

requires additional energy from an atom recombination or whether it occurs thermally. Alkali and alkaline-earth metals, zinc, mercury, cadmium, and magnesium have vapor pressures at 700 K sufficiently high to explain the observed absorption signals, whereas for copper, iron, silver, and cobalt additional energy will be needed to vaporize the solid metal.

Of course, the macroscopic observations made in this work will not allow elucidation of the complete lattice atomization mechanism, and it is clear that more data on the stoichiometry of the overall reaction are needed and additional information on the characteristics of the solid surface will be required.

Conclusions

When various solids come into contact with the afterglow products of microwave-induced plasmas, containing hydrogen, oxygen, nitrogen, or water, metal atoms are ejected from the solid phase as a result of heterogeneous interactions between the afterglow products and the solid sample. This phenomenon is called "lattice atomization", and it should be emphasized that it occurs with a broad variety of solids such as almost all alkali halogenides and a large number of sulfides, nitrates, carbonates, sulfates, and oxides of divalent metals.

In the first part of this study, several parameters influencing the effect were investigated. Although this lattice atomization occurs at moderate temperature between 400 and 800 K, increasing the temperature of the solid markedly enhances the metal atom formation rate. A very sensitive parameter, determining the magnitude of the metal atom concentration in the gas phase $[M_g]$, is the distance z between the microwave discharge zone and the

solid. It was found that the concentration sharply increases when this distance becomes shorter. Once formed, the metal atoms are transported together with the remaining afterglow products downstream of the solid. Their concentration diminishes only slowly.

The second part of this study was devoted to a determination of possible precursors in this lattice atomization process. It was found that the influence of charged species, excited atoms, or molecules is negligible, whereas, on the other hand, ground-state hydrogen, oxygen, or nitrogen atoms are definitely required in order to observe measurable M_g concentrations. The efficiency for creating lattice atomization increases according to the sequence $H > O$ or N atoms, and an attempt is made to explain this trend in terms of two different reaction mechanisms.

In order to establish a detailed reaction mechanism, further work on the stoichiometry of the overall process and on the physicochemical behavior of the surface of the powders is currently planned.

Finally, since in some cases a coloration of the solid was observed, this study may also have a more fundamental importance in the field of formation of color centers and crystal defects.

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A Study by He I Photoelectron Spectroscopy of Monomeric Nitrosomethane, the Cis and Trans Dimers, and Formaldoxime

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A combination of in situ He I photoelectron and quadrupole mass spectroscopy has been used to study monomeric nitrosomethane, the cis and trans isomers, and formaldoxime. In contrast to earlier results it is shown that cis- $(CH_3NO)_2$ sequentially gives $CH_2=NOH$ and CH_3NO upon vaporization. A photoelectron spectrum of the cis dimer was not observed. In addition, a previous spectrum of "monomeric" CH_3NO is shown to belong to the trans dimer. The assignments of the measured ionization potentials for these species are supported by semiempirical HAM/3 results. A breakdown of Koopmans' theorem is confirmed for CH_3NO by a calculation involving perturbation corrections.

Introduction

The dimer of nitrosomethane, $(CH_3NO)_2$, exists at room temperature in two isomeric forms, cis and trans, which undergo isomerization relatively easily. The cis dimer has been synthesized by the pyrolysis¹⁻³ or photolysis^{4,5} of *tert*-butyl nitrite, or the periodate oxidation of *N*-

methylhydroxylamine,⁶ while the trans isomer has been prepared by the photolysis of *tert*-butyl nitrite.¹ The cis dimer converts easily to the trans dimer upon heating¹ or simply by dissolving in a solvent with a low dielectric constant, e.g., $CHCl_3$,^{1,6} the reverse occurs upon irradiation with ultraviolet light.¹

Formaldoxime, $CH_2=NOH$, another structural isomer of nitrosomethane is always present in the synthesis of the nitrosomethane dimer¹⁻⁶ and can be generated directly by heating the solid dimer or its solution.¹ It is a colorless

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TABLE I: Experimental and Theoretical Results^a for Monomeric Nitrosomethane with the Proposed Assignments

orbital symmetry	exptl ^b	theor					
		HAM/3 ^c	MINDO/3 ^c	CNDO ^d	CNDO ^e	ab initio ^f	ab initio ^g
10a'	9.68 ± 0.05	9.56	9.11	11.8	11.75	11.50	10.39
2a''	14.3	14.00	12.86	14.7	15.33	14.94	15.16
9a''	13.8	13.96	11.75	16.0	16.21	15.59	15.62
1a''	16.9 ^h	16.18	15.35	19.5		17.93	17.52
8a'	15.8	15.60	14.26	19.8		18.21	18.26
7a'	16.9 ^h	16.83	15.40	20.2		19.23	19.16
6a'		20.90	21.07			23.88	23.43

