ACC JOURNAL 2016, Volume 22, Issue 1 DOI: 10.15240/tul/004/2016-1-004

RELEAVING REFRACTORY OXIDIZED ORGANIC POLLUTANTS BY PHOTOELECTROCHEMICAL TREATMENT USING FORMIC ACID AS SOLVENT

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Abstract

Unlike most organic compounds which undergo ready mineralization on illuminated and oxygenated semiconductors like TiO_2, nitroarenes (from dye-, explosives- or polymer production), nitriles or multiply halogenated solvents are inert towards this kind of attack. However, they can be processed if strongly reducing entities are produced in such a semiconductor system. It is shown that the above kinds of refractory pollutants can be treated in formic acid (HCOOH) due to visible irradiation if combined with W, Nb or Bi oxide semiconductor slurries. Toxic functional groups are often removed entirely, e.g. with Hal ($\neq$ aliph. F), CN whereas nitrobenzenes turn into anilinium ions and benzyl groups undergo rearrangement at Nb_2O_5. The method is broadly applicable and cheap.

Keywords

Formic acid; Photoelectrochemical reduction; Decomposition of organic pollutants; Semiconducting oxides; PEC rather than hydrogen storage.

Introduction

Halocarbons and nitroaromatics, formerly commonly used as solvents or being residues of polymer- or explosive productions (e.g., perchloroethylene, TNT, picrates or toluene diisocyanate) are hard to treat- and refractory residues in the environment. Unlike with other kinds of organics, their oxidation by either direct electron transfer or by using OH radicals is difficult to impossible. However, hydrogenating enzymes like hydrogenases can process some of these pollutants, and a more convenient reductant can be produced by illuminating a HCOOH solution[1] simply subjecting the solvent to photoelectrochemical attack. Previous experiments (Fränzle et al. [4]) dealt with degradation of more complicated aromatic compounds, namely diphenyl amine derivative diclofenac™ (Na salt, readily soluble in HCOOH) and its possible fragmentation products like 2,6-dichloroaniline. The purpose of the study (also see Zeisig [10]) reported here was to understand the specific responses and relative reaction kinetics of various functional groups in both aliphatic and aromatic compounds which, unlike diphenyl amines, are very hard to oxidize but might undergo hydrogenation removing the very substituents causing both toxicity and often compromising more classical methods of degradation or mineralization, covering a broad range of moieties in both aliphatic and aromatic organics. This can be done using visible in semiconductors having band gaps near 3 eV.

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[1] HCOOH is a very polar solvent the physicochemical parameters of which are very similar to those of water. Accordingly, while nitrobenzenes are fully miscible with formic acid, alkanes like hexane or benzene or toluene do not mix in cold, and solubilities of most chlorinated (except for CH_2Cl_2 or $CHCl_3$) or brominated hydrocarbons in HCOOH are comparable to those in water.

1 Theoretical Considerations

Generally speaking, the most likely reducing agent in the conc. HCOOH medium, namely CO_2^- could either be produced by direct reduction of CO_2 at some – 1.8 V (Stanbury [9]) or by (anodic- or hole-induced) oxidation of HCOOH (the structure [more stable tautomer?] of COOH formed in this manner is unknown while CO_2H^+ is protonated at oxygen only). Of course, like all simple C_1 and C_2 compounds and –anions photoelectrochemical as well as electrochemical transformations of HCOOH were investigated before (e.g. Reichert et al. [8] and quotations in this paper), with a focus on fuel-cell use of formic acid (Okamoto et al. [7]). It turned out that neat HCOOH cannot be oxidized at Pt anodes without some water being present (ibid.), probably because then there is a stable cover of the electrode surface by CO (with methanol, methyl formate forms instead). The adsorption of CO to oxide interfaces will be less pronounced than to PGM or gold electrodes, suggesting removal to be easier to accomplish in neat HCOOH even if the co-processed substrates are not strongly adsorbed.

