Highlighting the research of Dr. Andraž Šuligoj, Prof. Dr. Urška Lavrenčič Štangar, Prof. Dr. Nataša Novak Tušar and coauthors from Slovenian research institutions, the National Institute of Chemistry, the University of Ljubljana, the Jožef Stefan Institute and the University of Nova Gorica, as well as of Prof. Dr. Pegie Cool from the University of Antwerp in Belgium.

Surface modified titanium dioxide using transition metals: nickel as a winning transition metal for solar light photocatalysis

Ni and Zn provide a winning combination of redox potential and band gap position for TiO₂ supported metal-oxo-nanoclusters with enhanced solar-light activity. However, Ni is the only metal, which has a positive effect on solar photoactivity in both oxidation and reduction reactions.
Surface modified titanium dioxide using transition metals: nickel as a winning transition metal for solar light photocatalysis†

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Titanium dioxide has been widely used as an antimicrobial agent, UV-filter and catalyst for pollution abatement. Herein, surface modifications with selected transition metals (Me) over colloidal TiO2 nanoparticles and immobilization with a colloidal SiO2 binder as composite films (MeTiO2/SiO2) on a glass carrier were used to enhance solar-light photoactivity. Colloidal TiO2 nanoparticles were modified by loading selected transition metals (Me = Mn, Fe, Co, Ni, Cu, and Zn) in the form of chlorides on their surface. They were present primarily as oxo-nanoclusters and a portion as metal oxides. The structural characteristics of bare TiO2 were preserved up to an optimal metal loading of 0.5 wt%. We have shown in situ that metal-oxo-nanoclusters with a redox potential close to that of O2/O2− were able to function as co-catalysts on the TiO2 surface which was excited by solar-light irradiation. The materials were tested for photocatalytic activity by two opposite methods; one detecting O2− (reduction, Rz ink test) while the other detecting *OH (oxidation, terephthalic acid test). It was shown that the enhancement of the solar-light activity of TiO2 by the deposition of transition metal oxo-nanoclusters on the surface depends strongly on the combination of the reduction potential of such species and appropriate band positions of their oxides. The latter prevented excessive self-recombination of the photogenerated charge carriers by the nanoclusters in Ni and Zn modification, which was probably the case in other metal modifications. Overall, only Ni modification had a positive effect on solar photoactivity in both oxidation and reduction reactions.

1. Introduction

Titanium dioxide (TiO2) is widely used as a photocatalyst for both water and air depollution as well as in self-cleaning surfaces and sensor technology. However, due to its band gap of 3.2 eV it is only able to absorb UV light, i.e. λ ≤ 390 nm, thus limiting its activity under solar light. To overcome this problem, several strategies can be used: (i) doping of the TiO2 bulk to extend the absorption edge or (ii) TiO2 surface modification, to employ surface–interface charge transfer (IFCT). The latter, with the use of transition metals coated on the surface of TiO2, was proposed1 to enhance electron–hole separation, while, in addition, the metal ion clusters located on the surface of TiO2 also serve as co-catalysts being able to be reduced by the electrons from the conduction band of TiO2 and later on to be involved in the production of superoxide anions (O2−). The surface of titania commonly exhibits coverage with titanol (Ti–OH) groups which with their electron donor capability offer a good surface for modification with positively charged transition metal ions. Different transition metals have already been applied as surface nanoclusters such as Cu(II),2 Fe(III),2 and Zn(II).3 Cu(II)-1,3,4 and Fe(III)-surface2 modified TiO2 have been well described in air cleaning photoreactor set-ups. Increased photocatalytic activity under solar irradiation was ascribed to IFCT from EVB (TiO2) to metal nanoclusters on the surface with the subsequent formation of O2− radicals via eqn (1). These then help the photocatalytic process in addition to hydroxyl radicals (·OH) and/or holes (h+) themselves.
\[
O_2 + e^- \rightarrow O_2^{2-} \tag{1}
\]
\[
2O_2^{2-} + 2H_2O \rightarrow \cdotOH + OH^- + O_2 \tag{2}
\]

Yet, in a liquid system dye degrading Cu\(^{2+}\) surface sites showed a general trend of decreasing the photoactivity of TiO\(_2\) due to the thermodynamically favourable transition of \(e^-\) and \(h^+\) to the band edges of CuO which are bracketed by those of TiO\(_2\) and hence higher recombination is promoted.\(^3\) A positive effect of small additions of copper (0.1 wt\%) for phenol degradation was also found\(^4\) and was explained by the transfer of \(e^-\) from CuO to TiO\(_2\) via Ti–O–Cu bonds, with the addition of particles being smaller and having a higher number of surface OH groups. Thus, it remains unclear why surface modification of TiO\(_2\) with some transition metals shows improvement with other, this is not the case.

Additionally, photoreactivities are commonly measured in air photoreactors towards air-borne alcohols, in oxygen rich atmospheres, which facilitates the above-described mechanism (eqn [1]).\(^1\) However, one should notice that active oxygen species are significantly less reactive compared to hydroxyl radicals, \(i.e.\) their reduction potential at pH 7 is 0.94 V while for \(\cdotOH\) this value is more than doubled, 2.34 V.\(^1\) The contribution of \(O_2^{2-}\) to the activity of catalysts should hence be far less than that of \(\cdotOH\). However, \(\cdotOH\) can be generated from \(O_2^{2-}\), where the additional restraint is the presence of water (eqn [2]).\(^1\) However, more experiments are needed to elucidate the role of \(O_2\) presence in the reaction mixture, be it in air or in aqueous environments.

Also, more research should be done in the field of immobilised catalysts in the form of films on carriers such as metal, glass, paper, cellulose fibres, etc. if we are to increase the number of commercial applications of such materials on a large scale.\(^7\) Titania catalysts in the form of films with a high surface area have not been used in such kinds of studies, supposedly having too small nanoparticles for enough metal clusters to be formed on them, which represents another gap in the experimental data reported.

