Visible Light Induced Degradation of Methylene Blue on Titanium Oxo Ethoxo Clusters of Type $Ti_{16}O_{16}(OEt)_{32}$

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Titanium-oxo-ethoxo cluster, $Ti_{16}O_{16}(OEt)_{32}$ (Ti_{16}-cage) has been used as a nano-building block for advanced materials. Photocatalytic application may also be possible due to its molecular structure consisting of an inorganic titanium oxide core. However, the Ti_{16}-cage is too unstable to examine its photocatalytic properties under atmospheric conditions. Herein it is shown for the first time that the aforementioned Ti_{16}-cage is capable of/can be used for the degradation of organic dyes under visible light irradiation. A possible mechanism of this photocatalytic reaction is proposed.

Key Words: Photocatalysis, Ti-cage, Titanium oxo ethoxo cluster, $Ti_{16}O_{16}(OEt)_{32}$.

INTRODUCTION

Titania-based materials exhibit a number of interesting and potentially valuable photo-induced properties when illuminated with light below 370 nm[1,2]. It is desirable to produce completely new materials and/or modify the existing ones so that they can be activated by the visible portion of the solar spectrum or by ambient light within buildings. The development of solar powered photo-activated materials would have a major impact on future applications, such as catalysis, electrocatalysis, photochromism and superhydrophilicity.

An attractive strategy for creating visible light active photocatalysts is the controlled synthesis of doped, photoactive titania-based materials. Doping TiO_2 with low levels of main group elements results in a red-shift of its absorption spectrum and detectable activity under visible light, which is still not sufficient for practical applications. Fundamental questions about the mechanisms of the reactions still remain unanswered.

The synthesis of entirely new forms of titanium/oxygen materials with well-controlled composition and unusual structures provides a good starting point. Hybrid organic-inorganic materials are promising compounds[3,4]. Numerous hybrid organic-inorganic materials have been developed, mainly by taking advantage of the mild chemical conditions of the sol-gel process[5,6]. Existing hybrid materials, such as $Ti_{16}O_{16}(OEt)_{32}$, with good photostability and a very fast photochromic response have been reported[7]. However, such materials have never been explored with respect to their photoinduced catalytic activity.

Additionally, such hybrid monomers could be used as single-source precursors for the photo-functionalization of surfaces by covalent tethering and deposition of visible light-active nanoparticles, low dimensional structures and thin films of doped titania-like materials, in which the composition and nanoscopic structure can be varied in a controlled way.

The study of the titanium oxo ethoxo cluster $[Ti_{16}O_{16}(OEt)_{32}]$ as a well-defined nano-building block has been reported[7]. Due to its limited dimensionality and structural variability (Ti coordination varies between 4 and 6), the associated electronic structure and electron/hole migration, recombination rates are likely to be very different from those of bulk TiO_2 (Fig. 1). The study is an unprecedented approach to the visible light activated hybrid organic-inorganic materials. Both doped and un-doped $Ti_{16}O_{16}(OEt)_{32}$ can offer very interesting possibilities as light-harnessing species for the photocatalysis and photoelectrocatalysis of a range of reactions.

Simple organometallic and coordination complexes have found many important commercial applications in homogeneous catalysis, where they are highly esteemed due to their high reactivity and selectivity. Properties such as chirality, size and the production of branched or linear products can readily be influenced by ligand design.

In this paper it is proven for the first time that the $Ti_{16}O_{16}(OEt)_{32}$ cluster has a capacity of the colour degradation capability of the solutions of organic dyes under visible light irradiation.
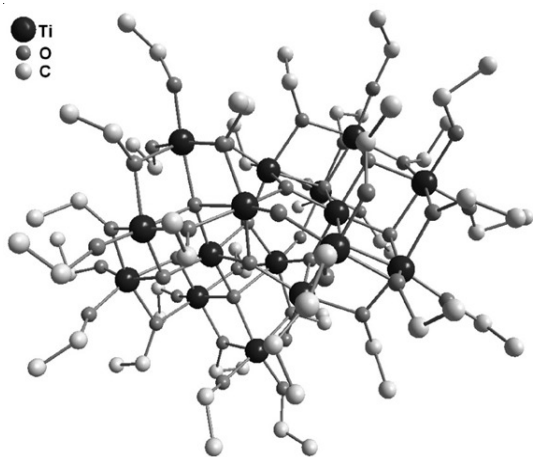
Fig. 1. Structure of the cage [$Ti_{16}O_{16}(OEt)_{32}$] (H-atoms and the disorder in some of the EtO groups are omitted for clarity) taken from ref. 14 and 15