^a All values in eV. ^b All IP's ± 0.1 eV except as specified. ^c This work. The geometry is taken from ref 9. ^d Reference 19. ^e Reference 8. ^f Reference 12. ^g The nitroso group is eclipsed to the methyl group as in c.²⁸ ^h The 1a'' and 7a' ionizations are unresolved.

liquid which trimerizes at room temperature to hexahydro-1,3,5-trihydroxytriazine.

Some experiments have been performed on nitrosomethane including the determination of the electronic spectrum^{7,8} and the microwave spectrum,^{9,10} and in addition, several theoretical investigations have been performed particularly related to the structural isomers,¹¹ electronic spectrum^{8,12-14} rotational barrier,^{15,16} and the photoelectron spectrum.¹⁷⁻¹⁹ The photoelectron spectrum displayed in ref 18 differs from that given in ref 17 and the high-temperature spectrum of ref 19. Heating the cis dimer into a photoelectron (PE) spectrometer gave a spectrum of monomeric CH₃NO with ionization potentials (IP's) in reasonable agreement with CNDO^{8,17} and ab initio¹² calculations. However, heating the trans nitrosomethane dimer gave an entirely different spectrum¹⁸ with three IP's below 12 eV. To compound the problem further, additional work on XNO type molecules¹⁹ gave the same spectrum of the CH₃NO monomer as in ref 17, but the spectrum there assigned to the starting material cis-(CH₃NO)₂ is, as we shall show, that of formaldoxime.²⁰

In this work we wish to clarify the confusion relating to the PE spectra of nitrosomethane, the cis and trans dimers, and formaldoxime. To assist in the identification of these species we have performed mass spectroscopic measurements under the same conditions as the PE experiments by means of a quadrupole mass spectrometer attached to the ionization chamber of the PE spectrometer. Finally, we have also performed some semiempirical HAM/3^{21,22} calculations and an ab initio calculation including perturbation corrections to Koopmans' theorem²³ (PCKT) for

CH₃NO to support our conclusions.

Experimental Section

cis-(CH₃NO)₂. The best method for synthesizing *cis*-(CH₃NO)₂ turned out to be the periodate oxidation of *N*-methylhydroxylamine.⁶ Pyrolysis and photolysis of *t*-BuONO were also tried but with limited success. The white solid obtained melted at 99–99.5 °C and gave UV and IR spectra identical with those of the *cis* dimer.¹ The sample was introduced into the ionization chamber of a PE spectrometer by heating at 4 cm from the ionization point. This experiment was repeated, but with a longer inlet tube packed with glass wool which could also be heated. PE and mass spectra were recorded in both instances under a variety of conditions.

trans-(CH₃NO)₂. The trans dimer was obtained by dissolving the *cis* dimer in CHCl₃ and then slowly evaporating the solvent.⁶ The colorless crystals melted in 126.8–127.0 °C and gave an IR spectrum identical with that of the trans dimer.¹ Sampling procedures similar to those described above were used to obtain PE and mass spectra.

Formaldoxime. CH₂=NOH was synthesized by the condensation of formaldehyde and hydroxylamine.²⁴ The white solid obtained sublimed between 90 and 134 °C and did not give a melting point even in a sealed tube. The IR spectrum was identical with that described in the literature.¹ The sample was heated into the spectrometer at about 43 °C and the PE and mass spectra were obtained. The PE spectrum, even after passage of the vapor through glass wool at temperatures up to 200 °C, was identical with that obtained by Dargelos et al.,²⁰ and to that purporting to be the *cis*-(CH₃NO)₂ species.¹⁹

Instrumentation. The photoelectron spectrometer is a modification of one previously described.²⁵ The photoionization point has been raised by incorporation of a three-element einzel lens which serves to focus electrons into the 180° hemispherical analyzer. Ions produced by the photoionization process are extracted in the opposite direction into a quadrupole mass spectrometer (EAI Quad 150) mounted vertically above the ionization point and are counted with a channel electron multiplier (CEM). The two spectrometers are controlled by an LSI 11/03 microcomputer. At present the experiments are not done in coincidence, but we can switch from one mode to another within seconds, thus enabling both PE and mass spectra to be recorded under virtually identical sampling conditions. In common with all such quadrupole mass spectrometers there is discrimination at higher *m/e* ratios. Since it is often essential to obtain a parent peak for species identification, we have expanded our mass range

