Cu-decorated Raschig-TiO$_2$ rings inducing MB repetitive discoloration without release of Cu-ions under solar light

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**Abstract**

The methylene blue (MB) discoloration on innovative photocatalysts made up of Raschig-rings coated by pre-formed TiO$_2$ nanoparticles decorated with CuOx (RR@TiO$_2$-Cu) is presented. The MB-discoloration was drastically accelerated by the subsequent addition of 0.044% Cu. This Cu-content being ∼3000 times below the TiO$_2$ present in the RR@TiO$_2$ samples led to MB-discoloration in shorter times. The Cu-ions released from the RR@TiO$_2$-Cu 0.004% were determined <1ppb by inductively coupled plasma mass-spectrometry (ICP-MS). Cu-percentages >0.018% decreased the MB-discoloration kinetics due to the Cu acting as recombination sites for the photogenerated charges. The total organic carbon (TOC) reduction concomitant with the MB-discoloration is reported as well as the effect of the initial MB-concentration and pH on the discoloration kinetics. The Cu-addition shifted significantly the TiO$_2$ absorption into the visible region even when added in sub-microgram quantities (0.004%) to RR@TiO$_2$ as detected by diffuse reflectance spectroscopy (DRS). The Cu level added to RR@TiO$_2$ was too low to be detected by X-ray diffraction (XRD). The roughness of the RR@TiO$_2$-Cu (0.018%–0.081% Cu) presented Rg-values between 11.8 nm and 23.9 nm. The RR@TiO$_2$-Cu presented agglomerate sizes of ∼200 nm for TiO$_2$ and for the Cu aggregates sizes of ∼20 nm. The MB discoloration kinetics and reuse of the RR@TiO$_2$-Cu suggest the potential as a supported catalyst in environmental cleaning process. A reaction mechanism is suggested taking into consideration the role of the Cu$^{+2+}$ intra-gap states involving redox catalysis as detected by X-ray photoelectron-spectroscopy (XPS).

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1. Introduction

TiO$_2$, doped TiO$_2$ and decorated TiO$_2$ either in colloid form or powder have been reported to degrade pollutants under band gap irradiation. Some studies report TiO$_2$ on glass/polymer and metal plates leading to pollutants. This subject has been the focus of recent reviews [1–6]. This type of catalysis/photocatalysis is used to degrade pollutants resistant to biological degradation at low concentrations involving reactions driven by solar light. In this case, the source of energy is free but its utilization requires facilities that involve capital investment. The reactions when light reaches the semiconductor surface (TiO$_2$) in the presence of O$_2$ (air) leads to the generation of charges and radicals not needing any additional reactant to abate the organic pollutant. In this study, we have selected as a probe the dye methylene blue (MB). Glass in the form of Raschig rings, was used as a low cost inert support for the TiO$_2$. TiO$_2$ coated Raschig rings have been used for the degradation of pollutants in dilute solutions under band-gap irradiation to abate the dye direct-red 16 [7]. This approach has also been used to degrade several aromatic compounds in aqueous solution [8–10]. Our laboratory has reported Raschig rings coated by TiO$_2$ as a catalyst to degrade phenol-compounds [11], phenol [12] and chlorophenols [13]. This study addresses the preparation of Raschig rings coated with TiO$_2$ but adding small amounts of a 3d-transition element like Cu/Cu-ions to extend its absorption into
the visible region with the objective of increasing the dye degradation kinetics under solar light.

We address the simple preparation of a low-cost RR@TiO2-Cu photocatalyst and its testing with the degradation of MB. Supported TiO2 avoids the separation of the catalyst from the solution at the end of the dye degradation process. The degradation kinetics of Cu-decorated TiO2 Raschig rings, the reaction mechanism, the Cu-ions leaching from the catalyst surface and the characterization of the optimized photocatalyst surface will be systematically investigated in the course of this study.