EXPERIMENTAL

Synthesis of the catalyst: The synthesis of $Ti_{16}O_{16}(OEt)_{32}$ was performed following a previously described procedure, which leads to a pure product with > 60 % yield[8-11]. $Ti_{16}O_{16}(OEt)_{32}$ (labeled Ti_{16}-cage) was used as prepared. All solvents were dried by distillation in the presence of 4 Å molecular sieves. Distilled water and ethanol were previously degassed by bubbling with nitrogen over 24 h. Methylene blue ($C_{16}H_{18}N_3SCl$, λ_{max} = 660 nm) was obtained from Aldrich. The dye was used without further purification.

Air had a dramatic effect on the solubility of the Ti_{16}-cage. Once the Ti_{16}-cage was exposed to air, it became insoluble in water. All samples were prepared under anaerobic condition. The choice of solvent can have a dramatic effect on the stability and reactivity of the Ti_{16}-cage. Several organic solvents were tested as a solvent for the Ti_{16}-cage, which is highly insoluble in water. An appropriate solvent should have the following properties: it must be inert to the material under investigation and transparent in the desired wavelength region. Toluene and ethanol were employed as useful solvents for the Ti_{16}-cage and methylene blue, respectively. It was reported that the Ti_{16}-cage is stable in toluene and ethanol[11]. A block of the Ti_{16}-cage without grinding showed very low solubility. Therefore, ground Ti_{16}-cage was prepared under inert conditions and placed in Schlenk tubes. The solvent of interest was transferred to the Schlenk tube by syringe. The dry solvent was added until the Ti_{16}-cage sample completely dissolved.

Characterization: Titanium oxo ethoxo clusters, Ti_{16}-cage, have not previously been tested for photocatalytic activity. In this study, a simple test method for the photocatalytic degradation[12] of methylene blue under visible light was investigated.

Methylene blue (MB) was employed as a reagent to investigate the photocatalytic capacity of the Ti_{16}-cage. A methylene blue-ethanol solution (1.0×10^{-5} mg/L) was freshly prepared for each photocatalytic study. The effective volume of the photoreactor cuvette (4.0 cmL × 1.0 cm W × 1.0 cm H) was approximately 3 mL. The prepared samples were then placed inside the box and irradiated while constant magnetic stirring was applied.

The experiments were performed at 25-26 ºC regulated by an electric fan. The reactant solution in the transparent quartz cuvettes was stirred magnetically.

Ti_{16}-cage-toluene solution (5.0×10^{-3} g/mL) and methylene blue-ethanol solution (1.0×10^{-5} g/mL) were prepared under inert conditions, with care being taken not to expose them to light for longer than necessary. The cuvettes were cleaned for 0.5 min in an ultrasonic bath (sonomatic 2800) with ethanol, washed with distilled water and dried in an oven at 90 ºC for 1 h. Subsequently, they were sealed with a rubber septum and saturated with nitrogen gas. Each solution (1.5 mL each) was transferred to the quartz cuvette (3 mL) *via* syringe and magnetically stirred before and during irradiation.

The control experiment without Ti_{16}-cage was conducted under the same reaction conditions. Distilled toluene and methylene blue-ethanol solution (1.5 mL each) were transferred to a quartz cuvette, which was saturated with nitrogen gas. The reactant solution was irradiated under anaerobic conditions by the same light source.

The reactant solution was illuminated with visible light (≥ 420 nm) from a 1 kW Xe lamp. For the analysis of the samples a Varian UV-VIS spectrometer 4000 and a Philips PW1820 X-ray powder diffractometer with copper radiation (CuK_α) source were used.

RESULTS AND DISCUSSION

According to UV-VIS diffuse reflectance absorption spectra, the Ti_{16}-cage absorbs mostly in the UV spectral region as shown in Fig. 2. The photoexcitation threshold of the Ti_{16}-cage can be estimated from plots of the square root of Kubelka Munk functions F(R) *versus* photon energy[13]. This procedure yields a value of approximately 3.2 eV.
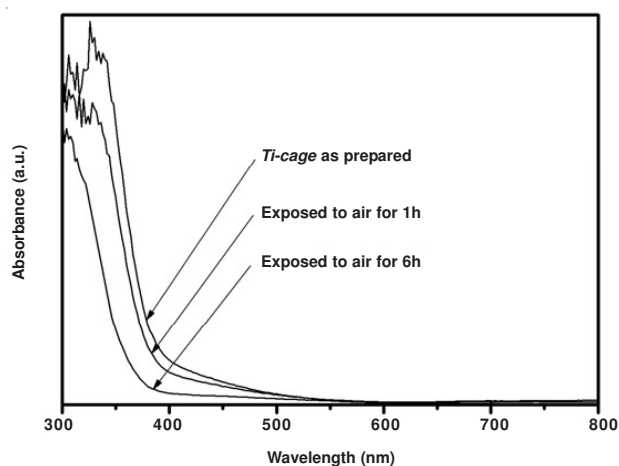