Semiconductors are solids distinguished by a band gap in between the valence band (-s [several ones except for cubic crystal structures]) and the conduction band; in solution or even some gaseous phase both e^-_{cb} and holes (h^+_{vb}) can bring about redox reactions with substrates of suitable redox potentials (for 1e-potentials of organics see e.g. Miller et al. [6]). With organics, these agents often cause decay of carbon backbones. Accordingly, key reactions in HCOOH are:

$$4\ \mathrm{HCOOH} + 2\ e^-_{cb} \rightarrow H_2\uparrow + 2\ \mu\text{-}H(HCOO)_2^- \qquad (1)$$

$$\mathrm{HCOOH} + h^+_{vb} \rightarrow \mathrm{HCOO} + H^+_{solv} \leftrightarrow CO_2^- + 2\ H^+_{solv} \qquad (2)$$

CO_2^- activity is thus controlled mainly by autoprotolysis or purity of solvent. Unless there is complete cleavage of either kind of charge carriers by dissolved or adsorbed species, like in photochemical solar cells, p-type materials should undergo oxidation with time while in *n*-type solids the anion partial lattice tends to become destroyed and cations get reduced. Unlike the potentials of both conduction and valence band edges, band gaps do not respond to the change of medium unless surface protonation or partial exchange of either cat- or anions take place. The band gaps of the applied semiconductors are given in Tab. 1.

The spectral emission of the used power-LED [(Ga,Al)N] is not very narrow, let alone monochromatic. Absorption of a substantial part of the radiation by each applied semiconductor is likely. There were no attempts to estimate quantum yields as the focus on identifying products and reaction pathways was possibly (and actually) influenced by the kind of semiconductor (rather than its conduction mode).

Tab. 1: *Photophysical data on the semiconductors used in this experimental series*

Semiconductor	Band gap [eV], conduction mode	Absorption edge / spectrum	Theoretical absorption edge [nm]	Remarks
Bi_2O_3	2.9; p	Indirect transition near 414 nm; direct at $\lambda \leq 370$ nm	428	BiOX have larger band gaps.
Nb_2O_5	About 3.2 (see remarks); n	≥ 400	390?	Data on band gap of Nb_2O_5 do differ considerably (BG ≈ 3.1 – 3.8 eV); material is not bright white, suggesting BG < BGrutile, that is < 3.1 eV. Protonated forms, like alkali niobates, should have smaller band gaps (i.e., ≤ 3 eV). Nb (and highest-oxidation state Hf, **W**, Ta) oxides are impossible to dissolve in acids ≠ HF ("valve metals").
WO_3	2.8; n	Some 450	443	Bright yellow, turns green upon irradiation in HCOOH within 2 min; tungsten bronzes are *n*-type materials also.