2. Materials and methods

2.1. Materials and synthesis of RR@TiO2-Cu, reactor set-up, MB-discoloration, total organic carbon (TOC), X-ray fluorescence (XRF) and irradiation source

The Raschig rings that served as support for the RR@TiO2-Cu were 4 × 4 mm in size and 1 mm thick, were made out of soda lime glass composed by: 70% SiO2, 10% (Na2O, CaO, MgO K2O) and 5% (Fe2O3, Al2O3). TiO2 used in the suspensions was Degussa P25 and the CuNO3 · 3H2O was Acros Organics. The polyethylene-graft-maleic anhydride powder (PEGMA) was a Sigma–Aldrich No.456624, Mw ~ 14000. The reagent 3, 7-bis (Dimethylamino) phenazatnium chloride or Methylene Blue (MB from now) was Sigma-Aldrich and used as received. NaN3 (Fluka) was used as a possible oxygen singlet scavenger (O2), 1, 4-benzoquinone (BQ) and methanol were used respectively as O2* radical scavenger and OH* scavengers [14]. Ethylenediamine tetra-acetic acid (EDTA-2Na) was used as TiO2yb hole scavenger [15].

The supported catalyst preparation was prepared according to the following sequence: The Raschig rings were washed with detergent and then treated with HNO3 30% for 10 min at 50 °C, then drained and rinsed with Milli-Q water. The clean Raschig rings were subsequently immersed in PEGMA dissolved in toluene 5% (wt/wt), then drained and dried overnight at room temperature. The dry Raschig rings with PEGMA on their surface were dipped in TiO2 suspensions (5 g/l) and Cu(NO3)3·3H2O was added according to the amount selected to decorate the RR@TiO2. The rings were drained and dried at 110 °C for 1 h. The latter step was repeated 3 times and the RR@TiO2-Cu was calcined at 500 °C during 10 h to eliminate the PEGMA, the interfacial binder. TiO2/Cu was deposited on the external and internal surfaces of the Raschig rings. The reproducibility of the amount of Cu deposited on the RR@TiO2 was ± 20% and it was kept by following the preparation protocol.

The UV–vis spectra during MB discoloration were followed in a Schimadzu single beam instrument. The total organic carbon (TOC) was determined in a Shimadzu TOC 5000 equipped with an ASI auto-sampler. The Ti and Cu content in (RR@TiO2-Cu) was evaluated by X-ray fluorescence in a PANAlytical PW 2400 unit. The TiO2 and Cu weight percentages on the RR@TiO2 rings are reported in Table 1 and were determined by X-ray fluorescence spectroscopy. By this technique, each element emits a defined X-ray wavelength that is associated with the particular atomic number of each element. The different TiO2-Cu suspensions used to prepare the rings were 0.05% up to 3% w/w Cu/TiO2.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>%wt TiO2</th>
<th>%wt Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR@TiO2</td>
<td>11.30</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>RR@TiO2-Cu 0.004%</td>
<td>11.98</td>
<td>0.004</td>
</tr>
<tr>
<td>RR@TiO2-Cu 0.018%</td>
<td>22.67</td>
<td>0.018</td>
</tr>
<tr>
<td>RR@TiO2-Cu 0.053%</td>
<td>18.73</td>
<td>0.053</td>
</tr>
<tr>
<td>RR@TiO2-Cu 0.081%</td>
<td>13.04</td>
<td>0.081</td>
</tr>
</tbody>
</table>

Photolysis experiments were performed in the cavity of a solar simulated Hanau Suntest Lamp with a tunable light intensity attachment equipped with an IR filter to remove IR radiation >800 nm. The UV-radiation <305 nm was removed by the Pyrex wall of the reaction vessels. The Raschig rings used to fix the TiO2-Cu were positioned between a central Teflon cylindrical tube and the reactor wall; in this way the photocatalytic bed was fixed inside the reactor. The Teflon support was fitted with small holes (2 mm diameter) to allow diffusion of the solution in the reactor. In the bottom of the reactor, and concentrically to both the Teflon tube and the reactor, a magnetic stirrer was positioned to keep the diffusion of the reactive species. The Suntest solar simulator (Heraeus, Hannau, Germany) is shown in Fig. 1a. The reactors cavity was ~ 30 cm wide, 20 cm long and 20 cm high. The distance between the Xe-lamp and the photo-reactor lid was 10 cm. The photo-reactor was 7 cm high without the lid and 11 cm high with the lid. Before each photocatalytic run the MB-solution (70 ml) was equilibrated in the dark with the RR-TiO2-Cu (35 g) for 30 min.

