diffuse reflectance spectrum and the photocurrent action spectrum. The action spectrum obtained with $31Bi_2O_3 \cdot Nb_2O_5$ is given also in Fig. 3. It is seen clearly that the mixed oxide is sensitive to light of much lower energy. Indeed, the photocurrent onset is located at about 540 nm and, again, the action spectrum and the diffuse reflectance spectrum match closely.

These measurements show that the mixed oxides, especially those containing low levels of $Nb_2O_5$, are photoelectrochemically active at much longer wavelengths than found for either of the pure oxides. The dopant modifies the band gap of the bulk material due to changes in the crystal lattice, although it might also modify the space charge depth and the minority carrier transport properties. These latter properties would affect the efficiency of photoinduced charge separation but not the wavelength response. Comparison of the band gaps with the known structural properties of these mixed oxides (*1*), as shown in Fig. 2, suggests that the crystal structure is the dominant factor in determining the photoelectrochemical onset wavelength for this family of compounds. It is interesting to note that, whereas undoped $Bi_2O_3$ is a direct semiconductor, the dopant appears to render the material somewhat less direct.

Because of the unfavorable position of the flat-band potential, the $Bi_2O_3 \cdot Nb_2O_5$ system lacks the ability to photodissociate water. Irradiation of the mixed-oxide solid solutions suspended in aqueous solution at pH 9.2 containing chloroplatinate ($2 \times 10^{-3}$ *M*) did give small yields of $O_2$, but quantum

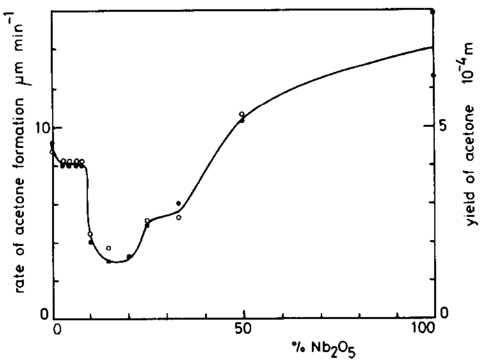

FIG. 4. Initial rate (○) and total yield (●) of acetone formation upon photolysis of the oxides in 1 : 1 water : propan-2-ol solution.

yields were very low and irreproducible. However, the ternary oxides showed more activity upon irradiation in 50% aqueous propan-2-ol solution. Upon illumination, acetone and $H_2$ were detected as reaction products. For pure $Nb_2O_5$, the ratio of products was consistent with dehydrogenation of the alcohol (at least over the early stages of reaction):

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2$$

Partial platinization of the $Nb_2O_5$ surface gave a dramatic increase in the rate of product formation (*7*). With the $Bi_2O_3 \cdot Nb_2O_5$ solid solutions, acetone but not $H_2$ was detected during the early stages of irradiation (Fig. 4). After an induction period, $H_2$ began to evolve but at a slow rate, and the molar ratio of acetone to $H_2$ always exceeded ca.5. This suggests that the major photoreaction is the oxidation of propan-2-ol by valence band holes giving rise to 1-hydroxy-1-methylethyl radicals and forming Bi at the surface of the semiconductor. The C-centered organic radicals disproportionate in the bulk solution to form acetone:

$$Bi_2O_3 + 3(CH_3)_2CHOH \rightarrow 2Bi + 3(CH_3)_2CO + 3H_2O$$

The 1-hydroxy-1-methylethyl radicals are known to reduce water to $H_2$ on the surface of a suitable catalyst, and it appears that Bi functions in that role since further irradiation results in formation of detectable yields of $H_2$.

The rate of acetone production does show some dependence upon the composition of the material (Fig. 4). Interestingly, the rate does not simply reflect the depth of the valence band but depends upon the precise structure of the ternary oxide, the materials with low levels of $Nb_2O_5$ doping again exhibiting relatively high photoactivity.

In related experiments, we have shown that irradiation of the ternary oxides suspended in aerated water containing 4-chlorophenol (0.1 *M*) at pH 9.2 results in formation of $Cl^-$ ions and $CO_2$, products that are consistent with dehalogenation and subsequent destruction of the aromatic molecule. Such reactions may have applications in water purification.

In all the above photochemical experiments, it was found that incorporation of low levels (<10%) of $Nb_2O_5$ into the $Bi_2O_3$ structure renders the material more active towards visible light. Thus, neither $Nb_2O_5$ nor $Bi_2O_3$ absorbs significantly above 440 nm. Incorporation of <10% $Nb_2O_5$ into $Bi_2O_3$ pushes the absorption threshold out to ca. 540 nm, such that a reasonable fraction of the solar spectrum is collected. This is achieved by subtle structural modification, not by doping with colored material; the resultant semiconductor retains the primary properties of the parent $Bi_2O_3$. Although $Bi_2O_3$ itself is not a useful, or indeed stable, photocatalyst the enormous range in composition of oxide solid solutions derivable from it suggests that a range of semiconducting compounds can be generated by this method. Furthermore, it might be possible to identify an oxide solid solution in which the flat-band potential can be tuned over a wide range by structural modification in the same way that $Nb_2O_5$ alters the valence band level of $Bi_2O_3$. Further work along these and related lines is underway.

*Experimental.* Samples of pure Bi were sealed into glass tubes and the open end was finely polished and anodised at 0.6 V vs SCE. Solid samples of $Bi_2O_3$ were pressed into disks (2 mm thick and 0.8 $cm^2$ in surface area) under high vacuum and high pressure. The disks were sintered in air at 800°C for 8 hr before being cooled, powdered, and resintered. The disks were sealed into Teflon holders with epoxy resin and the back of the disk was coated with a thick film (ca. 1 mm) of pure Bi, which was applied by *rf* sputtering. A contact wire was soldered to the Bi film and the whole electrode was sealed into a glass tube with epoxy resin. Electrodes were made from the solid solutions, synthesized previously, in the same manner and at least three electrodes were tested for each sample.

## Acknowledgment

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