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TABLE II: Experimental and Theoretical Results^a for Monomeric Formaldoxime

orbital sym- metry	exptl ^b	theor			
		HAM/ 3 ^c	MINDO/ 3 ^c	4- 31G ^d	ab initio ^e
2a''	10.59 ± 0.02	10.60	10.04	11.33	11.16
10a'	11.12 ± 0.05	11.49	9.38	12.04	12.24
1a''	14.3	14.23	13.80		16.27
9a'	14.9	15.06	12.57		16.27
8a'	16.1	15.76	14.35		17.71
7a'	17.5	17.53	16.64		21.06
6a'	18.3	19.93	20.28		22.64

^a All values in eV. ^b All IP's are ±0.1 eV except as specified. ^c This work. Geometry is taken from ref 30. ^d Reference 20. ^e The hydrogen of the hydroxyl group is trans to the coplanar hydrogen of the methylene as in c.²⁸

TABLE III: Experimental and Theoretical Results^a for the *trans*-Nitrosomethane Dimer

orbital symmetry	exptl ^b	HAM/3 ^c	SCF-CI (CNDO) ^d
3a _u	8.63 ± 0.05	8.92	10.58
10a _g	9.91 ± 0.01	9.93	11.96
9b _u	10.77 ± 0.05	10.94	13.07
2b _g	11.5	12.51	14.18
2a _u	13.6	13.98	
9a _g		14.02	
8b _u		14.33	
1b _g		14.86	
8a _g	15.41 ± 0.05	15.35	
7b _u	16.91 ± 0.05	17.30	
1a _u		18.15	
7a _g		18.55	
6b _u		18.68	
6a _g		22.60	

^a All values in eV except as specified. ^b All IP's ±0.1 eV. ^c This work. Geometry is taken from ref 31. ^d Reference 8.

from 150 to 300 amu and reduced the discrimination by replacing the original radiofrequency coil. Of much more use is our ability to use light sources other than He I (21.22 eV), e.g., Ne I (16.67 and 16.85 eV), Ar I 11.62 and 11.83 eV, and H L_α (filtered, 10.20, or unfiltered, 10.20 with H L_β, 12.09 and H L_γ, 12.75 eV). This reduces ion fragmentation, thereby simplifying the mass spectrum and enhancing the parent ion peak. Such a system has now proved invaluable for the identification of novel transient and unstable molecules.

Molecular Orbital Calculations. Calculations were performed on monomeric nitrosomethane, the *cis* and *trans* dimers, and formaldoxime by using the semiempirical HAM/3 method²¹ which has been shown to give excellent IP values for a wide variety of molecules.²² The calculated IP's, experimental IP's, and geometries used for the calculations are given in Tables I–IV. For comparison purposes other types of calculations previously given in the literature are included.

We have also calculated the vertical IP's of CH₃NO using Rayleigh–Schrodinger perturbation theory to obtain corrections to Koopman's theorem based on a self-consistent-field (SCF) calculation from the GYAUSSIAN 70 system of programs.²⁶ Details of this procedure have been given by Chong et al.²⁷ and the results are summarized in Table V for a truncation parameter of $T = 2.6$. The earlier geometry of ref 9 was adopted instead of ref 10 for the

TABLE IV: Theoretical Results^a for the *cis*-Nitrosomethane Dimer

orbital symmetry	HAM/3 ^b	SCF-CI (CNDO) ^c
3b ₁	8.13	12.42
10a ₁	9.11	12.09
9b ₂	9.68	13.58
2a ₂	11.28	10.19
8b ₂	13.78	
2b ₁	13.96	
7b ₂	14.81	
1a ₂	15.42	
9a ₁	15.55	
8a ₁	16.32	
1b ₁	17.47	
7a ₁	18.41	
6b ₂	19.02	
6a ₁	24.12	
5b ₂	24.69	
5a ₁	27.89	
4b ₂	29.64	

^a All values in eV. ^b This work. Geometry is taken from ref 30. ^c Reference 8.