The light intensity reaching the photo-reactor was 90 mW cm−2 and was detected at the top of it. This light intensity was determined by a light dosimeter that measures the integrated photons in the Suntest simulator between 290 nm and 800 nm. The spectral range of photons generated by the Xe-lamp is shown in the Supplementary Fig. S5. The light in the Suntest cavity is reflected several times by the polished Al-walls.

2.2. ICP-MS determination of Ti-ions and Cu-ions leached out during MB discoloration

The determination by inductively coupled plasma mass-spectrometry (ICP-MS) of the Ti and Cu eluted during MB degradation was carried out by an ICP-MS FinniganTM unit equipped with a double focusing reverse geometry mass spectrometer. It has an extremely low background signal and a high ion-transmission coefficient. The discoloured MB solution in contact with RR@TiO2-Cu was digested with nitric acid 69% (1:1 HNO3 + H2O) to remove the organics in the solution and to insure that there were no adhered ions remaining on the flask wall. The samples droplets were introduced to the ICP-MS trough a peristaltic pump to the nebulizer chamber at ~7700 °C. This allows the complete sample evaporation. The Ti and Cu found in the nebulizer droplets were subsequently quantified by mass spectrometry (MS).

2.3. RR@TiO2-Cu microstructure: surface properties

The atomic force spectroscopy (AFM) image signals were acquired in contact mode using a PSIA Xe-100 AFM. Silicon nitride cantilevers were used with feedback set points close to 1.0 nN. The AFM scanner and position sensors were calibrated using standard samples from Mikromash. The experimental error in the roughness was below 10%. The mean surface roughness (RMS) was calculated for scanned areas of 2 × 2 μM.

X-ray diffraction (XRD) of the RR@TiO2-Cu Raschig rings were recorded on a Philips X’Pert PRO diffractometer equipped with an X’Celerator detector and a Ni-filtered Cu K radiation operating at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) of the RR@TiO2-Cu was carried out in an AXIS NOVA photoelectron spectrometer (Kratos Analytical, Manchester, UK) provided for with monochromatic AlKα (hν=1486.6 eV) anode. The surface atomic concentration was determined from peak the XRD areas using the electrostatic correction according to Shirley [16–18]. The carbon C1 s at 284.6 eV was used as reference for the peak positions of Ti, C, and O the XPS spectragram as well [16].
3. Results and discussion

3.1. MB discoloration kinetics

Table 1 presents the percentage of Cu and TiO$_2$ on the Raschig-rings obtained by X-ray fluorescence (XRF).

Fig. 1b, traces (1) and (2) show the MB adsorption in the dark on the RR@TiO$_2$-Cu 0.004% surface and on bare Raschig rings. There is no significant difference between runs (1) and (2) shown in Fig. 1b due to the low percentages of TiO$_2$ and Cu on the support (~15% TiO$_2$ and 0.004% Cu). Fig. 1b, trace (3) shows the low light effect on MB-discoloration in presence of Raschig rings during 240 min. A
displayed and involve (see charge states Cu ions released during MB-discoloration up to the 5th use cycle and Cu-ions released during MB-discoloration up to the 5th use cycle. Suntest light set at 90 mW cm\(^{-2}\)

**Fig. 2.** (a) Rate constants \(k\) for the repetitive MB \(4 \times 10^{-3}\) mol L\(^{-1}\) discoloration by RR@TiO\(_2\)-Cu-0.053% photocatalyst (trace 4)) shows no complete discoloration after 240 min. RR@TiO\(_2\) is presented in trace (5), it displays a higher initial degradation rate compared to the RR@TiO\(_2\)-Cu-0.053% photocatalyst (trace 4)). RR@TiO\(_2\)-Cu-0.004% (trace 6)) is seen to lead to a faster discoloration compared to RR@TiO\(_2\)-Cu-0.053% (trace 4)) despite the lower Cu content (13.5 times less Cu). Also, RR@TiO\(_2\)-Cu-0.004% (trace 6)) performs better than RR@TiO\(_2\) (trace 5) with higher initial degradation rate and being able to reach complete discoloration. These observations suggest that the Cu-sites deposited on the RR@TiO\(_2\) surface may involve to intra-gap sites facilitating the TiO\(_2\) charge transfer to MB under band-gap irradiation. However, at higher concentrations of Cu on the TiO\(_2\) surface the Cu-sites may act as charge recombination centers decreasing the amount of photogenerated charges [1-6]. The position of the potential energy level of the Cu-intra-gap states lies between the TiO\(_2\) vb (3.1 eV) and the TiO\(_2\) cb (\(-0.1\) eV) and can be estimated to be close to 0.15 eV [19]. The Cu\(^{1+2}\) on the TiO\(_2\) under band-gap irradiation would work as an electron acceptor enhancing MB-degradation [20].