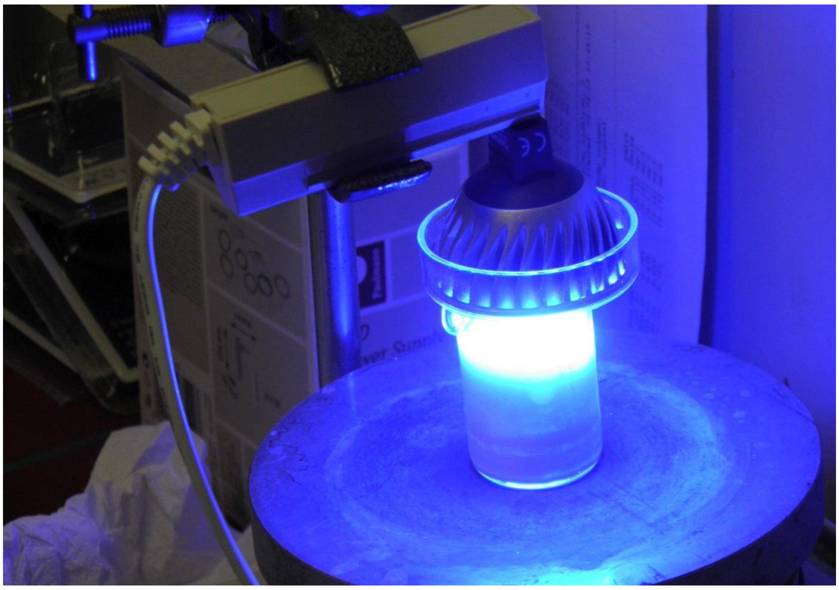
Source: Own

2 Materials and Methods

- 97% formic acid (Merck)
- Bi_2O_3
- Nb_2O_5
- WO_3 (all from Sigma-Aldrich)
- $NaBPh_4$ (Fluka)
- Solvents: pentane, hexane
- Substrates: several halogenated hydrocarbons, nitriles and ketones, including
  - 1,3-dichloroacetone,
  - 1,1,1,2,3,3,3-heptachloropropane,
  - highly halogenated ethanes,
  - unsaturated chlorohydrocarbons such as chlorobenzene, bromobenzene,
  - benzyl chloride, $CClX{=}CCl_2$ (X = H or Cl),
  - 1,2-chlorofluorocyclohexene and –naphthaline,
  - 4-Y-C_6H_4-NO_2 (Y = H, F…I, OH),
  - nitriles PhCN, $PhCH_2CN$, hexane nitrile and 6-bromohexane nitrile.

2 g of dried semiconducting oxide are suspended in 20 ml HCOOH in which 1 mmol of the test compound was dissolved before and irradiated by some blue-emitting high-luminosity

LED (3.5 W) [Fig. 1] for one hour on a magnetic rotary stirrer[2] at RT (evaporation hood [HCOOH vapors!]). Due to the kind of the selected light source, heating of the suspension during the experiment is negligible.



Source: Own

Fig. 1: *Blue-light photolysis of some halogenated organic material dissolved in HCOOH in presence of niobia (stirred off-white* Nb_2O_5*)*

The bright white area in the picture is due to partial over-exposition (light scattered by suspended particles) of the photograph. There is a limited access of air oxygen; the stirred reaction beaker is not completely sealed by the front “window” cover of the LED. Any peroxocarbonate radicals thus forming would reconvert into CO_2^- by decaying into OH and CO_3^- before either reacting with more HCOOH.

Then 1 ml of the solution is taken off and extracted by 1 ml of a Na tetraphenylborate solution in n-pentane which is not miscible with HCOOH, stirred for 30 min [Fig. 2] before separating the upper liquid phase.

20 µl of this pentane solution is then injected into an Agilent/Saturn 3000 GC/MS system (temperature range of separation 80 – 210°C) using a chiral (cyclodextrine-based) column for separation. MS permits identification of products due to fragmentation patterns which is important here as there are some unexpected pathways in the reactions (see below). The traces of HCOOH passing into the unpolar phase are kept from loading the mass spectrometer by a time lag until switching on of 4.5 min (then, T = 116°C [slightly above the common b. p. of HCOOH]).

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[2] As aliphatic CF bonds are not attacked in this system, PTFE coatings of magnetic stirrer bars will not be attacked.

Source: Own

Fig. 2: *Extraction of analytes from HCOOH into n-pentane after irradiation and deposition of the SC particles. The yellow color of the more dense formic acid phase is neither due to remaining nitroaromatics (reduction is complete) nor to metal ion dissolution but points to unidentified red to brownish organic decomposition products.*

Of course, doing photoelectrochemistry in aggressive media such as concentrated acids requires that the semiconducting phases be insoluble therein which obviously might pose a problem concerning the SCs fairly commonly employed in PEC, such as pnictides (III-V-SCs like GaP, AlAs, InP) or chalcogenides (ZnS, ZnSe, oxides). There even is a paper in the literature describing PEC production of molecular fluorine from anhydrous HF using $SrTiO_3$; given the rather high solubility of SrF_2 and ease of formation of TiF_6^{2-} in this solvent, stability of the photoelectrode is doubtful at best. Considering HCOOH-based media, oxides of valve metals like n-type WO_3 and Nb_2O_5 and p-type Bi_2O_3 fulfill this condition. However, it should be noted that, regardless of high acidity and polarity of 97% HCOOH, also other SC oxides such as Fe_2O_3 do not dissolve in this medium regardless of illumination. In the latter cases, however, effective PEC is unlikely, therefore these systems were no further pursued and investigated.

3 Results

3.1 Alterations of Semiconductors

Upon illumination in HCOOH, yellow WO_3 rapidly turns green but never becomes blue; i.e. a tungsten bronze will not form. Bi_2O_3 is slowly bleached indicating water uptake to produce BiO(OH) but no reduction[3] of Bi(III) takes place. Otherwise the semiconductors proved stable much beyond expectation (holds for both n- and p-type materials), also when irradiated much longer (e.g. overnight).