Titania in combination with porous silica (TiO\(_2\)/SiO\(_2\)) with a large surface area was studied in our previous work.\(^8\) Here, we report the fundamental reasons for the improvement of solar light activity to be the suitable band positions of metals (Me) which are deposited on the surface of colloidal TiO\(_2\) and immobilised with colloidal SiO\(_2\) as films on a glass carrier (MeTiO\(_2\)/SiO\(_2\)). Colloidal titania was decorated with selected transition metals spanning from manganese to zinc due to their ability to accept/release electrons and the different positions of their valence (\(E_{\text{VB}}\)) and conduction bands (\(E_{\text{CB}}\)). This enabled discussion on the electronic nature of surface nanocluster mechanisms which elucidated the reasons for increased solar-light activity while immobilisation on the soda-lime glass by using colloidal SiO\(_2\) enabled comparison of optical properties of the same samples which were then used in reactions. Two different reaction pathways were used to provide a general assessment of the solar-light activity of the catalysts. First, the \(O_2^{2-}\) radicals, and consequently the reduction activity, of the modified TiO\(_2\) surface were assessed in the test with Resazurin ink, while the direct formation of \(\cdotOH\) (oxidation) was monitored via oxidation of terephthalic acid.

## 2. Experimental

Unless stated otherwise all chemicals were used as purchased: tetraethyl orthosilicate (TEOS, 98%) from Acros Organics; acidic TiO\(_2\) colloidal suspension CCA 100 AS from Cinkarna company (Slovenia); P-25 TiO\(_2\) powder from Evonik Degussa; terephthalic acid (TPA) from Alfa Aesar; hydrochloric acid (37%) and 2-propanol from Carlo Erba; hydroxethyl cellulose (HEC) from Fluka; ethanol (96%) from Itrij; Levadol 200/30% from Obermeier; 1-propanol from Sigma-Aldrich; and NaN\(_2\) from WWR. Glycerol (99.5%, Sigma-Aldrich) and hydroxethyl cellulose (Fluka) were used for the preparation of the Rz ink. Resazurin (dye content ~92%) was supplied by Sigma-Aldrich. FeCl\(_3\)-6H\(_2\)O, NiCl\(_2\)-6H\(_2\)O and ZnCl\(_2\) were purchased from SigmaAldrich, MnCl\(_2\)-4H\(_2\)O from Riedel-de Haen, and CuCl\(_2\) and CoCl\(_2\)-6H\(_2\)O from Merck.

### 2.1 Photocatalyst preparation

The modification of the surface of TiO\(_2\) was done according to a modified process, described previously.\(^9\) Namely, to the acidic CCA 100 AS colloidal TiO\(_2\) suspension (pH = 1.1, 20 mL) an appropriate amount of metal chloride (hydrate) was added in order to obtain a metal loading (m/m) of 0.05, 0.075, 0.1, 0.5, 2, 5, 7.5 and 10% (MeTiO\(_2\)). Metal chlorides were chosen instead of nitrates, because removal of the latter requires high temperatures (ca. 300–500 °C), while chlorides can be removed by washing at room temperature. High-temperature post-treatment may cause the favourable formation of metal oxides plus the additional growth of anatase particles which reduces the specific surface area.\(^10\) The suspension was then heated to 90 °C and stirred at this temperature for 1 h in a round flask in order to coat the surface of TiO\(_2\) with metal-oxo-nanoclusters. Importantly, the pH did not rise above 2 during the synthesis, because metal ions are prone to form oxides at higher pH values, which do not enhance the photocatalytic activity remarkably, due to their rigid structure and hence lesser availability to receive and donate electrons. Washing to remove chlorides was done by centrifuging the suspension at 9000 rpm for 2 min. The supernatant was then removed along with Cl\(^-\) ions. The AgNO\(_3\) test was performed and if proven positive, dH\(_2\)O (2 mL) was added followed by centrifugation and decantation. The process was repeated until the AgNO\(_3\) test was negative. Later, EDX analysis was performed on pressed pellets in order to confirm the absence of Cl\(^-\) on the surface of TiO\(_2\). All samples were chlorine-free.

Prior to conducting photocatalytic tests, the catalysts (MeTiO\(_2\)) were immobilised in the form of films on objective glass slides using a colloidal silica binder (MeTiO\(_2\)/SiO\(_2\) composite films). The idea of the so-called glass frit was introduced already in the eighties\(^11\) where the crucial condition for good adhesion is the chemical compatibility of surfaces to be bonded, i.e. glass and a SiO\(_2\) mesh. Hence, at room temperature, TEOS was added to HCl as a catalyst, diluted with
isopropanol (iPrOH) and then left to hydrolyse for 30 min in a molar ratio of TEOS : HCl : iPrOH = 0.075: 0.003 : 1. However, in order to preserve the high permeability of the films, colloidal SiO2 (Levasil 200/30%, 25 nm, 0.15 mol) particles were added to the TEOS silica mesh12,13 and left to mix vigorously overnight. This SiO2 mixture was added to the colloidal MeTiO2 suspension (1.5 M) in a Ti : Si molar ratio of 1 : 1 and mixed vigorously for 5 min. As a reference TiO2 catalyst, the P-25 suspension (1.5 M) was made by suspending 2.4 g P-25 in 10 mL H2O. The composite, made of SiO2 and MeTiO2, was then sonicated in a cold ultrasonic bath for 10 min.

The glass slides were cleaned with ethanol and deionized water. They were then coated with this catalyst suspension using dip coating at a withdrawal speed of 2 cm min\(^{-1}\). Thermal stabilisation of the films was done at 150 °C for 1 h (ED 23, Binder). The process was then repeated 8–12 times to achieve a surface density of 1 mg cm\(^{-2}\). Thermal treatments at higher temperatures (e.g. 500 °C) were not conducted as this may cause a decrease in the surface area due to sintering, to avoid the detrimental diffusion of sodium ions from the glass support at higher temperatures14 and to minimise the environmental impact.

### 2.2 Characterization

All physicochemical characterizations were conducted on metal modified TiO2 samples, which were immobilised on a glass carrier using a silica binder (SiO2 50 mol%), which generally preserved structural properties. It should be noted here that silica addition caused the “dilution” of the active TiO2 component, which after this constituted 50 mol%. However, two measurements were conducted on modified TiO2 only, i.e. without the addition of SiO2: (i) isoelectric point measurements to better pinpoint the differences between the samples and (ii) X-ray absorption spectroscopy measurements (XAS) due to the sensitivity of the method with which 0.5 wt% of the investigated metal vs. TiO2 in the sample is just enough to observe the impact.