**Fig. 1c** shows the pseudo-first order rate constant \(k\) of MB-discoloration as a function of the Cu-amount added to RR@TiO\(_2\). **Fig. 1c** shows that the \(k\) for the MB-discoloration by RR@TiO\(_2\)-Cu-0.004% is higher compared to the \(k\) by the RR@TiO\(_2\)-Cu-0.018% photocatalyst and the other photocatalysts used to discolor MB (see **Fig. 1c** caption). This is the evidence for the RR@TiO\(_2\)-Cu-0.004% sample acting as a trap for the TiO\(_2\)vb (h\(^+\)) increasing the charge separation and concomitantly decreasing the electron-hole recombination in TiO\(_2\). Higher amounts of Cu decorating RR@TiO\(_2\) above Cu 0.004% act as charge recombination sites/centers decreasing the \(k\) values during MB-discoloration (see **Fig. 1c**). The MB-discoloration kinetics as a function of the initial MB-concentration and the initial pH are reported in Supplementary material S2 & S3.

**Fig. 1d** presents the changes in the MB-absorbance spectra between 200 and 800 nm for MB solutions \(4 \times 10^{-3}\) mol L\(^{-1}\) in contact with RR@TiO\(_2\) rings decorated with different amounts of Cu under Suntest light. The spectra in **Fig. 1d** (a-d) show that the MB-peak at 664 nm decreases more slowly as the Cu-content increases, which is consistent with results reported above in **Fig. 1c**. The MB-bands between 600 and 700 nm correspond to the conjugated \(\pi\) system comprising MB monomers/dimers [21]. The aromatic ring bands \(< 300\) nm were observed also to disappear after around 120 min reflecting the progressive cleavage of the MB-aromatic ring. The small absorbance \(< 300\) nm is assigned to long-lived organic intermediates left in solution [22]. The existence of long-lived intermediates in solution is further confirmed by the TOC results presented next for MB-discoloration/degradation in **Fig. 1e**.

Total organic carbon (TOC) decrease during the photocatalytic degradation of MB \(4 \times 10^{-3}\) mol L\(^{-1}\) mediated by RR@TiO\(_2\)-Cu-0.004% under Suntest light (90 mW cm\(^{-2}\)) at initial pH values \((\text{pH} 5.7\) and \(\text{pH} 10\) is presented in **Fig. 1e**. For the two pH-values investigated the initial TOC drops by 75%. The mineralization varied only in a narrow range on the Cu amounts added on the RR@TiO\(_2\) rings. This information is available in Supplementary material S4.

### 3.2. Repetitive MB-discoloration and evidence for the RR@TiO\(_2\)-Cu-0.004% stability

**Fig. 2a** shows the kinetic constants during the discoloration of MB by RR@TiO\(_2\)-Cu-0.004% up to the 5th use cycle. The \(k\) values vary only 10% up to the 3rd cycle and became lower in the 5th cycle. The photocatalyst rings were carefully washed and dried after each cycle. **Fig. 2b** shows by ICP-MS the Ti-ions leached after each recycling, the values reported in **Fig. 2b** were far below the allowed limit set by sanitary regulations for the toxicity on mammalian cells, up to one gram TiO\(_2\) [23]. **Fig. 2c** shows the ICP-MS amounts of the Cu-ions leached during the MB-discoloration into the solution. The values of 1 ppb of Cu detected after the 5th cycle were far below the limit of 25 ppb set by some sanitary regulations [24]. The low levels found for the release of Ti and Cu indicate that we are in the presence of an oligodynamic effect involving catalysis by contact with metal and/or oxides and taking place with an almost negligible release of ions [25].

