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[13] We have already synthesized from **14** the tetrakis(diphenylphosphanyl oxide) compound, which can be reduced to tetraphosphane.

Modified, Amorphous Titania—A Hybrid Semiconductor for Detoxification and Current Generation by Visible Light**

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Although titania (titanium dioxide, TiO_2) absorbs only 2 – 3 % of the solar light reaching the surface of the earth, it is the best investigated semiconductor in the field of chemical conversion and storage of solar energy. While early work was predominantly concerned with photoelectrochemical conversion,[1–3] later investigations focused on chemical processes, especially on water cleavage.[4] More recently, detoxification of water has become the main topic since upon UV irradiation in the presence of oxygen titania is able to oxidize most organic and inorganic contaminants to harmless products such as carbon dioxide and mineral acids.[5, 6]

According to the proposed mechanism, the light-generated electron-hole pair in titania is trapped at surface sites at which interfacial electron transfer occurs from and to adsorbed substrates.[7] To obtain a more efficient utilization of solar light ($\lambda_{max} = 500$ nm), diverse efforts were made to shift the light sensitivity of titania ($E_{bg} = 3.2$ eV, $\lambda \leq 390$ nm) into the visible region. A classical example is the photosensitization of the photocurrent by dyes and transition metal complexes of the type $[RuL_3]^{2+}$ (L = a substituted 2,2′-bipyridyl ligand).[8, 9] Doping with ions of V, Cr, Mn, Fe, Co, Ni, and Cu results in a shift of light absorption into the visible range, but only in very few cases does it also enable generation of a current or a chemical reaction by visible light.[10] An example is the decomposition of NO_x, although it is unclear whether or not this process occurs through a semiconductor photocatalysis mechanism.[11] It was further reported that colloidal titania doped with 0.1 to 50 atom % of iron induces the degradation of dichloroacetate with visible light. However, concomitant cathodic dissolution of the iron(III) oxide occurs, which can be avoided only by addition of oxidizing agents like hydrogen peroxide.[12]

Typical for all mentioned investigations is that the crystalline modifications anatase and rutile were involved, while amorphous titania was reported to not be photoactive.[13] In connection with our work on the use of amorphous zinc and cadmium sulfide as photocatalysts for new chemical syntheses,[14] we have now found that amorphous, microporous titania (AMM-Ti) modified with transition metal salts induces a photocurrent and photocatalyzes the degradation of 4-chlorophenol with visible light.

The new hybrid photocatalysts were prepared by a sol – gel procedure through controlled hydrolysis of titanium alkoxides in the presence of disodium hexachloroplatinate, rhodium(III) chloride, and gold(III) chloride[15]. The obtained microporous powders display specific surface areas in the range of 160 – 200 m^2g^{-1} and a pore-size distribution with a maximum at 0.78 nm, and are amorphous according to X-ray diffraction. In agreement with the latter, no crystalline parts could be detected by high-resolution transmission electron micrography. The ESCA and EXAFS investigations (ESCA = electron spectroscopy for chemical analysis, EXAFS = extended X-ray absorption fine structure) of a sample of AMM-Ti doped with 1.1 % Pt^{IV} (**1**) revealed that platinum is present in the oxidation state IV and surrounded by four chloride ions. The EDX analyses (EDX = energy dispersive X-ray) with a lateral resolution of 1 – 2 nm do not give any evidence for the presence of discrete platinum particles. Therefore, it is assumed that platinum tetrachloride is homogeneously distributed in the matrix of amorphous titania.[16]

The diffuse reflectance spectrum of **1** resembles that of unmodified AMM-Ti, but exhibits an additional absorption in

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1433-7851/98/3721-3034 $ 17.50+.50/0

the range of 400–550 nm, which is assigned to the platinum(IV) chloride centers (Figure 1).[17] When an electrode coated with **1** was irradiated at different wavelengths in a standard photoelectrochemical cell, a photocurrent was observed also in the visible region; that was not the case when unmodified titania was employed. It is evident from Figure 1 that the wavelength dependence of the photocurrent follows the absorption spectrum. The same result was obtained when the action spectrum was measured not potentiostatically but under short-circuit conditions to ensure careful exclusion of any external voltage.