3.2 Organic Substrates and Products Obtained

Unlike other compounds insoluble in water, the highly polar (4-substituted) nitrobenzenes do completely mix with HCOOH. There are no intermediate or remanent discolorations

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[3] Bi colloids turn green to black; they do readily form in thermochemical reactions with even CO at T < 200°C and likewise if triplet aromatics form photochemically on Bi_2O_3 (Fränzle et al. [3]).

suggesting intermediate formation of nitrosobenzenes, azobenzenes, or aromatic hydroxyl amines. When nitrobenzenes are reduced, one must consider that anilines are fairly strong bases in HCOOH. GC/MS analysis by extraction into pentane thus will occur only if tetraphenylborate assists extraction of the large cation. In addition, an effective extraction can be determined by its by-product in GC/MS; while the aniline (displaying both dehalogenation and nitro group reduction) is directly identified by MS fragmentation patterns, BPh_4^- decomposes right at the injector interface to yield biphenyl already at $T > 130°C$; biphenyl of course produces another distinctive GC/MS signal.

Upon photolysis of the semiconductor slurry/HCOOH/organic pollutant mixture, the probable intermediate CO_2^- reacts with various organics partly reducing them in this strongly acidic ($H_0 \approx -3.3$) medium, e.g. producing anilinium ions from nitrobenzenes. Functional groups undergoing complete cleavage are:

- cyanogroups from all aliphatic, benzonitriles and benzyl cyanides (phenyl acetonitrile) are completely cleaved, probably forming HCN,
- nitrogroups in nitrobenzenes undergo partial loss of nitro group,
- there is cleavage of methyl or substituted methyl groups of benzyl compounds if irradiated using niobia/HCOOH, e.g. producing some chlorobenzene from benzyl chloride whereas phenyl acetonitrile in the same medium partly rearranges to produce aniline; the fate of exocyclic carbon atoms is unknown so far.

C-halogen bonds do respond differently:

- Aliphatic **C-F** bonds are not cleaved (a disadvantage in treating CFCs, of course) while aromatic ones do readily react (e.g. 4-fluorophenol, 4-fluoronitrobenzene)
- Both aromatic and aliphatic C-Hal bonds (Hal = Cl, Br or I) are cleaved, with
- Reactivity sequence of dechlorination is $-\mathbf{CCl}_3 < -CHCl_2 < -CHalY-$ or $=CCl_2$, that is, symmetrical 1,1,1,2,3,3,3-heptachloropropane (which, again, is difficult to dissolve in HCOOH) does not provide substantial amounts of chiral product on any semiconductor tried; hexachloroethane does only slowly react while pentachloroethane mainly affords 1,1,1,2-tetrachloroethane (plus trichloroethylene) rather than symmetrical tetrachloroethane (for benzyl halogenides see above)
- **C-Br** bonds, as far as investigated, behave very similarly to C-Cl bonds
- Both **iodo**aliphatics and iodoaromatics produce a dark-colored oily phase which readily separates form HCOOH but does, however, contain little if any I_2

Attempts were done to get a chiral product from processing 1,3-dichloroacetone, racemic 1-chloropropanol-2 to be resolved by using a chiral GC-column into two peaks but to no avail: unlike 1-chloroacetone, the above product was not obtained at all, neither was its formate ester. Likewise, other ketones do **not** undergo hydrogenation, in stark contrast to the (non-PEC) HCOOH-based hydrogenation of immonium ions (Eschweiler-Clarke reaction) or transformations catalyzed by organoiridium complexes splitting HCOOH into H_2 and CO_2 (Hull et al. [5]).

4 Discussion

Both cyano- and nitro groups can be completely removed from an organic compound by this reaction. NO_2 will then undergo reduction, like nitrate[4] but unlike NO_2^- (which is fairly stable in HCOOH). The mechanism of cyano group cleavage is unclear; yet it should be noted that a) heating nitriles with oxides such as CaO causes CN removal and b) cyanide addition to aldehydes, ketones, imines and the like is reversible. From degradation of phenyl acetonitrile (benzyl cyanide) by Nb_2O_5/HCOOH/hν, nothing else than toluene and aniline could be obtained by GC/MS.