X-Ray diffraction (XRD) patterns were recorded on a PANalytical X’Pert PRO high-resolution diffractometer using CuK\(_\alpha\) radiation (1.5406 Å) in the 2θ range from 5 to 60° (100 s per step of 0.034°) using a fully opened X’Celerator detector.

The elemental composition was determined by the energy-dispersive X-ray (EDX) analysis with an INCA Energy system attached to a Zeiss Supra 3 VP field emission gun (FEG) microscope, operating at 20 kV.

Isoelectric points were determined using a Zetasizer nano ZS instrument (Malvern) with electrophoretic light scattering technology in the pH range of 2–12 adjusted by the addition of either 0.1 M NaOH or 0.1 M HCl and measured using a digital pH meter (Mettler Toledo).

Nitrogen adsorption measurements were done at 77 K on a Tristar 3000 Micromeritics volumetric adsorption analyser. Before the adsorption analysis, the samples were outgassed under vacuum for 2 h at 473 K in the port of the adsorption analyser. The BET specific surface area\(^{15}\) was calculated from the adsorption data in the relative pressure range from 0.05 to 0.25. The total pore volume was estimated on the basis of the amount adsorbed at a relative pressure of 0.97.\(^{16}\) The pore size distributions (PSDs) were calculated from the nitrogen adsorption data using a BJH algorithm based on the ideas of Barrett et al.\(^{17}\) The maxima on the PSD are considered as the primary mesopore diameters of the given samples.

Diffuse reflectance and transmittance UV-VIS spectra were measured using a UV-VIS spectrophotometer equipped with an integrating sphere (LAMBDA 650 UV/Vis with a 150 mm integrating sphere, Perkin Elmer, USA). Indirect band-gap energies were determined by plotting the Kubelka–Munk transformation of the original diffuse reflectance spectra vs. photon energy.\(^{18}\)

Transmission electron microscopy (TEM) was performed on a 200 kV field emission gun (FEG) microscope (JEOL JEM 2100). For ARM 200 CF studies a drop of an ethanol diluted nanoparticle solution was placed on a copper grid and dried at room temperature. The specimens were additionally coated with carbon in order to prevent excessive charging and decomposition of the sample under the electron beam (80 kV).

A conventional continuous wave (cw) electron paramagnetic resonance spectrometer operating at a Larmor frequency \(\nu_{L} = 9.6\) GHz was employed to detect the electron spin resonance. The spectrometer is equipped with a standard Varian E-101 microwave bridge, a Varian rectangular TE102 resonance cavity, and an Oxford Cryogenics continuous-flow helium cryostat. Prior to analysis the samples were annealed at 120 °C overnight.

### 2.3 Photocatalytic activity

The direct formation of ·OH (TPA test) was carried out by a method of oxidation of terephthalic acid (TPA) to hydroxy-terephthalic acid (HTPA) (Fig. 1) as described elsewhere.\(^ {19}\) The tests were done in a UV/Vis photo chamber reactor equipped with 2 LUMILUX L 15W/840 CoolWhite 590 × 38 mm (Osram) solar light lamps. The samples were first preirradiated for 2 h under UVA light. Briefly, a solution of sodium terephthalate was prepared by mixing together TPA (500 mg) and an aqueous solution of NaOH (31 mL, 0.201 M), followed by dilution with ethanol to obtain 50 mL of the TPA solution. Separately, an aqueous solution of HEC (2 wt%, 10 mL) was mixed with ethanol (96%, 30 mL). The final solution was obtained by mixing TPA solution (10 mL) with HEC solution (20 mL). The films of TPA were deposited onto photocatalytic films at 22 °C using a dip-coater with a pulling speed of 10 cm min\(^{-1}\). The films were dried using a hair dryer immediately after the deposition of the film. The kinetics of ·OH formation was calculated using

\[
\frac{d[HTPA]}{dt} = k_1 - k_2[HTPA],
\]

where by solving the differential equation one obtains \([HTPA] = k_1/k_2(1 - e^{-k_2t})\). Measurements of fluorescence (excitation @320 nm and emission @430 nm) using a microplate reader (Infinite F200, Tecan, Switzerland) were used for quantification.

The second photocatalytic assessment was performed by following the reduction of Rz ink to Resorufin (Fig. 1a).\(^ {20}\) The
dye is reduced by photogenerated electrons, while holes oxidise the sacrificial electron donor, i.e., glycerol and thus do not interfere with the reaction; hence this test directly follows reduction by e\(^-\) since oxygen is not directly present in the reaction. In heterogeneous photocatalysis the rate (proportional to \(k_{\text{app}}\)) of the process is dependent on the radiant flux (\(I\)). \(\theta\) is a constant with a value of usually 0.5 under high-intensity conditions where recombination dominates or 1.0 under low-intensity conditions where surface reactions dominate.\(^{21}\) An excess of glycerol ensures electron–hole recombination is not the dominant process, thus ensuring \(\theta \rightarrow 1\). Briefly, to HEC (1.5 wt%), 20 g) glycerol (2 g) was added. Resazurin (20 mg) and Tween 20 (20 mg) were then added and mixed overnight to completely dissolve the dye. The ink (50 \(\mu\)L) was applied on the films, preirradiated for 2 h under UVA light by a doctor blade method. 3 M tape (Scotch\(^\circ\)) was taped on the two sides of the films, preirradiated for 2 h under UVA light by a doctor blade method. This part of the spectrum is responsible for the generation of holes with high oxidation power, which oxidise adsorbed hydroxyls or water to form °OH which is then detected as fluorescent HTPA. In this way, nanoclusters impede the electron–hole recombination. By using a UV-cutoff filter (Fig. S6\(^\dagger\)) it was shown that this (h\(^+\) oxidation via UV-illumination) is the major pathway for TPA oxidation, which is in agreement with other authors.\(^{29}\)