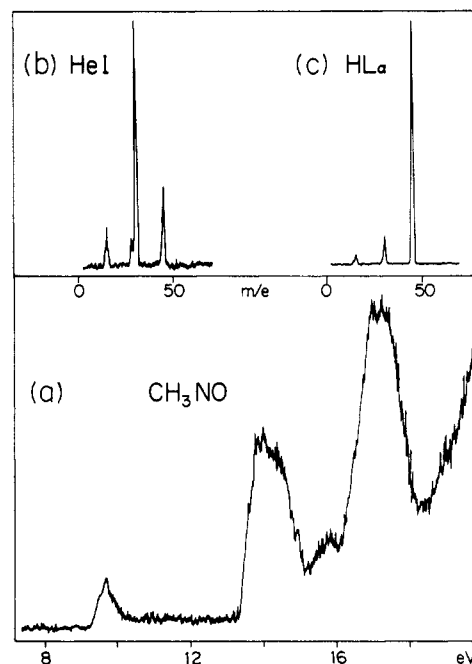


Figure 1. (a) The He I photoelectron spectrum of nitrosomethane, CH₃NO, together with photoionization mass spectra recorded with (b) He I and (c) unfiltered H L_α (H L_{αβγ}) radiation.

above calculation since it gave a superior SCF total energy.

Results

The results of the above experiments may be summarized as follows.

Heating *cis*-(CH₃NO)₂ into the PE spectrometer gives monomeric *formaldoxime*, CH₂=NOH, up to ~80 °C, and at ~95 °C monomeric *nitrosomethane*, CH₃NO, is the major product in the vapor phase. The species described by Bergmann et al.¹⁹ as the *cis* dimer is, in actuality, CH₂=NOH, although they did obtain a spectrum of CH₃NO at higher temperatures. The spectrum shown in ref 17 is correctly identified as CH₃NO. The PE spectrum of CH₃NO and its corresponding quadrupole mass spectrum obtained under the same conditions are shown in Figure 1. Heating the sample further over pyrex wool gave no change in the spectrum.

Further verification of CH₂=NOH as the low-temperature species can be established by trapping this vapor en

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TABLE V: Comparison of Observed and Theoretical IP's^a Calculated by PKKT for CH₃NO

orbital symmetry	exptl ^b	GAUSSIAN 70 ^c		perturbation corrections results			
		STO3G	STO4-31G	3rd order	$\Delta(E^{GA})$	$\Delta(E^{GA})^e$	SP ^d
10a'	9.68 ± 0.05	8.40	11.20	9.24	9.10	9.5	9.67
9a'	13.8	13.36	15.32	13.69	13.65	14.0	
2a''	14.3	12.30	14.65	14.00	14.00	14.2	14.26
8a'	15.8	15.89	18.14	16.37	16.05	16.4	
7a'	16.9	16.83	18.95	16.39	16.30	16.6	
1a''		16.13	17.65	16.39	16.39	16.6	
6a'		21.79	23.58	20.58	20.46	20.9	

^a All values in eV. ^b All IP's ±0.1 eV except as specified. ^c Geometry taken from ref 9. ^d Scaled perturbation, see text. ^e Extrapolated.

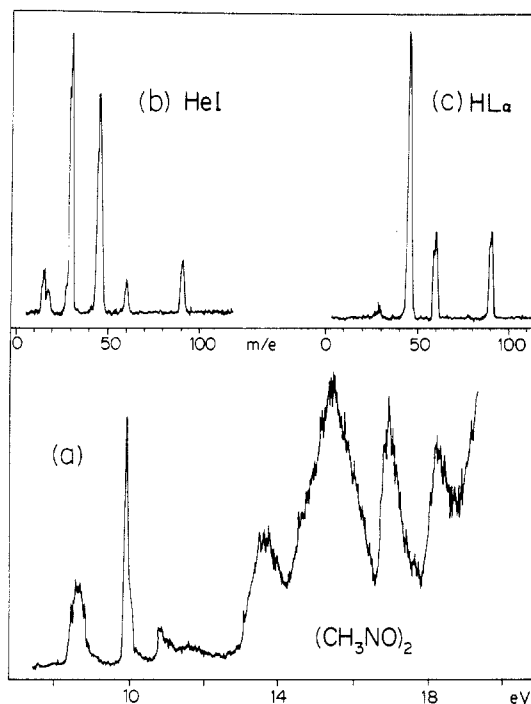


Figure 2. (a) The He I photoelectron spectrum of the *trans*-nitrosomethane dimer, (CH₃NO)₂, together with (b) the He I and (c) the unfiltered H L α photolysis mass spectra.

route into the spectrometer. A white solid is deposited which melts at room temperature and then resolidifies. This white solid gives subliming characteristics and an IR spectrum identical with those of trimeric formaldoxime.