There are several possible reducing products of HCOOH when the latter undergo hole oxidation in photoelectrochemistry, including H atoms, CO, and CO_2^-. Redox potentials known from aq. solutions can be extrapolated to HCOOH by a formula from data on redox potentials of many metals and hydrogen in HCOOH, $HCONH_2$, simple alcohols, CH_3CN, etc. (Fialkov [1]), namely (3):

$$\varepsilon_{HCOOH} = 0.986\, \varepsilon_{H2O} - 0.45 \tag{3}$$

V vs. NHE in the respective medium is given in Tab. 2.

Tab. 2: *Redox chemistry in various solvents*

solvent	**a**	**b**
water	**1**	**0**
CH_3OH	0.971	0.06
C_2H_5OH	0.930	0.19
HCOOH	0.986	-0.45
HCO-NH_2	0.967	0.11
HCO-NH(CH_3)	0.899	-0.12
CH_3CN	0.937	-0.05
neat N_2H_4, excluding hydrogen electrode	0.808	1.09

Source: Calculated by this author using data collected by Fialkov [1].

The potential shift **b** here depends on basicity of solvent relative to that of water; see HCOOH vs. $HCONH_2$ and N_2H_4 or from phase transfer potentials. Among these, only H atoms can reduce Yb^{3+} or Eu^{3+}. There is no color change during PEC (or sonochemical) processing of the system.

Control experiments were done to ascertain that a "live" photoelectrochemical process rather than a catalytic dehalogenating hydrogenation or some based on HCOOH decomposition[5] does occur indeed; reductions like those described before were not observed with either stirring the solution in darkness nor using some batch of PEC oxide which had been previously irradiated (cp. the green discoloration of WO_3) but now exposed to substrate in the dark only. Besides of these control experiments, some by-reactions shows the contribution from hole oxidation of contaminants dissolved in HCOOH and/or adsorbed to the solid, namely additions of residues from preparing the semiconductors:

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[4] Dissolving solid silver nitrate in conc. HCOOH gives rise to a peculiar yet somewhat dangerous kind of clock reaction (Fränzle [2]):

1) there is reduction of nitrate producing mainly NO, then
2) after about 30 – 50 s evolution of nitrogen oxides from the meanwhile boiling solution stops, and only then brownish colloidal silver is formed

[5] Both decay pathways of HCOOH into CO and water (the dominant and spontaneously occurring one) and into CO_2 and H_2 (to be catalyzed by iridocene phenanthroline derivative complexes (Hull et al. [5]) are exothermic whereas HCOOH vapor UV photolysis mainly yields HCO and OH radicals

unsaturated aliphatic substrates such as tri- and tetrachloroethylene do not just undergo halogen cleavage but, provided one uses n-type oxides which contain some halide residues from preparation, e.g. Nb_2O_5. After short irradiation of a slurry containing niobia and C_2Cl_4 in HCOOH, thus some pentachloroethane and hexachloroethane are obtained besides of tri- and dichloroethylene. In HCOOH, both chlorine and bromine, unlike nitrogen oxides or nitrate ion, are unexpectedly metastable, hence will add to a C=C double bond rather than oxidize HCOOH directly if formed from halide ions by photoelectrochemical hole oxidation. Some boiling water extraction of the niobia used here yielded levels of 350 µg/g Cl and 20 µg/g F, with the common preparation of niobia being hydrolysis (either by liquid water or hot vapor) of $NbCl_5$ produced by either the Kroll process and fractionated distillation/sublimation separation from Ti, Ta etc. or HCl gas treatment of fluoroniobates. The presence of substantial amounts of fluoride in the samples argues for the latter method of preparation; absence of CFCs from the product mixture obtained from C_2Cl_4 or C_2HCl_3 can be accounted for as the holes do not directly oxidize C=C double bonds nor fluoride ion, that is:

$$2\ Cl_{-ad}s \rightarrow Cl_2^-,\ \text{no } FY^-\ \text{species} \rightarrow \text{chlorination of C=C bonds only} \qquad (4)$$

no fluorine introduced; $k_{Cl2-/C=C} >> k_{-Cl}$ in C_2Cl_4

Conclusion

The broad range of organic compounds which are very difficult to oxidize by either valence band holes, OH radicals or anodes, however, undergo the process described here, and the various possible chemical/technical origins of these suggest to use them in remediation of residues especially as HCOOH is cheap and products, some of which are toxic still, like anilines, are then much more accessible towards microbiological secondary treatment. The cleavage of cyano groups and of exocyclic benzylic C atoms (cp. indanes) in the HCOOH/niobia system could probably be used in preparative organic chemistry, e.g. that of alcohols and (chiral) phenyl propanoic- or -acetic acids.