### 3.3. Light intensity effects on the MB-discoloration kinetics and ROS detected during the MB-degradation

**Fig. 3a** shows the effect of light intensity on MB discoloration in the presence of RR@TiO\(_2\)-Cu. The faster MB-discoloration kinetics was observed under a higher applied light intensity increasing the photogenerated charges in TiO\(_2\) making up 99.9% of the RR@TiO\(_2\)-Cu 0.004%. The run shown in **Fig. 3a**, trace 4) at 90 mW cm\(^{-2}\), was carried out in the presence of a cut-off filter 400 nm to block the UV light. Although the UV-light is present in a relation of about 1:20 compared to the photons in the Suntest simulated light cavity emitting light in the visible range (400–800 nm), their high energy is sent to contribute to the MB-discoloration up to ~50%. Only semiconductor materials show an increased amount of photogenerated charges due to a higher applied light intensity. **Fig. 3a** shows that TiO\(_2\) and not the Cu intra-gap absorbers are responsible for the observed MB-discoloration. This suggests that the TiO\(_2\)-be-
reacting with the adsorbed O₂ is the main channel leading in later stages to MB-discoloration.

Fig. 3b shows the scavenging of the intermediate radicals generated on the RR@TiO₂-Cu 0.004% surface: a) trace (2) MB-discoloration in the presence of methanol 20 mM L⁻¹ quenching the OH-radicals, b) trace (3) MB-discoloration in the presence of NaN₃ 20 mM L⁻¹, a scavenger of oxygen singlet O₂ [26,27], c) trace (4) MB-discoloration in the presence of benzoinone 20 mM L⁻¹ [1,2] a quencher of O₂⁻/HO₂⁺ [28,29], d) trace (5) MB-discoloration in the presence of 20 mM L⁻¹ ethylenediamine tetra-acetic acid disodium salt (EDTA-2Na), a widely used TiO₂vb (h⁺) scavenger [1,6]. Trace (1) shows MB-discoloration without the addition of scavengers.

Results in Fig. 3b show that the scavenging follows the series: vb (h⁺)→ O₂⁰⁺/HO₂⁻→ O₂→ OH⁻. The dissolved O₂ (8 mgL⁻¹) is not only a TiO₂ electron scavenger but its presence is necessary to generate the HO₂⁻. At pH > 4.8, more than 50% of the HO₂⁻ is present in the form of O₂⁰⁺. This form of the HO₂⁻ radical predominates, since the initial pH of the MB-solution was ~6.0 decreasing during the MB-discoloration to a value of 4.7. The OH⁻ radicals scavenged by methanol in Fig. 3b, trace 2) imply one electron reduction OH⁻(OH⁻ with Eq. 1.90 V NHE and show a smaller scavenging effect compared to O₂⁻/HO₂⁻ with a lower potential of Eq. 0.75 V NHE. The lifetime and concentration of the OH⁻ radicals is much lower compared to the less energetic O₂⁻ / HO₂⁻ [30].

Azide NaN₃ has been generally reported as a singlet O₂ scavenger [1,2]. However, it also reacts with OH-radicals with a similar rate as it does with singlet O₂ [3,15]. For this reason, the data reported in Fig. 3b wouldn’t indicate in a specific way the effect of the singlet oxygen during MB-discoloration. Another issue to consider is that the CuO(OH)⁻ could react in two ways: a) directly with O₂ leading to O₂²⁻ or b) reducing the CuO to Cu⁺, as noted in Eqs. (1) and (2) below:

\[
\text{CuO(cbe}^-) + O₂ \rightarrow \text{CuO} + O₂^{2-} \quad (1)
\]

\[
\text{CuO(cbe}^-) \rightarrow \text{CuO}^\text{(Cu⁺)} \quad (2)
\]

Reaction (2) is much faster than the CuO dissolution [19,20], shown in Eq. (3). The reaction (Eq (3)) involves CuO(Cu⁺) and could possibly lead to the reaction of CuO with the holes TiO₂vbh⁺.

\[
\text{CuO(Cu⁺)} \rightarrow \text{CuO vacancy} + \text{Cu⁺} \quad (3)
\]

EDTA is used generally as a hole scavenger in TiO₂ photocatalysis. But it may not play this role in the case of CuO mediated photocatalysis. We observed that by scavenging TiO₂vbh⁺ with EDTA, the MB became colorless. After contacting the MB-solution with fresh air (O₂), the solution became blue again. This suggests that while blocking the TiO₂vbh⁺, MB gets reduced to the leuco form of methylene blue (LMB).