### 3.1 Photocatalytic activity towards oxidation

The photocatalytic formation of °OH measured via HTPA formation for TiO2 with a modified surface is shown in Fig. 2. It was shown before\(^{24}\) that reactions that are not specific, e.g. dye degradation, can show even higher improvement of degradation rates for similar modification of the TiO2 surface. The photocatalyst approach is focused on the generation of oxygen radicals on the active sites located on the surface of metal clusters (eqn (1)), while to generate °OH radicals further steps are needed (eqn (2)). However, since the lamps in the tests were simulating solar light, they also had a portion of UVA light intensity (Fig. S1\(^\dagger\)). This part of the spectrum is responsible for the generation of holes with high oxidation power, which oxidise adsorbed hydroxyls or water to form °OH which is then detected as fluorescent HTPA. In this way, nanoclusters impede the electron–hole recombination. By using a UV-cutoff filter (Fig. S6\(^\dagger\)) it was shown that this (h\(^+\) oxidation via UV-illumination) is the major pathway for TPA oxidation, which is in agreement with other authors.\(^{29}\)

#### 3.1.1 Dependence on the dopant content

In Fig. 2b and c it can be seen that—in a series of different loadings of metal clusters (Ni and Zn)—lower concentrations, i.e. lower than 2 wt%, show an increase in photocatalytic degradation rates while higher loadings notably decrease the activity. This could be due to the formation of larger clusters at higher loadings and higher shading effect of the TiO2 surface. Also, the larger clusters possess less structural flexibility, and hence are less capable of receiving/losing e\(^-\). Therefore, 0.5% loading was chosen for modifications with other transition metals.

Fig. 2a shows that the solar light activity of colloidal TiO2 (marked with a dashed line) was by itself far better than the activity of the P-25 reference material. Interestingly, 0.5% modifications of the titania surface with Mn, Fe, Co and Cu decreased the activity by 86, 21.7, 58.9, and 63.9%, respectively. On the other hand, modifications with Ni and Zn led to the increase of the photocatalytic rate by 33.6 and 82%, respectively.

### 3.2 Photocatalytic activity towards reduction

In Table 1 the results of the reduction of Rz ink are presented. For this reaction, an optimum metal loading of 0.5 wt% was chosen. The time taken to bleach (ttb) may be estimated by

![Fig. 1 Mechanism of photocatalytically sensitized (a) reduction of Rz ink (blue) to Resorufin (pink) and (b) oxidation of TPA to HTPA (fluorescent). (c) UV/VIS photo chamber reactor which allows UV or visible light illumination – with the red line area under investigation being marked and (d) cross-cut SEM micrograph of the colloidal TiO2 film on glass onto which test molecules from (a) and (b) were loaded.](image)

![Fig. 2 Photocatalytic results of the oxidation of terephthalic acid under visible light irradiation. Activity of the 0.5% modified TiO2 samples with selected transition metals (a) and the dependence of activity on the concentration of metal loading for Ni (b) and Zn (c). For comparison, the activity of P-25 TiO2 immobilized with the same binder is presented. The dashed line represents the activity of unmodified colloidal TiO2. Error bars present the standard error of the mean (N = 3).](image)
Table 1. Measured ttb values for Rz ink reduction using visible light irradiation for different modified photocatalytic films (lower is better). Metal deposition on the surface was 0.5 wt%.

<table>
<thead>
<tr>
<th>Sample (x-TiO₂)</th>
<th>ttb (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal TiO₂</td>
<td>39 ± 2</td>
</tr>
<tr>
<td>P25 TiO₂</td>
<td>141 ± 3</td>
</tr>
<tr>
<td>Mn</td>
<td>34 ± 5</td>
</tr>
<tr>
<td>Fe</td>
<td>46 ± 4.5</td>
</tr>
<tr>
<td>Co</td>
<td>61 ± 3.5</td>
</tr>
<tr>
<td>Ni</td>
<td>30 ± 4</td>
</tr>
<tr>
<td>Cu</td>
<td>53 ± 0.3</td>
</tr>
<tr>
<td>Zn</td>
<td>53 ± 1</td>
</tr>
</tbody>
</table>

Table 2. Lattice parameters and the crystallite size of bare TiO₂ and titania with a decorated surface obtained by Rietveld refinement. Numbers in brackets indicate an error of the last decimal place. x in x-TiO₂ denotes the metal which was used for 0.5 wt% modification on the surface.

<table>
<thead>
<tr>
<th>Sample (x-TiO₂)</th>
<th>a = b (Å)</th>
<th>c (Å)</th>
<th>Cell volume (Å³)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal TiO₂</td>
<td>3.803(5)</td>
<td>9.51(3)</td>
<td>137.5(9)</td>
<td>8(1)</td>
</tr>
<tr>
<td>Mn</td>
<td>3.811(2)</td>
<td>9.550(5)</td>
<td>138.7(1)</td>
<td>13(1)</td>
</tr>
<tr>
<td>Fe</td>
<td>3.798(10)</td>
<td>9.51(3)</td>
<td>137.2(8)</td>
<td>10.0(9)</td>
</tr>
<tr>
<td>Ni</td>
<td>3.800(9)</td>
<td>9.52(2)</td>
<td>137.5(8)</td>
<td>8(1)</td>
</tr>
<tr>
<td>Cu</td>
<td>3.806(8)</td>
<td>9.51(2)</td>
<td>137.5(8)</td>
<td>8(1)</td>
</tr>
<tr>
<td>Co</td>
<td>3.802(12)</td>
<td>9.52(3)</td>
<td>137.7(10)</td>
<td>9(1)</td>
</tr>
<tr>
<td>Zn</td>
<td>3.801(1)</td>
<td>9.519(4)</td>
<td>137.5(1)</td>
<td>9(3)</td>
</tr>
</tbody>
</table>

Fig. 3 XRD patterns of (A) TiO₂ nanoparticles modified with metal-oxo-nanoclusters at 0.5 wt% loading, and patterns of TiO₂ particles modified with (B) Ni and (C) Zn nanoclusters.