Fig. 2. *in situ* UV-VIS absorbance spectra of Ti_{16}-cage powders as prepared and exposed to air for different times.

The spectrum of Ti_{16}-cage powder, as prepared, reveals the absorption shoulder at 400 - 520 nm, which is characteristic of a material that may be photocatalytically active under visible light. This absorption shoulder is similar to that observed in our previously reported anion-doped titania[16-18]. However, upon exposure to air, the absorption shoulder of the Ti_{16}-cage disappeared and the spectra shifted to shorter wavelengths as

a function of time. This implies that atmospheric moisture/oxygen rapidly reacts with Ti_{16}-cage powder.

As shown in Fig. 3, *in situ* XRD patterns of the air- and moisture-sensitive Ti_{16}-cage powder were taken as soon as prepared in the glove box. The XRD patterns of Ti_{16}-cage powder as prepared shows a peak occurring at 7°, which is reported in literature[11]. On the other hand, the intensity of the XRD peaks for the sample exposed to air decreased as time went on and disappeared after 64 h. From the absorption spectra and XRD patterns, it is clear that atmospheric moisture (or oxygen) reacts with the Ti_{16}-cage, possibly forming a material similar to amorphous titania.
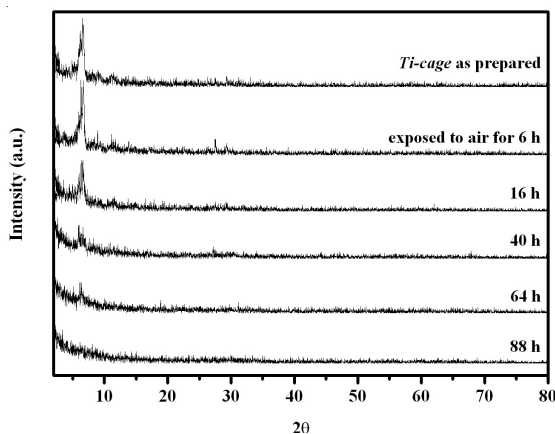

Fig. 3.   *in situ* XRD patterns of Ti_{16}-cage powders as prepared and exposed to air for different times.

Methylene blue was employed as a reagent to investigate the photocatalytic activity of the Ti_{16}-cage. The reactant solution was illuminated with visible light (= 420 nm) from a 1 kW Xe lamp. Upon irradiation of the Ti_{16}-cage-methylene blue solution, the initial blue colour (absorption peak at 660 nm) was seen to bleach and to shift to shorter wavelengths slowly. The blue colour completely disappeared after 1 h as shown in Fig. 4 (blank circles). During illumination, the absorption maximum of the solution exhibited a gradual hypsochromic spectral shift from 660 to 611 nm[19]. The rate of disappearance of the blue colour was a bit slower than that of methylene blue solution without the Ti_{16}-cage (blank squares).
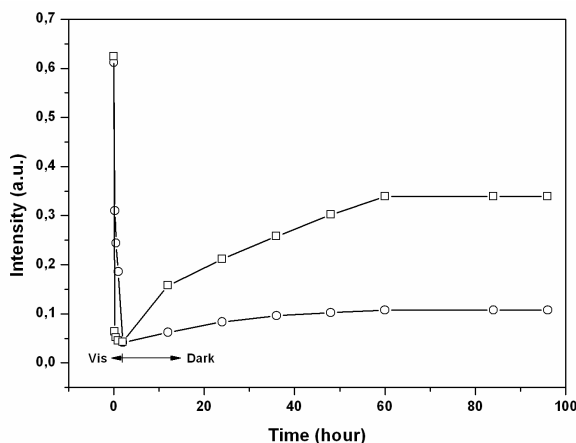

Fig. 4.   Photobleaching and recovery profiles of methylene blue solution with Ti_{16}-cage (blank circles) and without Ti_{16}-cage (blank squares) under visible light and dark conditions

When left in the dark subsequently, the re-colouration of both solutions was observed, which was associated with the re-appearance of the absorption band of the methylene blue dimer (MBD) at 610 nm. The re-colouration of both solutions stopped after 60 h in the dark. In case of the Ti_{16}-cage-methylene blue solution, *ca.* 60 % of methylene blue was irreversibly bleached by the photocatalytic reaction and *ca.* 40 % of methylene blue was regenerated as methylene blue dimer in the dark. However, in the case of the methylene blue solution, *ca.* 10 % of methylene blue was irreversibly photo-bleached naturally and *ca.* 90 % of methylene blue was regenerated as methylene blue dimer in the dark.