Heating *trans*-(CH₂NO)₂ into the PE spectrometer at ~28 °C gives a spectrum identical with that obtained by Egddell et al.¹⁸ As we shall see later this is indeed the *trans* dimer and not the monomeric as claimed.¹⁸ The IP values are the same as those for the *trans* dimer published by Bergmann et al.¹⁹ The PE and mass spectra are shown in Figure 2, the mass spectrum unequivocally showing the presence of the dimer. When this species is passed over Pyrex wool at ~220 °C the PE spectrum obtained is that of monomeric CH₃NO. At lower temperatures the PE spectrum shows a mixture of the *trans* dimer and monomer, with no evidence for CH₂=NOH.

The PE spectrum of formaldoxime is similar to that obtained previously²⁰ and is shown in Figure 3 together with the mass spectrum. The cracking pattern obtained by using both the He I and unfiltered H L α (H L $\alpha_{\beta,\gamma}$) serves to distinguish CH₂=NOH (Figure 3) from CH₃NO (Figure 1). This species does not isomerize up 200 °C.

In addition to the PE and mass spectroscopy results, the HAM/3 calculations (Tables I-IV) provide additional confirmation for the correct identification of all species. In the absence of a PE spectrum for the *cis* dimer, the calculation (Table IV) provides some indication of the

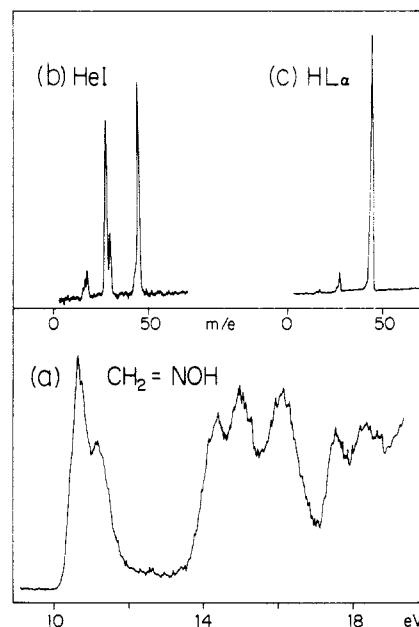


Figure 3. (a) The He I photoelectron spectrum of formaldoxime, CH₂NOH, together with (b) the He I and (c) the unfiltered H L α photolysis mass spectra.

position and ordering of IP's. These values are expected to be much more accurate than the previously obtained CNDO results.⁸

The GAUSSIAN 70 STO4-31G calculations (Table V) give an ordering of the first seven occupied molecular orbitals of CH₃NO as 10a', 2a'', 9a', 1a'', 8a', 7a', and 6a', and a 3a'' low-lying unoccupied molecular orbital, which is consistent with some other previous *ab initio* results (Table I). The perturbation corrections decreased all the IP's obtained by the 4-31G calculations, but the two IP's corresponding to the two a'' orbitals retained relatively higher values due to the interactions with the 3a'' orbital. The ordering of ionization is 10a', 9a', 2a'', 8a', 7a', 1a'', and 6a', with the IP's for 7a' and 1a'' orbitals predicted quite close together. Only two IP's are reported for the scaled perturbation calculations because these calculations estimate very good IP values for the highest occupied molecular orbital of each symmetry species, but not for the rest.

Discussion

We have now established that the *cis*-(CH₃NO)₂ species gives CH₂=NOH up to ~80 °C and CH₃NO above 90 °C. Heating to a higher temperature over Pyrex wool gave the CH₃NO monomer unchanged, indicating that the isomerization of the *cis*-nitrosomethane dimer to formaldoxime occurs probably while the *cis* dimer is still in the solid state. The formation of the CH₂=NOH species at a temperature some 10 °C below that at which *cis*-(CH₃NO)₂ dissociates completely into the monomeric form is rather unusual.

The thermal dynamics of this complicated system have to be studied again before a proper mechanism of isomerization can be developed.