Based on these findings, the design of a reactor with a RR@TiO₂-Cu photocatalyst may consider two factors: a) good contact between the photocatalyst and the solution and b) good mixing inside the reactor for oxygen diffusion, which will improve the oxygenated radicals’ formation.

3.4. Suggested reaction mechanism, involvement of Cu intra-gap states

Metals/oxides have been shown to increase the charge separation on semiconductors [16,19] leading to new interfaces. The discoloration mechanism is suggested to proceed initially by the photogenerated TiO₂ electrons transferred to the TiO₂cb by the Cu intra-gap states in the TiO₂ as suggested in Fig. 4.

\[
\text{TiO}_2 + \text{Cu} + h\nu \rightarrow \text{vb} (h^+) + \text{cb} (e^-) \quad (4)
\]

The direct photosensitization of MB in the presence of RR@TiO₂-Cu under Sun test simulated sunlight shown in Fig. 4 may be suggested as:

\[
\text{MB} + \text{[RR@TiO₂-Cu]} + h\nu \rightarrow [\text{MB}^\text{••} \cdots \text{RR@TiO₂-Cu}] \rightarrow \text{MB}^{\text{••}} + \text{[RR@TiO₂-Cu]} + \text{cb} (e^-) \quad (5)
\]

Under sunlight irradiation, both the MB and TiO₂ are photosensitized, MB injects electrons into the TiO₂cb and in parallel converts MB to the MB⁺ cation radical. The electron injected by the MB into the TiO₂ reacts with O₂ and generates highly oxidative radicals leading to the discoloration/degradation of MB as shown in Fig. 4 [20]. The low laying Cu intra-gap states promote the indirect transition of the electron from TiO₂ vb (h⁺) to the TiO₂cb. This is consistent with the results reported in Fig. 1b for RR@TiO₂-Cu 0.004% photocatalyst. The Cu¹⁺ two intra-gap states also interact with the RR@TiO₂-Cu 0.004% adsorbed O₂. In this way, the recombination rate of the TiO₂ e⁻/h⁺ pairs is hindered improving the photocatalyst MB-degradation. The addition of

![Fig. 3](image-url)
Cu > 0.004% makes the Cu-act as a recombination center because the thickness of the space layers decreases with increasing Cu-content [19]. The Cu\(^{3+}\) would also reduce the air (O\(_2\)) consuming electrons or re-oxidize to Cu-ions by the photogenerated TiO\(_2\) holes to Cu\(^{2+}\) [20,31,32].

The Cu\(^{1+}/2+\) and Ti\(^{3+}\) intermediate donor levels may be present due to the back charge transfer reaction: e\(-\) + Ti\(^{4+}\) \rightarrow Ti\(^{3+}\) following the reaction stated above in Eq. (4) [33]. The vb\((h + v)\) reacts with the TiO\(_2\) O-vacancies formed concomitant to the Ti\(^{3+}\) trough the channel: h\(^+\) + O\(_2\) \rightarrow O\(^-\) leading subsequently to the re-population of Cu\(^{1+}\) in the Cu\(^{1+}/2+\) intra-gap states. Sputtered Cu-polystyrene was reported to present initially predominantly Cu\(^{1+}\) states followed in later reaction stages by Cu\(^{2+}\) [15]. Cu intra-gap sates in a TiO\(_2\)/Cu sputtered catalyst surface were reported to lead to more OH\(^{-}\)-radicals, due to additional vb\((h + v)\) [16]. As long as the RR@TiO\(_2\)-Cu 0.004% in Fig. 4 is photoactivated by light, it will continuously produce cbe- reacting with O\(_2\) leading to the formation of oxidative intermediate radicals.

3.5. Surface properties of RR@TiO\(_2\)-Cu

3.5.1. Diffuse reflectance spectroscopy (DRS)

Fig. 5 shows the DRS spectra of the samples in Kubelka-Munk units. Cu is seen to move the RR@TiO\(_2\) absorption drastically into the visible region. Similar optical modifications were found by Kapilashrami et al. [34] when doping TiO\(_2\) with non-metals. Trace (1) shows the DRS spectrum of TiO\(_2\) Degussa P-25 on glass. The Cu\(^{2+}\) ionic-radial are larger than the one of Ti\(^{4+}\), and therefore it would be difficult for the Cu\(^{2+}\) to replace Ti\(^{4+}\) in the crystal lattice [33,35]. The Cu-species may decorate the surface of the TiO\(_2\) matrix. If Cu-cations would be incorporated in the TiO\(_2\) lattice by substituting Ti\(^{4+}\), the electro-neutrality demand would require the additional formation of O-vacancies. Peaks between 320 and 440 nm in Fig. 5, traces 2, 3 have been attributed to (Cu–O–Cu)\(^{2+}\) clusters in highly dispersed states. The peaks between 400 and 500 nm (Fig. 5, traces 4, 5) were assigned to three dimensional Cu\(^{1+}\) clusters in CuO [36,37].