3.3 Characterization

To rule out that metal ions did not enter the lattice of titanium dioxide, Rietveld refinement of the X-ray diffraction patterns was used to obtain the parameters of the anatase unit cell (Table 2). The results (Fig. 3) showed no major differences among the samples, regardless of the type or weight fraction of the transition metal loaded on the surface of TiO₂. Interestingly, metal oxides were not detected even at higher grafting concentrations; probably due to their sizes being too small. All samples showed peaks at 25.3°, 37.9°, 48° and 54° 2θ, corresponding to the anatase structure (ASTM card #00-021-1272). Surface metal-oxo-nanoclusters did not cause any shift of the diffraction peaks; hence, the synthesis temperature (90 °C) did not cause the diffusion of metal ions into the structure of titania. Also, the lattice parameters are very similar among the samples (Table 2) as well as the crystallite sizes. Instead, the metal species are grafted as nanoclusters on the surface of TiO₂ nanoparticles.

Modifying the surface of small TiO₂ nanoparticles should change the surface area as well as the pore structure and volume due to the occlusion of the micropores. This is clearly seen at higher loadings (higher than 2 wt%) in Fig. 4b and c. The type IV isotherm, which is observed for the parent TiO₂ material and typical for mesoporous adsorbents, gradually changes to type II isotherms, which indicates nonporous or macroporous materials. Also, at higher loadings, the H2 hysteresis loop is visible which indicates the complex pore structure where network
effects are important. Moreover, the gradual decrease in the
desorption curve indicates a broad size distribution of the pore
necks. From these data, we can assume that grafting nano-
clusters onto the surface of TiO₂ at high concentrations
changed the morphology and pore structure of the samples,
where the trend is towards a more plate-like particle
morphology. Also, in general, the complex pore structure in low
loadings is being partially filled, resulting in simpler pore
connectivity.

However, lower loadings (0.05–0.5 wt%) of metal-oxo-
nanoclusters on the surface (Fig. 4a) maintained the H1
adsorption hysteresis, typical for pore channels without
obstructions.²⁵ Hence, the pores were uniform and easily
accessible either by the adsorption or desorption part of the
isotherm; although a decrease in pore size is seen consistently
throughout all grafting metals (Table 3). Also, the relatively
narrow hysteresis implies that the necks of the pores were not
eoggled, confirming the accessibility of the pores. This coin-
cides well with the catalytic activities, which showed the largest
activities at these concentrations (0.5 wt%) as seen in Fig. 2. The
specific surface areas did not differ significantly among
different modifications (Table 3), on the basis of which we can
conclude that pore distribution and surface area are not the
factors influencing the activity.

The ATR FT-IR analysis showed that the bare TiO₂ surface is
more hydroxylated than those which have been modified for all
samples (Fig. S3†) as observed by the intensity of the O–H rs
vibration at 3350 cm⁻¹. This can be ascribed to the higher
number of surface –OH in bare TiO₂, while a partial occupancy
of these sites by metal-oxo-nanoclusters can be expected in
surface modified samples.

Because photocatalysis involves surface reactions, the
surface charge of the catalyst was assessed by measuring the
zeta (ζ) potential (Fig. S2†). The modification of the surface of
titania shifted the isoelectric point to higher values in all
samples (Table 4) due to the presence of positively charged ions
on the surface of titania. Moreover, all oxides of transition
metals used in this study have higher IEPs,²⁶ which contribute to the
observations in ζ-potential measurements. This phenomenon was most significant in modifications with copper
and zinc, which also possess the highest IEP, i.e. 9.5 and 8.8 for
CuO and ZnO, respectively.²⁶ This means that the acid character
is extended to higher pH values, which has a consequence of
less negative potential at neutral pH. In other words, after
modification, the surface became more positive as in bare TiO₂.
Hence, anionic dyes can be adsorbed on the surface at pH closer
to neutral in comparison to bare TiO₂.

This decrease was the most prominent in Ni- and Zn-
modified samples, which implies a more uniform coating of
the surface by small nanoclusters leading to higher shading of
the titanol groups on TiO₂.

Photocatalytic activity can be discussed in terms of the
relative energy of valence and conduction bands (E_{CB} and E_{VB},
respectively). If we know the values of the band gap (E_{g})
and absolute electronegativity of the semiconductor (χ), which
can be determined by the geometric mean of the electronegativities
of constituent atoms,²⁶ E_{CB} can be determined as follows:

\[ E_{VB} = \chi - 4.5 + 0.5 \times E_{g} \tag{3} \]

where −4.5 eV is the Fermi level of the NHE with respect to
the vacuum level. From the DRS measurements (Fig. S5†) the E_{g}
of bare TiO₂ was determined to be 3.31 eV and thus E_{CB} equalled
−7.46 eV. The band gap values of the modified samples differ
only slightly. As a rule, if the band gap depends on the dopant
content in the TiO₂ matrix, it may be attributed to the dopant
introduction in substitutional positions. Here, this is not the
case (Table S2, Fig. S5†) and a gradual increment in Ni-
concentration shifted the absorption edge to higher wave-
lengths non-linearly, again proving that the metals were not
incorporated into the titania framework.

However, since films appeared semi-transparent (i.e. matt),
suggesting partial transmittance of the visible light, light scat-
tering in the visible region is important in terms of maximising
light harvesting. Reflection on non-transparent films (which is
the case in this research) results from scattered and reflected
radiation on macroscopic particles. Thus, the sum of trans-
mittance (T) and reflectance (R) spectra enables the calculation of
the true absorbance (A) of TiO₂ films at a certain wavelength.
It must be emphasised that in this study films which were tested for
diffuse reflectance had identical surface properties in both
experimental set-ups (DRS and photocatalytic tests). This
enables us to directly link optoelectronic properties to their
catalytic performances. In most publications this is not the case

### Table 3 Structural parameters of TiO₂ modified with 0.5 wt% of selected transition metals. The isotherms were recorded for samples which contained 50 mol% SiO₂, and thus real samples which were used also in photocatalytic tests.

