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# Effects of different Cu loadings on photocatalytic activity of TiO<sub>2</sub>-SiO<sub>2</sub> prepared at low temperature for oxidation of organic pollutants in water

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Abstract: The objective of this research is to examine how copper modification can improve the photocatalytic activity of TiO<sub>2</sub>-SiO<sub>2</sub>, and to explain the correlation between Cu concentration and chemical state of Cu cations in the TiO2-SiO2 matrix, and the photocatalytic activity under the UV/solar irradiation. The Cu-modified TiO2-SiO2 photocatalysts were prepared by a low temperature sol-gel method based on organic copper, silicon and titanium precursors with varied Cu concentrations (from 0.05 to 3 mol%). The sol-gels were dried at 150 °C to obtain the photocatalysts in the powder form. The photocatalytic activity was determined by a fluorescence-based method of terephthalic acid decomposition. Up to three times increase in photocatalytic activity is obtained when TiO<sub>2</sub>-SiO<sub>2</sub> matrix is modified with Cu in a narrow concentration range from 0.05 to 0.1 mol%. At higher Cu loadings the photocatalytic activity of Cu modified photocatalyst is smaller than in the unmodified reference TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst. XRD analysis shows that all Cu modified TiO2-SiO2 composites with different Cu concentrations have the same crystalline structure as unmodified TiO<sub>2</sub>-SiO<sub>2</sub> composites. The addition of Cu does not change the relative ratio between anatase and brookite phase or unit cell parameters of the two TiO<sub>2</sub> crystalline structures. The Cu K-edge XANES and EXAFS analysis is used to determine valence state and local structure of Cu cations in Cumodified TiO2-SiO2 photocatalyst. The results elucidate the mechanism responsible for the improved photocatalytic activity. In the samples with low Cu content, which exhibit largest activity, Cu-O-Ti connections are formed, suggesting that the activity enhancement is due to Cu(II) cations attachment on the surface of the photocatalytically active TiO<sub>2</sub> nanoparticles, so Cu(II) cations may act as free electron traps, reducing the intensity of recombination between electrons and holes at the TiO2 photocatalyst's surface. At higher Cu loadings no additional Cu-O-Ti connections are formed, instead only Cu-O-Cu connections are established, indicating the formation of amorphous or nanocrystalline Cu oxide, which hinders the photocatalytic activity of TiO<sub>2</sub>.

## Introduction

Titanium dioxide is one of the most popular photoactive materials and it has been widely used for water purification, degradation of air pollutants, removal of residual pesticides, self-

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cleaning glass, etc.<sup>[1-3]</sup> Photocatalytic activity only appears under UV light irradiation since TiO<sub>2</sub> cannot absorb visible part of sunlight due to its wide band gap (3.0 - 3.2 eV). Addition of SiO<sub>2</sub> to TiO<sub>2</sub> improves mechanical strength and thermal stability of the photocatalyst, increases the surface area and pore volume and, in some cases, inhibits the charge carrier surface recombination and the crystallization of anatase phase, and therewith, increases photocatalytic activity of pure TiO2.<sup>[4]</sup> Dong et al.<sup>[5]</sup> studied the photocatalytic degradation of Rhodamine-B dye under UV-light by nano-ordered two-dimensional hexagonal mesoporous  $TiO_2$ -SiO<sub>2</sub> composite materials that have been synthesized by organic-solvent evaporation method, and found that TiO<sub>2</sub>-SiO<sub>2</sub> composite materials have better photocatalytic activity than pure TiO<sub>2</sub> (Degussa P25) because of the synergetic roles of coupled adsorption and photocatalytic oxidation. Anderson and Bard<sup>[6]</sup> studied the photocatalytic degradation of Rhodamine-6G (R-6G) under UV-light and described the effect of incorporation of SiO<sub>2</sub> on the behaviour of a TiO<sub>2</sub>-based photocatalyst prepared by a sol-gel method from organometallic precursors. TiO<sub>2</sub>-SiO<sub>2</sub> catalysts were heated to 200 °C for 12 h. They demonstrated that a ratio TiO<sub>2</sub>/SiO<sub>2</sub> of 30/70 produces a catalyst about 3 times more active than Degussa P25 TiO<sub>2</sub>. Higher photocatalytic activity relates to the preferential adsorption of R-6G on SiO2 which increases the surface concentration of R-6G at or near the TiO<sub>2</sub> sites promoting more efficient oxidation by photogenerated species. They suggest that the photogenerated intermediate oxidants on the TiO<sub>2</sub> sites (hydroxyl radical or perhydroxyl radical) must diffuse and react with R-6G on the SiO<sub>2</sub> sites.