3.5.2. X-ray diffraction (XRD)

The XRD-spectrograms in Fig. 6 are shown for RR@TiO\(_2\)-Cu 0.018% in trace (1) and for RR@TiO\(_2\)-Cu 0.053% in trace (2). The presence of TiO\(_2\) Degussa P-25 is confirmed by the peaks at 25° and 27.5° for anatase and rutile respectively, as reported by Hanaor et al. [38]. The size of the anatase crystals was assessed based on the (101) reflection in the spectra (1) and (2) and the calculations lead to particle size of ~20 nm in both cases. The calculations were made by means of the Debye-Scherrer equation, noted in Eq. (6).

\[
D = \frac{k\lambda}{\beta\cos\theta}
\]

Fig. 4. Suggested scheme for RR@TiO\(_2\)-Cu intra-gap mediated electron transition under sunlight irradiation leading to MB-discoloration/degradation. For further details see text.

Fig. 5. DRS spectra for different Cu weight percentages in RR@TiO\(_2\), (1) RR@TiO\(_2\), (2) RR@TiO\(_2\)-Cu 0.004%, (3) RR@TiO\(_2\)-Cu 0.018%, (4) RR@TiO\(_2\)-Cu 0.053% and (5) RR@TiO\(_2\)-Cu 0.081%.

Fig. 6. XRD for different Cu weight percentages in RR@TiO\(_2\) and references of TiO\(_2\), Cu and Cu oxides. (1) RR@TiO\(_2\) – Cu 0.018%, (2) RR@TiO\(_2\) – Cu 0.053%. Reference XRD: (3) Anatase (R100013), (4) Rutile (R040049), (5) Copper (R061078), (6) CuO (R050384), (7) CuO (R120076) [42].
Fig. 7. (a) AFM-topography of RR@TiO$_2$–Cu 0.018% taken at a resolution of (2 × 2 μM), (b) AFM-topography of RR@TiO$_2$–Cu 0.081% taken at a resolution of (2 × 2 μM).

For Eq. (6), D stands for the crystal size in nm, $\kappa$ as the shape factor which is usually fixed as 0.89, $\lambda$ as the wavelength which is taken as 0.154 nm, $\beta$ is the full width at half maximum for the prominent peak, and $\theta$ as the Bragg’s diffraction angle in radians [39,40]. The characteristic peaks of Cu and Cu oxides between 35° and 40° in Fig. 6, traces (1) and (2) appear as overlapping peaks of anatase (trace (3)), Cu (trace (5)), Cu$_2$O (trace (6)) and CuO (trace (7)). Cu-oxides peaks were found by XRD for higher Cu doping percentages (>5%) by Bensouici et al. [41]. The Cu and Cu-oxide peaks in Fig. 6 are referenced to the RRUFF database [42]; they appear between 35° and 40° for Cu, Cu$_2$O and CuO. In the course of this study, we could not sort out the different Cu-oxide species due to the extremely low amounts of Cu deposited on the catalyst surface.

3.5.3. Atomic force microscopy (AFM) and roughness (Rg)

Fig. 7 shows AFM-topography images of RR@TiO$_2$–Cu 0.018% (a) and RR@TiO$_2$–Cu 0.081% (b) for two scanning areas of 2 × 2 μM. The topography of RR@TiO$_2$–Cu 0.004% sample is not presented because the low amount of Cu could not be detected; only TiO$_2$ aggregates presented adequate signals. Fig. 7a) shows TiO$_2$ and Cu-agglomerates of ~200 nm ~20 nm in size respectively. The RR@TiO$_2$–Cu 0.018% samples presents a roughness (Rg) $\approx$ 11.8 nm. In this case, the topography of the AFM contour in Fig. 7a) shows peaks relatively closely packed to each other providing the contact points with MB [43]. Fig. 7b) illustrates the TiO$_2$–Cu 0.081% sample. TiO$_2$ and Cu agglomerates of ~200 nm and ~20 nm in size respectively were observed. The RR@TiO$_2$–Cu 0.081% sample presents roughness (Rg) $\approx$ 23.9 nm. The topography of the AFM contour in Fig. 7b) shows deeper and wider valleys to accommodate the MB dye providing less surface contact between the photocatalyst and MB.