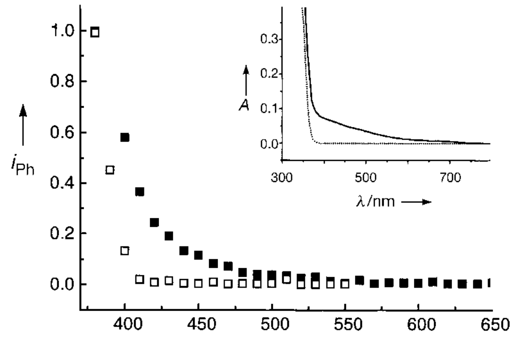


Figure 1. Photocurrent action spectrum for TiO_2 (Degussa P-25) (□) and **1** (■; in both cases the semiconductor powder was precipitated onto the ITO glass electrode (ITO = indium tin oxide) from an aqueous suspension. The photocurrent i_{ph} (arbitrary units) was measured in a conventional three-electrode arrangement (platinum and Ag/AgCl as counter and reference electrode, respectively, 0.1 M NaOH as electrolyte), and a potential of 0.5 V (Ag/AgCl) was applied to the photoelectrode. The insert shows the diffuse reflectance spectra of TiO_2 (Degussa P-25, ••••) and **1** (——); the absorbance *A* is plotted as a Kubelka–Munk function.

To test the photocatalytic activity, the degradation of 4-chlorophenol, an ubiquitous contaminant in water, was investigated; it is well known that upon irradiation with UV light crystalline titania catalyzes complete mineralization to water, carbon dioxide, and hydrogen chloride.[5] Surprisingly, **1** enables this reaction to occur even with visible light ($\lambda \geq$ 455 nm, Figure 2), and the wavelength dependence of the apparent disappearance quantum yield is comparable with its absorption spectrum (Figures 1, 3). Even after an irradiation time of 6 h the photocatalyst was deactivated only to a minor extent, since the degradation rate decreased only by 10% when the photocatalyst was employed in a second experiment. AMM-Ti powders modified with gold(III) choride and rhodium(III) chloride have similar photocatalytic properties.

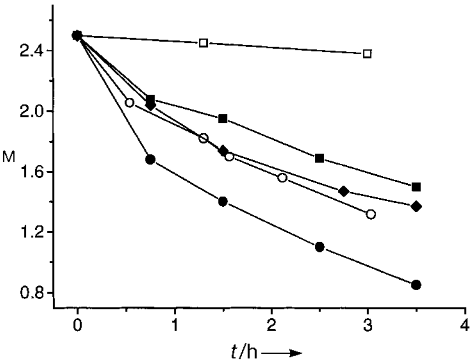


Figure 2. The decrease in 4-chlorophenol concentration ($c_0 = 2.5 \times 10^{-4}$ M) upon irradiation of an aqueous suspension (0.5 gL^{-1}) of the semiconductor powder with visible light (Osram XBO 150-W xenon lamp, cut-off filter $\lambda \geq 455$ nm). □: TiO_2 (Degussa P-25); ■: 0.7% Pt^{IV}/AMM-Ti; ○: 1.1% Pt^{IV}/AMM-Ti, ●: 3.0% Pt^{IV}/AMM-Ti, ◆: 4.0% Pt^{IV}/AMM-Ti.

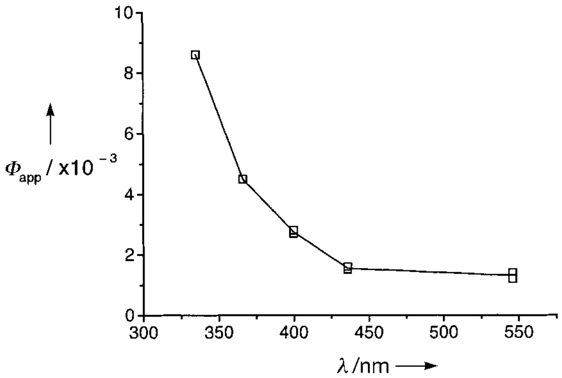
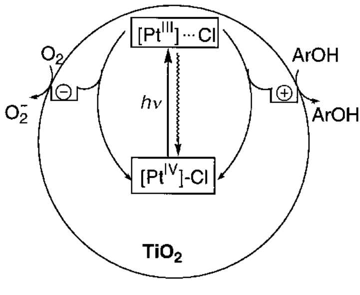


Figure 3. Wavelength dependence of the apparent disappearance quantum yield (Φ_{app}, uncorrected for light scattering) of the degradation of 4-chlorophenol photocatalyzed by **1**.