To improve the photocatalytic activity under solar light irradiation, and reduce high rate of recombination between photogenerated electrons and holes in TiO<sub>2</sub>, metal doping was introduced.<sup>[7]</sup> Improving photocatalytic activity can be achieved if more photo-generated electrons and holes move to the surface of the semiconductor particles before they recombine in bulk. Doping of TiO<sub>2</sub> with transition metals can introduce electron capture centres resulting in a decrease in electron/hole recombination centres.<sup>[8,9]</sup> The photocatalytic activity of TiO<sub>2</sub> and TiO2-SiO2 photocatalysts is improved if Pt, Pd, Au or Ag are used as dopants<sup>[10-13]</sup> or if Pt, Pd, Au or Ag are deposited on TiO2<sup>[14]</sup> but these metals are rare and expensive. Copper is a good candidate to replace expensive metals as dopants. Improved photocatalytic activity was found for Cu-modification under different reducing calcination atmospheres at low Cu concentrations (0.05, 0.1, 0.2, 0.5 and 1 mol% with respect to Ti).<sup>[15]</sup> The enhancement was attributed to Cu-ion participating in lengthening of electron hole pair recombination time, and due to creation of oxygen vacancy which helps to reduce the band gap.<sup>[15]</sup> Wu et al.<sup>[16]</sup> showed that Cu nanoparticles prepared by

wet impregnation, followed by low-temperature H<sub>2</sub> reduction, could improve the catalytic activity of TiO<sub>2</sub> under UV light. The catalytic activity of Cu-TiO<sub>2</sub> was about 10 times higher than that of TiO<sub>2</sub> at the optimum loading amount 1.5 mol% Cu. M. Tahir and B. Tahir<sup>[17]</sup> prepared Cu-modified TiO<sub>2</sub> nanocatalysts using modified sol-gel method and showed that CO production was higher than that of pure TiO<sub>2</sub> by more than 99 times when Cu concentration is 3.5 mol%. They also co-doped TiO<sub>2</sub> with Cu and In and showed that performance of 1.0% Cu and 3.5% In codoped TiO<sub>2</sub> catalyst for CO production is 113 times higher than un-doped TiO2. The enhanced conversion efficiency was attributed to improved charge separation in TiO<sub>2</sub>, where Cu and In species served as electron traps which suppressed electronhole recombination.<sup>[18]</sup> Momeni et al.<sup>[19]</sup> synthesized highly aligned TiO<sub>2</sub> nanotube films co-sensitized with Cu and W nanoparticles via chemical bath deposition method. Optimal performance was obtained with photocatalysts containing 0.04 mol% Cu and 0.06 mol% W. The enhanced photocatalytic activity was associated with the extended absorption in the visible light region and effective separation of photo-generated carriers by the co-sensitization of Cu and W nanoparticles. Zhang et al.<sup>[20]</sup> synthesized Cu-doped titanium oxide films by dc magnetron sputtering method using Ti and Cu mixed target. The Cu-doped TiO<sub>2</sub> films had different photocatalytic behaviour in accordance with the amount of doped copper. The optimum Cu doping concentration was 1.45 mol%, which showed the most effective photocatalytic activity. They suggested mechanism responsible for photocatalytic activity enhancement: the doped copper cation can provide a shallow trap for photo-generated electron and hole so as to inhibit the recombination and extend the lifetime of charge carrier. This optimum concentration can be explained by the balance of an increase in trapping sites leading to efficient trapping, and fewer trapped carriers leading to longer lifetimes for interfacial charge transfer.<sup>[7]</sup> In addition, the metal ion doping of TiO<sub>2</sub> has been used to induce the photoactivity in the visible light region.<sup>[14,21-25]</sup>

Improved photocatalytic activity of TiO<sub>2</sub> was found also in case of deposition of CuxO nanoclusters onto TiO2 surfaces by an impregnation technique at Cu concentrations from 0.001 to 0.02 mol%.<sup>[26]</sup> Under UV/Vis light irradiation, the electrons in the valence band of TiO<sub>2</sub> are promoted to Cu(II) species in Cu<sub>x</sub>O clusters, which results in the transformation of Cu(II) into Cu(I), while holes remain in the valence band.<sup>[26-28]</sup> Li et al.<sup>[29]</sup> showed that Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposites (with the molar ratio of Cu/Ti 0.01:1) prepared by a sol-gel method, calcined at 500 °C for 3h, exhibited higher photocatalytic activity than commercial  $TiO_2$  (Degussa P25) for the degradation of Rhodamine-B dye under both UV and visible light irradiation. They explained that addition of Cu enhanced the water absorption on TiO<sub>2</sub> surface, more OH<sup>-</sup> was formed and consequentially photocatalytic activity was increased. Cu species with divalent copper cations states, dispersed on the surface of TiO<sub>2</sub> nanoparticles, can effectively inhibit recombination of photoinduced charge carriers. Li et al.[30] and Xin et al.<sup>[31]</sup> concluded that metal to metal charge transfer in Ti-O-Cu complexes at TiO<sub>2</sub> surfaces enhance photoactivity through charge carrier separation. Li et al.[30] synthesized series of photoactive CuO-TiO<sub>2</sub> nanocomposites with different Cu concentration (0.1, 0.6 and 5 mol% Cu) via a deposition precipitation method. CuO-TiO<sub>2</sub> nanocomposite with a very low copper loading (0.1 mol%) demonstrated improved photoactivity