Unfortunately, little is known about such photocatalytic reactions in organic solvents under anaerobic conditions. A possible mechanism is illustrated in Fig. 5. Ti_{16}-cage is excited by visible light irradiation. When an alcohol is used as an sacrificial electron donor, the sacrificial electron donor scavenges holes in the occupied states, thereby decreasing the recombination rate of the photogenerated electron and hole. It is suggested that the photogenerated hole in the occupied states of an excited Ti_{16}-cage can cause oxidation of an alcohol to a corresponding radical, which can decompose methylene blue[20].
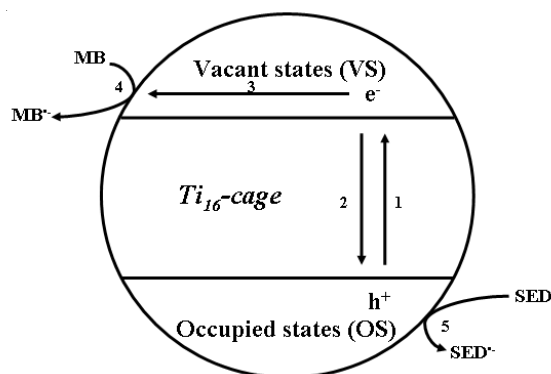

Fig. 5.   A possible reaction mechanism of photocatalytic reactions in organic solvent (the numbers represents the primary electronic pathways in the reaction): (1) excitation of Ti_{16}-cage; (2) recombination of electrons in the Ti_{16}-cage*; (3) electron migration within the lattice to the surface; (4) electron transfer to methylene blue (MB); (5) Ti_{16}-cage regeneration by sacrificial electron donors (SED) and/or oxidation of an SED by the photogenerated hole

While the vacant states act as a mediator for transferring the excited electrons to the methylene blue dye adsorbed on the Ti_{16}-cage surface, the occupied states might be regenerated by the sacrificial electron donor. If an electron transfer does take place from the excited adsorbed methylene blue to the semiconductor-like substrate, the methylene blue should, at least momentarily, be converted to a radical cation by this process. Methylene blue serves as both a sensitizer and a substrate to be degraded. After the illumination, remaining methylene blue radicals recombine to methylene blue dimer in the dark. Since the photoinduced electron injection gradually depletes the active sensitiser molecules on the surface of the Ti_{16}-cage, sacrificial electron donors regenerate the sensitizer[19,21,22].

Another possible scenario is the flow of electrons to the vacant states of the Ti_{16}-cage from sacrificial electron donor, *i.e.*, ethanol, rather than methylene blue. When electrons are injected from the sacrificial electron donor to the vacant states

of the Ti_{16}-cage, the sacrificial electron donor (SED) is oxidized to sacrificial electron donor (SED^+/SED^{2+}). The sacrificial electron donor radical cations are unstable and decompose methylene blue and methylene blue dimer. When the visible light is turned off, the blue colour of the remaining methylene blue dimer slowly returns.

The re-colouration of the methylene blue solution was detected at a blue-shifted position as the colourless solution was left in the dark. An aqueous solution of methylene blue is stable to visible light photoexcitation upon exposure to radiation with its absorption band[23]. However, little is known about the photochemical behaviour of methylene blue molecules in organic solvents.

The doubly reduced form of methylene blue, leuco-methylene blue is colourless[24,25]. The rapid reduction of methylene blue (blue colour) to leuco-methylene blue (colourless) by an electron donor (ethanol) and an electron scavenger (toluene) upon irradiation of the system under anaerobic condition might be a possible explanation for the aforementioned loss of blue colour. Subsequently the blue colour comes back slowly in the dark. A new absorption maximum appears at 638 nm, which is an example for metachromasy.