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OSVĚTLENÉ SUSPENZE POLOVODIČŮ V KYSELINĚ MRAVENČÍ: MOŽNOSTI FOTOCHEMICKO-REDUKTIVNÍHO ODBOURÁVÁNÍ HALOGENIZOVANÝCH, NITROVANÝCH ŠKODLIVIN A JINÝCH CHEMIKÁLIÍ

Na rozdíl od většiny organických sloučenin, které procházejí připravenou mineralizací na osvětlených a okysličených polovodičích, jako je TiO_2, nitroareny (z výroby barviv, exploziv či polymerní produkce), nitrily nebo halogenová rozpouštědla s násobnou vazbou jsou vůči tomuto druhu ataku inertní. Nicméně mohou být zpracovány v případě, kdy silně redukční entity jsou vyráběny v polovodičovém systému. Je zřejmé, že výše uvedené druhy žáruvzdorných znečišťujících látek lze zpracovávat pomocí kyseliny mravenčí (HCOOH) v suspenzi polovodivých oxidů, a to vzhledem k viditelné iradiaci v kombinaci s W, Nb nebo Bi. Toxické funkční skupiny jsou často zcela odstraněny, např. Hal (≠ alif. F), zatímco CN nitrobenzeny se promění na ionty anilinia a benzylové skupiny se přeskupí na Nb_2O_5. Tato metoda je široce použitelná a levná.

BELICHTETE HALBLEITERSUSPENSIONEN IN AMEISENSÄURE: MÖGLICHKEITEN ZUM PHOTOCHEMISCH-REDUKTIVEN ABBAU HALOGENIERTER, NITRIERTER SCHADSTOFFE U.A. CHEMIKALIEN

Während die meisten Organika an belichtetem und belüftetem TiO_2 photochemisch glatt mineralisiert werden, sind Nitroaromaten (aus der Herstellung von Farben, Sprengstoffen oder Polymeren), Nitrile und halogenierte Lösungsmittel in dieser Hinsicht inert. Sie reagieren allerdings dann, wenn in einem solchen Halbleitersystem stark reduzierende Intermediate freigesetzt werden. Daher sind die obigen refraktären Schadstoffe in Ameisensäure (HCOOH) gelöst an Suspensionen halbleitender Oxide von W, Nb oder Bi mit sichtbarem Licht abbaubar. Funktionelle Gruppen wie Hal (≠ aliph. F), CN werden vollständig abgespalten, Nitrobenzole zu Aniliniumsalzen reduziert, während Benzylgruppen an Nb_2O_5 umgelagert werden. Die Methode ist preisgünstig und auf sehr unterschiedliche Stoffe anwendbar.

OŚWIETLONE ZAWIESINY PÓŁPRZEWODNIKÓW W KWASIE MRÓWKOWYM: MOŻLIWOŚCI FOTOCHEMICZNEGO REDUKUJĄCEGO WYTRĄCANIA HALOGENIZOWANYCH, NITROWANYCH SUBSTANCJI SZKODLIWYCH I INNYCH SUBSTANCJI CHEMICZNYCH

W odróżnieniu od większości związków organicznych, które łatwo dają się mineralizować na oświetlonych i utlenionych półprzewodnikach, takich jak TiO_2, nitroaromaty (z produkcji barwników, materiałów wybuchowych lub polimerów), nitryle lub halogenowe rozpuszczalniki z układami wielokrotnych wiązań są wobec nich obojętne. Niemniej jednak mogą być przetwarzane w sytuacji, gdy dodane zostaną mocno redukujące produkty pośrednie. Dzięki temu wymienione odporne substancje szkodliwe rozpuszczone w kwasie mrówkowym (HCOOH) w zawiesinie tlenków półprzewodnikowych W, Nb lub Bi rozkładają się w świetle widzialnym. Grupy funkcyjne, takie jak Hal (≠ alif. F), CN zostają całkowicie usunięte, nitrobenzeny przekształcają się w anilinę a grupy benzylowe przegrupowują się w Nb_2O_5. Metoda jest tania i może mieć zastosowanie do wielu materiałów.