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relative to pure TiO<sub>2</sub>. In their opinion, one possible mechanism for the improved photocatalytic activity is that the surface/interfacial Cu(II) sites function as unique adsorption sites for methylene blue and facilitate the subsequent photocatalytic degradation. Xin et al.<sup>[31]</sup> prepared Cu-TiO<sub>2</sub> photocatalyst with different Cu dopant content (0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 1 and 3 mol%) by sol-gel method and showed that 0.06 mol% of Cu increased photocatalytic activity of Cu-doped TiO<sub>2</sub>. The increase of photocatalytic activity is ascribed to appropriate amount of oxygen vacancies and doped Cu(II) ions on the surface layer of TiO<sub>2</sub>, which can effectively capture the photoinduced electrons. Hussein et al.[32] used simulations to confirm experimental results about the reduction of Cu(II) to Cu(I) and how it may serve as a further mechanism through which the lifetime of surface holes may be extended.<sup>[30]</sup> Arana et al.<sup>[33]</sup> prepared Cu-TiO<sub>2</sub> by TiO<sub>2</sub> impregnation with CuSO<sub>4</sub> aqueous solutions (incipient wetness impregnation method) at 25 °C with Cu concentration 0.6 mol%. Catalysts were calcined at 500 °C for 5 h. They suggested that the presence of Cu(II) atoms on the TiO<sub>2</sub> surface generate the catalysts active centres and increase the photocatalytic activity because photo-generated oxidising species do not migrate far away from active centres where they are formed. Miyauchi et al.<sup>[34]</sup> and Irie et al.<sup>[35]</sup> demonstrated that visible light initiates interfacial charge transfer i.e., electrons in the valence band (VB) of TiO<sub>2</sub> are directly transferred to Cu(II) and form Cu(I), as well as holes in the VB of TiO2. The holes produced in the VB of TiO<sub>2</sub> efficiently oxidize organic contaminants. In contrast, the Cu(I) produced by electron transfer is likely to reduce adsorbed O2 through multielectron reduction, and thus electrons are consumed.

Jin et al.<sup>[36]</sup> used Cu(acac)<sub>2</sub> as a precursor to form molecular scale CuO clusters on the surfaces of TiO<sub>2</sub> particles (Degussa P25) in a highly dispersed state by chemisorption–calcination cycle technique and showed that the photocatalytic activity strongly depends on Cu loading. They explained that the effective mixing between the surface CuO cluster levels and the O2p states from the surface of TiO<sub>2</sub> yields a surface *d* sub-band that overlaps with the TiO<sub>2</sub> VB. The visiblelight absorption of CuO-TiO<sub>2</sub> can mainly be attributed to the interfacial electron transfer from the *d* sub-band to the conduction band (CB) of TiO<sub>2</sub>.

Xin et al.<sup>[31]</sup> reported that at heavy Cu doping concentration, *p*-type Cu<sub>2</sub>O can cover the surface of TiO<sub>2</sub>, which leads to decrease in the photocatalytic activity of photocatalyst. Li et al.<sup>[30]</sup> explained that at higher Cu concentration (>0.5 mol%) coupling between CuO and TiO<sub>2</sub> led to decreased photocatalytic efficiency due to the charge transfer from TiO<sub>2</sub> to CuO and subsequent charge recombination.

In our previous research<sup>[37]</sup>, we have developed a new lowtemperature sol-gel synthesis of Cu-modified TiO2-SiO2 photocatalysts, based on organic precursors. Colloidal solution of TiO2-SiO2 nanoparticles was prepared from titanium tetraisopropoxide, tetraethyl ortosilicate, and copper acetylacetonate as a source of Ti, Si and Cu, respectively. We examined how copper modifications at two copper concentrations (0.1 mol% and 3 mol%) processed at different temperatures (drying at 150 °C and additional calcining at 500 °C) affect the photocatalytic activity of TiO<sub>2</sub>-SiO<sub>2</sub> under the UV/solar irradiation. The enhancement of photocatalytic activity was obtained only in the photocatalyst modified with low Cu

# FULL PAPER

concentration (0.1 mol%), processed at low temperature. Calcination of Cu-modified  $TiO_2$ -SiO<sub>2</sub> photocatalysts at 500 °C induces significant structural changes and reduces its photocatalytic activity.