We have made many attempts to obtain the PE spectrum of the cis dimer using a variety of methods, including heating the dimer within 2 cm of the ionization point at minimal temperatures, and adiabatically expanding CH_3NO through a small nozzle. In both instances, $\text{C}_2\text{H}_2=\text{NOH}$ or CH_3NO alone are formed, and no evidence for the cis dimer was obtained.

The HAM/3 calculations serve as a basis for the assignments of the PE spectra and are presented in Tables I-IV. They will not be discussed in any detail here, except to say that those for $\text{CH}_2=\text{NOH}$ (Table II) are in agreement with the previous results,^{20,28} especially concerning the relative ordering of the first two closely spaced states. Those for trans- $(\text{CH}_3\text{NO})_2$ (Table III) closely fit our experimental spectrum (Figure 2) and Bergmann et al.'s experimental IP's.¹⁹ They also indicate that the earlier spectrum of Egdell et al.¹⁸ is actually that of the trans dimer.

CH_3NO presents an interesting assignment problem (Table I), since earlier calculations on HNO involving perturbation corrections to Koopman's theorem indicated that the theorem did not hold in this case.²³ This prediction was justified by our own PCKT calculation on CH_3NO . The low-lying unoccupied π level ($3a''$) in the SCF results caused a switching of $2a''$ with $9a'$ and $1a''$ with $8a'$ orbitals after corrections are applied. HAM/3 also predicted this ordering. The PCKT calculated IP's are all within 0.5 eV of the experimental values. A plot of predicted IP's against the values 10^{-T} (where T is the truncation criterion) shows that this discrepancy should

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decrease as more determinants are considered. An exception to this trend is exhibited by the small Pt band at 15.8 eV. Thus if the $8a'$, $7a'$, and $1a''$ ionizations are present in the band at 16.9 eV we might assign the 15.8-eV band to a shakeup satellite peak. This, however, is tentative and will have to be confirmed by a further extensive theoretical study.

Summary

It has been demonstrated that a combination of in-situ PE and quadrupole mass spectroscopy, combined with semiempirical HAM/3 calculations, can be successfully used to evaluate the ionization processes in a complicated gas-phase system, in the case, the CH_3NO , cis- and trans- $(\text{CH}_3\text{NO})_2$, and $\text{CH}_2=\text{NOH}$ mixture. This clarifies several ambiguities noted in earlier work.

We note that while this work was in its concluding stages, the authors of ref 18 have repeated their earlier work and now show²⁹ that the spectrum of CH_3NO is as described in this present manuscript. In addition, their configuration interaction calculations confirm the breakdown of Koopmans' theorem for this molecule. This work complements our present study where we have shown the interrelationship between the two dimer species, monomeric CH_3NO and $\text{CH}_2=\text{NOH}$.

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New Preparation Method for Doped Polycrystalline TiO_2 and Nb_2O_5 and Their Photoelectrochemical Properties

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Doped polycrystalline TiO_2 and Nb_2O_5 have been prepared by a new method and examined as photoanodes. Polycrystalline oxide films on metal substrates which are thick and porous are prepared by anodic oxidation accompanied by sparking in various electrolytes. It was found that cations in the electrolyte are doped into the oxide films during anodic oxidation, which has been proved by SIMS. Therefore, this is a new easy method of preparing doped polycrystalline TiO_2 and Nb_2O_5 . The TiO_2 film prepared in Na_2SO_4 solution at 100 V is a good photoanode, showing a relatively high photocurrent under visible-light illumination. The doping is carried out by addition of the doping ions in saturated Na_2SO_4 solution. The Cr-, Ir- and Rh-doped TiO_2 films exhibit a high visible photocurrent but a low UV photocurrent. The Cr-doped Nb_2O_5 films also exhibit similar spectral responses. An increase in the UV photoresponse and a decrease in the visible photoresponse by reduction are observed. The relationship in which the band-gap photocurrents decrease with increasing visible photocurrents is obtained for the doped oxide films. This suggests, with the reduction effects, that the impurity and the interstitial metal d bands or states bringing about the visible response also act as recombination centers.

Introduction

TiO_2 and Nb_2O_5 are suitable materials for photoanodes in the photoelectrolysis of water, especially in terms of stability in aqueous solutions. Polycrystalline oxide has the advantages of being easier to prepare and low in cost, and some forms of this material have photoelectrochemical

properties similar to those of a single crystal. Various preparation methods of polycrystalline TiO_2 have been reported: thermal oxidation of the metal¹⁻⁸ thermal de-

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