<table>
<thead>
<tr>
<th>Sample (x-TiO₂)</th>
<th>S\textsubscript{BET} a (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>V\textsubscript{tot} a (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>Pore size b (nm)</th>
<th>Band gap b (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal TiO₂</td>
<td>299</td>
<td>0.502</td>
<td>8.7</td>
<td>3.31</td>
</tr>
<tr>
<td>Mn</td>
<td>275</td>
<td>0.584</td>
<td>3.8</td>
<td>3.35</td>
</tr>
<tr>
<td>Fe</td>
<td>283</td>
<td>0.628</td>
<td>2.9</td>
<td>3.34</td>
</tr>
<tr>
<td>Co</td>
<td>267</td>
<td>0.567</td>
<td>3.7</td>
<td>3.33</td>
</tr>
<tr>
<td>Ni</td>
<td>269</td>
<td>0.654</td>
<td>3.6</td>
<td>3.29</td>
</tr>
<tr>
<td>Cu</td>
<td>289</td>
<td>0.466</td>
<td>3.6</td>
<td>3.34</td>
</tr>
<tr>
<td>Zn</td>
<td>264</td>
<td>0.535</td>
<td>3.1</td>
<td>3.29</td>
</tr>
</tbody>
</table>

a S\textsubscript{BET}, V\textsubscript{tot} and pore sizes determined by N\textsubscript{2}-sorption isotherms. b Band gaps determined from UV-vis diffuse reflectance spectra.

### Table 4 Isoelectric points of the bare TiO₂ and titania decorated with 0.5 wt% of selected transition metals.

<table>
<thead>
<tr>
<th>Sample (x-TiO₂)</th>
<th>Isoelectric Point</th>
<th>Potential at pH 7 (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal TiO₂</td>
<td>5.9</td>
<td>−23</td>
</tr>
<tr>
<td>Mn</td>
<td>6.7</td>
<td>−3.3</td>
</tr>
<tr>
<td>Fe</td>
<td>6.8</td>
<td>−2.7</td>
</tr>
<tr>
<td>Co</td>
<td>6.4</td>
<td>−12.5</td>
</tr>
<tr>
<td>Ni</td>
<td>6.2</td>
<td>−16</td>
</tr>
<tr>
<td>Cu</td>
<td>6.8</td>
<td>−4.7</td>
</tr>
<tr>
<td>Zn</td>
<td>6.8</td>
<td>−3.9</td>
</tr>
</tbody>
</table>
since light scattering in the sample occurring in DRS measurements is different from that in a photoreactor, especially if the catalyst is in powder i.e. suspension form.\textsuperscript{27}

From Fig. 5 it can be seen that the differences in reflectance spectra of colloidal TiO\textsubscript{2} films are quite subtle. This was expected since the absorption of photons directly depends on the number of titania particles, and consequently on the mass of the film on a given surface area, which was uniform among the samples. However, TiO\textsubscript{2} modified with zinc and iron had the highest scattering in the 400–450 nm region, followed closely by Co and then Ni, while Mn- and Cu-modified films showed the least scattering in that region. A quick drop in the reflectance value appeared towards larger values because of the small size of the nanoparticles due to the fact that lower wavelengths are scattered more efficiently, \textit{i.e.} by Mie theory\textsuperscript{28} scattering depends on the incident light wavelength and size of the particles. True absorption was shifted to longer wavelengths in all modifications, most notably in Ni, Co and Zn samples, although only by \textit{e.g.} 7 nm for Ni-modification. However, an additional increase of Ni (0.5% \(\rightarrow\) 1%) leads to increased absorption in the 400–450 nm part of the spectrum due to the 3d\textsuperscript{7} d–d transition in octahedral Ni\textsuperscript{2+} ions as suggested by EXAFS measurements (see below). Relatively high scattering in the 250–400 nm range and a red-shift in absorption make Zn and Ni the best candidates for photocatalystic tests; in the TPA test the highest activity was achieved by Zn- and Ni-modified samples, while in Rz ink reduction Ni modification resulted in the fastest bleaching under solar light.

Transmission electron microscopy of the Ni-modified sample revealed (Fig. 6) the distribution of nanoparticles and Ni-oxo-nanoclusters. A uniform distribution of nanoparticles is seen in Fig. 6A, with an average grain size of 6 nm. A portion of Ti was detected as Ti\textsuperscript{3+} by EELS analysis of the outside of titania particles (not shown). This is possible due to the presence of reducible Ni clusters which extract oxygen from the surface layer of TiO\textsubscript{2} to form NiO clusters thereby reducing titanium to Ti\textsuperscript{3+}. Both claims were also supported by \textit{in situ} EPR measurements (see below). The distribution of nanoclusters obtained from EDXS mapping and HAADF/STEM is shown in Fig. 6D and F (marked as bright spots), respectively, confirming that Ni is uniformly distributed on the surface of TiO\textsubscript{2} particles and that Ni is present in the form of oxo-nanoclusters.

For the most promising modification (Ni) X-ray absorption investigation was carried out. From the XANES study (Fig. 7a) it can be seen that the Ni-modified TiO\textsubscript{2} sample exhibits the same Ni K-edge energy position and a similar edge profile to those of the reference Ni\textsuperscript{2+} compounds Ni hyaluronate complex\textsuperscript{29} and NiO,\textsuperscript{30} where Ni\textsuperscript{2+} is octahedrally coordinated to 6 oxygens in the first coordination shell, indicating that Ni cations in the Ni-modified TiO\textsubscript{2} sample are also in a divalent state, octahedrally coordinated to 6 oxygen atoms in its first coordination sphere.

In the Fourier transform Ni K-edge EXAFS spectrum of the Ni-modified TiO\textsubscript{2} sample, contributions of Ni neighbour shells up to about 3 Å are resolved (Fig. 7b). The quantitative analysis of the EXAFS spectrum is performed with the IFEFFIT program package.\textsuperscript{31} Structural parameters of the local Ni neighbourhood (type and average number of neighbours, and the radii and Debye–Wallner factor of neighbour shells) were quantitatively resolved from the EXAFS spectrum by comparing the measured EXAFS signal with a model signal, constructed \textit{ab initio} with the FEFF6 program code\textsuperscript{32} from the set of scattering paths of the photoelectron in a tentative spatial distribution of neighbour atoms. The model comprised six oxygen atoms at the same distance in the first coordination shell and Ni and Ti atoms at two different distances in the second. The atomic species of neighbours are identified in the fit by their specific scattering factor and phase shift.