These results significantly differ from those for metal ion doped crystalline titania samples, which may absorb visible light but do not induce chemical transformations. The highest degradation rates were found when the platinum content in AMM-Ti was 3.0%. Formation of stoichiometric amounts of CO_2 and HCl was demonstrated by gravimetric and acidometric methods.[18] In the absence of air or upon reduction of Pt^{IV} to Pt^0, only negligible degradation was observed.[19] Platinum-free, white AMM-Ti exhibited only a very weak activity, irrespective of excitation in the UV or visible spectral region. The analogously prepared silica AMM-Si doped with 1.1% Pt^{IV} was inactive, while an aqueous solution of $PtCl_4$ induced a stoichiometric degradation.[20]

Both the photoelectrochemical and photochemical results suggest the presence of semiconductor photocatalysis, although a new mechanism of charge generation seems to operate. For a working hypothesis we propose that the titania matrix functions as a charge trap for the electronically excited platinum chloride component (Scheme 1).[21, 22] The thus formed surface redox centers (trapped charges) subsequently induce the multistep degradation of 4-chlorophenol by analogy with crystalline titania.[5, 23] In accordance with this



Scheme 1. Postulated mechanism of the photoinduced charge separation at amorphous, microporous **1**. Ar = 4-ClC_6H_4.

proposal the photocatalytic activity strongly depends on the electronic nature of the amorphous matrix.[20]

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[18] CO_2 as $BaCO_3$, HCl through measuring the pH value before (pH 7) and after irradiation (pH 2.7, after degradation of a 2.5×10^{-3} M solution of 4-chlorophenol).

[19] This is also a basic difference to crystalline TiO_2, the Pt^0 loading of which in general accelerates the rate of a photoreaction.

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[22] From Figure 1 a threshold wavelength of about 500 nm (2.5 eV) is extracted. From that one can estimate that the reactive TiO_2 surface centers are located around 0.7 eV below the conduction and valence band edges, respectively. The potential of Cl/Cl^- is 2.6 V (normal hydrogen electrode): S. D. Malone. J. F. Endicott, *J. Phys. Chem.* **1972**, *76*, 2223.

[23] Superoxide is involved also in the secondary reactions of the radical cation, most likely through hydrogen abstraction by the HO_2 radical formed by its protonation.[5a]

Synthesis, Electrochemistry, and Spectroscopy of Blue Platinum(II) Polyynes and Diynes**

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Conjugated polymers continue to attract great interest because of their potential use as organic semiconductors in optoelectronic devices such as light-emitting diodes,[1] lasers,[2] photocells,[3, 4] and field-effect transistors.[5] Organometallic conjugated polymers such as transition metal σ-acetylide polymers[6] provide information on the photophysical processes that occur in organic conjugated polymers.[7] Organometallic polymers of general formula **A** can be modified by

$$[\text{–M(L)}_n\text{–C}\equiv\text{C–X–C}\equiv\text{C–}]_\infty \qquad \mathbf{A}$$

(M = Fe, Ru, Os, Ni, Pd, Pt; L = phosphane or arsane, X = aromatic spacer)

changing the metal, the auxiliary ligands, or the spacer.[8, 9] Most metal polyyne polymers characterized so far have large band gaps in the range of 2.4–3.2 eV,[8, 10, 11] which compare unfavorably with those of some new conjugated organic polymers (<1 eV).[12, 13] These organic polymers were designed by using the concept[14] of alternating donor (electron-rich thiophene) and acceptor (electron-deficient thieno[3,4-*b*]pyrazine) units. With the aim of preparing a metal polyyne polymer with a band gap smaller than 2 eV, we synthesized a soluble donor–acceptor polymer in which an *n*-butylphosphane-substituted platinum(II) acetylene group acts as donor, and a thieno[3,4-*b*]pyrazine as acceptor.

The synthesis of the thieno[3,4-*b*]pyrazine ligand and of the platinum(II) polymer is summarized in Scheme 1. The compounds dibromo-5,7-diphenyl-2,3-thieno[3,4-*b*]pyrazine (**2**) and diphenyl-2,3-trimethylsilylethynyl-5,7-thieno[3,4-*b*]pyrazine (**3**) were prepared by literature methods.[15, 16] Treatment of **3** with four equivalents of K_2CO_3 afforded 2,3-ethynyl-5,7-thieno[3,4-*b*]pyrazine **4** as a brownish yellow, air- and light-sensitive solid in 75% yield. The polymeric and dimeric

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