The UV-VIS absorption spectra of solutions usually depend on the nature of the solvent. The wavelength of the observed UV-VIS peaks often depends on the solution's concentration as well as on the nature of the matrix to whose surface the dye is absorbed. If the molar absorption coefficients plotted against the wavelength, for any molecular species dissolved in a given solvent, yields a curve which is independent of the concentration of the solute, such a substance is said to obey the Beer-Lambert's law. However, the majority of organic dyes does not obey the Beer-Lambert's law, the discrepancy varying within wide limits among various dyes. Like the majority of organic dyes, the UV-VIS absorption characteristics of methylene blue significantly deviate from the Beer-Lambert's law. It is generally agreed that this deviation is due to a reversible formation of dye polymers, which are bound together by dispersion forces originating from the delocalized electrons of the individual dye molecules. The polymers exhibit an absorption spectrum different to that of the monomers[26,27].

Wotherspoon *et al.*[23] found a visible light induced spectral shift of thiazine dyes such as methylene blue. The absorption bands of the thiazine dyes were shifted to shorter wavelengths upon irradiation in the presence of polymethacrylic acid (PMA). The highly specific observation indicates that polymethacrylic acid could serve as a substrate for a special type of dye binding. Metachromasy of methylene blue in alcoholic solvents was reported in 1945[27]. In this study, toluene and ethanol can serve as substrates for a type of dye binding, thus explaining the observed shift.

Although the nature of the attractive forces ensuing in molecular aggregation seems understandable in a general, qualitative manner, no satisfactory quantitative theory has been established. A suggestion for a possible mechanism is illustrated in Fig. 6.

It is hypothesized that methylene blue reaches a singlet electronic excited state by illumination. Excited states are considerably stronger electron acceptors. In this case, a sacri-

ficial electron donor can easily participate in electron transfer processes. The sacrificial electron donor transfers electrons to methylene blue* and generates sacrificial electron donor (SED^{2+}). Methylene blue* is subsequently converted to leuco-methylene blue* (colourless). The toluene plays an important role in scavenging photogenerated electrons from methylene blue*/leuco-methylene blue*, thus reducing bleaching time. The methyl group increases the electron density in the π system of the benzene ring, especially in the *ortho* and *para* positions. Photogenerated electrons are transferred to the p system through the *meta* position and remain there. Toluene*, leuco-methylene blue and sacrificial electron donors (SED^{2+}) aggregate by dispersion forces originating from the delocalized electrons of the individual molecules. In the absence of light, the process are reversible. Sacrificial electron donors (SED^{2+}) are slowly converted back to sacrificial electron donor in the dark, but methylene blue aggregation remains, which results in a blue shift of the initial absorbance. The yield of methylene blue aggregation was estimated to be nearly 100 %[19].
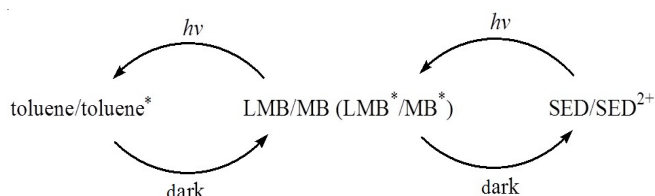

Fig. 6.   A possible reaction mechanism of methylene blue (MB) bleaching in organic solvents such as toluene.

The structure of the Ti_{16}-cage (metallic oxo core) is rigid due to the highly polar oxo-bridges between the titanium atoms, but the ethoxy groups present at the molecular surface are labile [6,7,11]. The rapid formation of a white precipitate, *i.e.*, TiO_2, may occur if there is any cluster fragmentation or decomposition, followed by homogeneous catalysis. However no precipitates were detected during and after the observed photocatalytic reaction.

Conclusion

Ti_{16}-cage has not, to date, been tested for photocatalytic activity. Photosensitized degradation of an organic dye has been carried out with the Ti_{16}-cage as a photocatalyst under visible light irradiation, where the organic dye served as both a sensitizer and the substrate to be degraded. It was thus proved for the first time that Ti_{16}-cage has the capacity for the colour degradation of solutions of organic dyes under visible light irradiation. It is believed that the colour degradation capability of Ti_{16}-cage was due to the fact that the visible light could excite the dye molecules adsorbed on the Ti_{16}-cage, followed by a series of photosensitizing reactions with a sacrificial electron donor.

It is inherently difficult to determine the mechanism of the described photocatalytic reaction because of the great number of possibilities. However, oxo-alkoxo-clusters of titanium such as the Ti_{16}-cage show potential as a new class of photocatalytic precursor. This new material is inexpensive and can reproducibly be synthesized.

ACKNOWLEDGEMENTS

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