Three variable parameters for each shell of neighbours are introduced in the model: the shell coordination number (N\textsubscript{s}), the distance (R\textsubscript{s}) and the Debye–Wallner factor (\(\sigma\textsuperscript{2}\)). In addition, a common shift of energy origin \(\Delta E\textsubscript{o}\) is also allowed to vary. The amplitude-reduction factor \(S\textsuperscript{2}\) is kept fixed at the value of 0.90. A very good agreement between the model and the experimental spectrum is found in the \(k\) range of 3.5–12.0 Å\textsuperscript{–1}, and the \(R\) range from 1.0 Å to 3.5 Å (Fig. 7b). The list of best-fit parameters is given in Table 5.

Ni cations are found to be coordinated to six oxygen atoms in the first coordination shell at 2.04 Å, and, on average, to one Ti and one Ni neighbour at larger distances. The Ni–O–Ti and Ni–O–Ni bridges detected in EXAFS analysis suggest that Ni\textsuperscript{2+} cations are partially attached to the surface of the photocatalytically active TiO\textsubscript{2} nanoparticles, and partially agglomerated with NiO nanoparticles.

To further elucidate the nature of such species, EPR spectra were recorded at 20 K. It showed the formation of oxygen...
radicals (O$_2^-$) and Ni$^{2+}$ centres upon visible light irradiation, depicted as the difference in Fig. S9. A broad signal at the low magnetic field was ascribed to very small Ni nanoparticles, with a $g_{\text{eff}}$ of 2.28. These can be observed since Ni-particles with a size significantly less than 50 nm (indicated also with TEM) may have non-stoichiometric nature resulting in a significant portion of Ni$^{3+}$ and thus exhibit paramagnetism. The presence of disorder in such clusters causes the reduction in size-dependent exchange interactions between two neighbouring Ni$^{2+}$ ions mediated through oxygen ions and induces anisotropy of Ni$^{3+}$. Upon irradiation, the presence of e$^-$ from TiO$_2$ increased the interactions in the nickel surrounding thus increasing the Ni$^{2+}$ signal, together with O$_2^-$ ($g = 2.002$). Ti$^{3+}$ centres weren’t seen since these are already present in some proportion in the parent (non-irradiated) materials, as indicated by the EELS from TEM. From the observation of these separate techniques we named the particles on the surface metal-oxo-nanoclusters.

### 3.4 Mechanisms of photocatalytic activity

Due to their electronic nature transition metals are capable of changing their oxidation states. This is also the main benefit with regard to their contribution to solar light photoactivity, and thus they serve as co-catalysts on the surface of titania. First, if a part of UV is present in irradiation (which in solar light...
TiO$_2$ $\overset{hv}{\longrightarrow}$ TiO$_2$(h$^+$, e$^-$) \hspace{1cm} (4)

Later the fate of charge carriers depends on their successful migration to the surface and reactions there. Nanoclusters are reduced by the photogenerated e$^-$ which leaves more h$^+$, which do not recombine, for oxidation reactions:

$$M^{n+} + e^{-} \rightarrow M^{(n - 1)+} \hspace{1cm} (5)$$

However, the same reduced metal sites on the surface can act as h$^+$ traps:

$$M^{(n - 1)+} + h^+ \rightarrow M^{n+} \hspace{1cm} (6)$$

In order to avoid such cyclic phenomena, the nanoclusters have to be well separated spatially, which is achieved by their low loading (see above). An additional reason for such low loadings to be optimal is the avoidance of shading effects in which species on the surface of TiO$_2$ would limit the penetration of light to titania nanoparticles.

With regard to the mechanism of clusters, iron, for example, gets reduced to Fe$^{2+}$ and then serves as the oxygen reduction catalyst:

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \hspace{1cm} (7)$$

$$4\text{Fe}^{2+} + \text{O}_2 + \text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^- \hspace{1cm} (8)$$

Copper which is reduced on the other hand has similar co-catalyst capabilities:

$$2\text{Cu}^+ + \text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{H}_2\text{O}_2 \hspace{1cm} (9)$$

$$3\text{Cu}^+ + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{Cu}^{3+} + 2\text{H}_2\text{O} \hspace{1cm} (10)$$

$$\text{Cu}^+ + \text{O}_2(\text{ads}) \rightarrow \text{Cu}^{2+} + \text{O}_2^{*-} \hspace{1cm} (11)$$

Zinc can promote photocatalysis by creating additional OH and O$_2^*$ as well. For instance:

$$\text{Zn}^+ + \text{O}_2(\text{ads}) \rightarrow \text{Zn}^{2+} + \text{O}_2^{*-} \hspace{1cm} (12)$$

$$\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{Zn}^+ + ^*\text{OH} \hspace{1cm} (13)$$

In the presence of Mn-clusters on the surface of TiO$_2$, the following reactions are possible:

$$\text{Mn}^{2+} + e_{cb}^- \rightarrow \text{Mn}^+ \hspace{1cm} (14)$$

$$\text{Mn}^+ + \text{O}_2(\text{ads}) \rightarrow \text{Mn}^{2+} + \text{O}_2^{*-} \hspace{1cm} (15)$$

$$\text{Mn}^{3+} + \text{OH}^- \rightarrow \text{Mn}^{2+} + ^*\text{OH} \hspace{1cm} (16)$$

However, it should be noted that Mn$^+$ and Mn$^{3+}$ are relatively unstable, compared to Mn$^{2+}$, which can have an effect on trapping the photogenerated e$^-$ (Mn$^{3+}$) and h$^+$ (Mn$^+$). This is probably the reason why manganese showed only minor results in the improvement of photoactivity.