3.5.4. X-ray photoelectron spectroscopy (XPS)

Fig. 8 and Table 2 show the peak variation and the surface percentage atomic concentration of the elements present in the RR@TiO$_2$–Cu 0.004% during discoloration/degradation of the MB diluted solution. The XPS signal at time zero was taken after the sample was contacted with the MB solution for 30 min in the dark. Fig. 8a) shows the Ti2p doublet shift from 456.98 eV to 457.15 eV. This provides the evidence for a redox reaction occurring during the MB-degradation involving Ti$^{3+}$/Ti$^{4+}$. The appearance of Ti$^{3+}$ species is associated to the peak initial shift of Ti$^{4+}$ >0.2 eV [3]. Redox behavior was also observed for Cu2p$_{3/2}$ and O1s since peak shifts from 930.68 eV to 931.08 eV and from 528.19 to 528.39 were observed for both elements respectively as shown in Fig. 8b) and Fig. 8c) [17,18]. Fig. 8d) shows the XPS C1s at time zero. It displays the contribution of several carbon bonds like C—C, C=C, COH, C=O, C—H etc., found in the MB such as C—C (sp$^2$), C—C (sp$^3$), C—N—R2 [44]. The XPS carbon peaks after 120 min irradiation (trace (2) in Fig. 8d) were less intense, meaning a decrease in atomic carbon, consistent with the values for C1s reported in Table 2, due to changes in the C—C (sp$^2$) and C—C (sp$^3$) during the MB degradation.

In Table 2 the percentage of C1s is seen to decrease within 120 min due to MB discoloration, but a strong residual C1s is noticed after 120 min. This observation is consistent with the TOC-results reported in Fig. 1d. No N-species adsorbed on the photocatalyst surface were detected by XPS as shown in Table 2 by the low atomic percentages found for N. The small amounts of
4. Conclusions

Cu-decoration seems to induce an intra-gap-electronic state in the TiO\textsubscript{2} facilitating the indirect electron transition in the TiO\textsubscript{2} band-gap and leading to an accelerated MB-degradation kinetics. The results obtained during MB discoloration showed that a Cu-addition of 0.004% on RR@TiO\textsubscript{2} led to the highest photocatalytic activity. The addition of Cu on RR@TiO\textsubscript{2} shifts strongly the photocatalyst absorbance into the visible region. The Cu intra-gap states in RR@TiO\textsubscript{2}–Cu could not be characterized due to the low amounts of Cu present in the photocatalyst. Higher Cu-levels on the TiO\textsubscript{2} surface seem to act as recombination centers for the photogenerated charges decreasing the rate of MB-discoloration. By the use of appropriate scavengers (TiO\textsubscript{2}vb (h\textsuperscript{+}) was found to be the most important intermediate species leading to MB-degradation. The XPS-shifts during the photocatalytic degradation of MB provides the evidence for redox events between CuO\textsubscript{x}/TiO\textsubscript{2} and the MB. The AFM results indicate that a low Cu-loading on the RR@TiO\textsubscript{2} rings showed a close packed contour compared to the wide-spaced contour obtained with higher Cu-loadings. A close packed contour in the low Cu-loading provides more contact points with MB leading to faster degradation.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jece.2016.12.006.

References


![Fig. 8. XPS signals of Ti (a), Cu (b), O (c) and C (d) at time zero (1) and after discoloration of a MB 4 × 10^{-5} mol L\textsuperscript{-1} solution on RR@TiO\textsubscript{2}–Cu 0.004% (2). Suntest irradiation set at 90 mW m\textsuperscript{-2}.](image-url)

Table 2

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<th>N1s</th>
<th>O1s</th>
<th>S2p</th>
<th>Ti2p</th>
<th>Cu2p \textsubscript{2,3d}</th>
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