We hypothesise that surface nickel species can react and help the photocatalytic process as follows:

$$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni} (-0.26 \text{ V}) \hspace{1cm} (17)$$

$$\text{Ni} + \text{O}_2 + 2\text{H}^+ \rightarrow \text{Ni}^{2+} + \text{H}_2\text{O}_2 \rightarrow 2e^- \rightarrow \text{Ni}^{2+} + 2\text{OH}^- \hspace{1cm} (18)$$

$$\text{Ni(OH)}_2 + 2e^- \rightarrow \text{Ni} + 2\text{OH}^- (-0.72 \text{ V}) \hspace{1cm} (19)$$

Nussbaum et al. doped BiOCl with Fe and Nb and argued that the reduction potential of the doped metals should be relatively low (Nb$^{5+}$/Nb$^{4+}$ is 0.35 V) and the location of the 4+ level is close to the O$_2$/O$_2^*$ level. This facilitates the reduction of oxygen to superoxide, thus back-flipping the 4+ state into the 5+ (for Nb at least). The mechanism is arguably particularly important under solar light, where the main active species are superoxides. Thus, in Fig. 8, $E_{\text{red}}^0$ for single e$^-$ (or 2 in the case of Ni) transfer are plotted on the right side. It can be seen that Zn, Co and Ni potentials are close to the O$_2$/O$_2^*$ level. This could lead to the above described back-flipping mechanism. However, it must be noted that those Ni cations that are bound to the surface of TiO$_2$ could change the valence band of TiO$_2$ and hence improve the absorption of visible light.

On the other hand, Li et al. argued that metal oxides whose band edges are bracketed by TiO$_2$ edges lead to the transfer of photogenerated charge carriers from TiO$_2$ which then recombine thus decreasing the overall activity of the materials. Hence, for Co VB and CB positions are bracketed by the $E_{\text{VB}}$ and $E_{\text{CB}}$ of TiO$_2$, which favours higher recombination of photogenerated charge carriers, thus reducing the activity under solar light. Interestingly, although the XRD, UV-VIS and XANES data clearly show that, in our case, the structures do not resemble the oxide structure of nanoclusters; it seems that the bracketing of VB and CB increases the recombination in metal-oxo-nanoclusters apart from Ni and Zn. In this study, nanoclusters are present as highly dispersed species on the surface of TiO$_2$, which are partially connected to Ti via oxygen bridges and partially forms M–O–M dimers or an amorphous M$_2$O$_3$ structure. The very small size of clusters facilitates electron transfer from the anatase surface, which in turn decreases the recombination if the above-mentioned constraints are fulfilled.

The second factor that limits the activity improvement is the potential of one electron reduction of OH to H$_2$O set at 2.31 V (vs. NHE). Holes created at levels lower than that do not have redox potential to contribute to activity significantly. Hence, if a hole is transferred to a metal oxide which has a low $E_{\text{red}}^0$, the latter probably serves to increase the e$^-$–h$^+$ separation at best or to increase the recombination of the charge carriers, which is more probable at higher loadings.

The valence band of ZnO (−7.39 eV) is just at the level of TiO$_2$ (−7.46 eV) which favours the transfer of h$^+$ to Zn clusters.
Hence, zinc is mostly active at oxidation reactions, which was clearly shown in the TPA test that follows the oxidation product of the model compound. Interestingly, nickel also showed improvement in oxidation photoactivity, although its $E_{\text{VB}}$ (7.5 eV) is slightly lower than $E_{\text{VB}}$ (TiO$_2$). On the other hand in the reduction reaction Zn acts as a charge trap site for photogenerated e$^-$ from TiO$_2$, which resulted in slower reaction kinetics. The same phenomena can explain lower solar activity toward reduction concerning Fe-, Cu- and Co-modified TiO$_2$ films, again, due to the bracketing of the CB and VB of the transition metal oxides by the bands of TiO$_2$, which results in metal oxides that act as recombination centres.

The experiments conducted by using a UV-cutoff filter showed that UV-excitation is still the dominant force driving the chosen reactions; this makes sense since the TPA oxidation proceeds via direct oxidation with holes. However, without the suitable band positions of the metal-oxo-nanoclusters, such charge carriers would only result in recombination at clusters. The latter was evident in the case of Mn-modification; its suitable CB-band position allowed for improved reduction of $\text{R}_2$, while the VB of MnO ($-7.09$ eV) is significantly lower than that of TiO$_2$, which makes such cluster traps for h$,^+$ hence limiting the oxidation of TPA to HTPA via holes. On the other hand, the EPR experiment showed that Ni-oxo-nanoclusters are centers for generating $\text{O}_2^\cdot$ radicals, while h$^+$ from TiO$_2$ are free to oxidize the reactants.

Hence, if such materials are to be used in aqueous media, the degradation of organic molecules would then proceed via direct attack by h$^+$ and via ‘OH$^-$ the former was experimentally proven by the TPA test. The superoxide radicals generated at the metal-oxo-nanoclusters would also add to the final degradation activity. The limiting factors are the aforementioned VB positions of the respective metal oxides and the spatial distribution of metal-oxo-nanoclusters on the TiO$_2$ surface.

4. Conclusions

We demonstrated that the enhancement of the solar-light activity of TiO$_2$ by the deposition of metal-oxo-nanoclusters on the surface depends strongly on the reduction potential of such species. The small size of metal-oxo-nanoclusters, synthesised in this study, allows dynamic acceptance/release of e$^-$ from TiO$_2$\text{VB}; this is governed mainly via the position of the reduction potential of such species as close as possible to the redox potential of $\text{O}_2$/OH$_2$; this is dependent on the position of the valence band of their corresponding oxides, since these are also present on the surface of TiO$_2$. We proved this by monitoring the formation of ‘OH, where the oxides of deposited metals whose bands were bracketed by TiO$_2$ bands resulted in a decreased solar-light activity, probably due to the higher recombination of e$^-$/h$.^+$, for which such clusters offered additional trapping sites. Additionally, the metal grafting shifted the absorption region in films toward lower energies and increased scattering in the films in the 400–450 nm region. This resulted in higher efficiencies to harvest solar light with a consequence of even higher photoactivity.

Ni and Zn showed a winning combination of redox potential and band positions of TiO$_2$ supported metal-oxo-nanoclusters for enhanced solar-light activity. However, Ni was the only metal which had a positive effect on solar photoactivity in both oxidation and reduction reactions. The results presented here open a new thinking paradigm for designing surface modification of semiconductors to enhance their solar-light photoactivity.

Conflicts of interest

The authors declare no conflicts of interest.
Acknowledgements

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