In this study we investigate the relation between Cu loading and photocatalytic activity of Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst, synthesized by low-temperature sol-gel synthesis, in order to optimize synthesis conditions and obtain the photocatalyst with highest photocatalytic activity under the UV/solar irradiation. The Cu concentrations are varied in the range from 0.05 to 3 mol%, at eight selected values: 0.05, 0.08, 0.1, 0.15, 0.3, 0.5, 1 and 3 mol%. The photocatalytic activity was tested by oxidative degradation of terephthalic acid (TPA) in aqueous solution. Increased photocatalytic activity was found only at low Cu loadings in a narrow range between 0.05 mol% to 0.1 mol%. To clarify mechanisms responsible for the photocatalytic activity enhancement at low Cu concentrations, and its decrease at high Cu loadings, different analytical and spectroscopic techniques were used. Crystal structures present in the unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts were investigated by X-ray diffraction. Specific surface area and average pore size was evaluated from N<sub>2</sub> sorption. Local structure and valence state of Cu cations in TiO2-SiO2 photocatalyst was determined by X-ray absorption spectroscopy (XAS) methods: extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). Correlations between the Cu cation local structure in TiO<sub>2</sub>-SiO<sub>2</sub> matrix and photocatalytic activity of the Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposites at different Cu loadings elucidate competitive mechanisms responsible for improvement or reduction of photocatalytic activity of the material.

## **Results and Discussion**

### Photocatalytic activity

The photocatalytic activity of the samples was measured by the fluorescence-based method of terephthalic acid (TPA) decomposition in aqueous solution, taking into account that 2hydroxyterephthalic acid (HTPA) is formed as an intermediate product. The formation rate constant of HTPA  $(k_1)$  is used to photocatalytic activity of the compare Cu-modified photocatalysts with an unmodified one. Modelling of the experimental data of HTPA concentrations as function of UV/Vis illumination time (Figure 1) was performed according to a simplified kinetics analysis for the initial degradation curve, where oxidation of TPA to HTPA under UV/solar irradiation can be described by zero-order kinetics ([HTPA] =  $k_1 \cdot t_1$ ).<sup>[37,38]</sup> Best fit values of the rate constants  $k_1$ , obtained for unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> catalysts with different Cu loadings and relative photocatalytic activities of Cu-modified compared to unmodified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst are presented in Table 1.

The results suggest that there is up to three times increase in photocatalytic activity when  $TiO_2$ -SiO<sub>2</sub> matrix is modified with low Cu concentrations in a narrow range from 0.05 to 0.1 mol%. In this range photocatalytic activity increases with Cu concentration reaching maximum activity in the interval between 0.08 and 0.1 mol% Cu. With increase of Cu concentrations above 0.1 mol%, photocatalytic activity first quickly drops to the values lower than in the unmodified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst and

further proportionally decreases with the increase of Cu concentration.

### Structural properties

The BET surface areas of unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> samples as determined by nitrogen adsorption and desorption analysis are given in Table 1. All Cu-modified samples exhibit same or very similar specific surface area as unmodified TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite. About 10% increased value is found for the two Cu modified TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposites, TS\_0.08Cu and TS\_0.1Cu, which are the most photocatalytically active. However, the increased photocatalytic activity in these two samples compared to the unmodified one cannot be attributed only to this small increase in their specific surface area. Average pore size in Cu modified TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite is the same (within error-bars) as in the unmodified one, at all Cu loadings.

The XRD patterns of unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> samples are shown in Figure 2. Anatase is the major crystal phase in all samples, with a minor amount of brookite phase. The broad peak that appears at  $2\theta$  around  $22^{\circ}$  can be attributed to glass-like amorphous silicate nanoparticles.



**Figure 1.** HTPA concentrations as function of UV/Vis illumination time for unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> powder catalysts with different Cu concentrations (from 0.05 to 3 mol%). (Dots – experiment, solid line – best fit model ([HTPA] =  $k_1 \cdot t$ ))

**Table 1.** Specific surface area, average pore size, and the rate constants of hydroxyterephthalic acid (HTPA) formation  $k_1$  of unmodified and Cumodified TiO<sub>2</sub>-SiO<sub>2</sub> samples. Relative photoactivity of the photocatalysts, i.e.  $k_1$  constant of the photocatalyst compared to the  $k_1$  constant of the reference unmodified photocatalyst is given in the second column. Uncertainty of the last digit is given in parentheses.

Sample	<i>k</i> ₁ [10 <sup>-6</sup> M min <sup>-1</sup> ]	Relative photoactivity	Specific surface area [m <sup>2</sup> g <sup>-1</sup> ]	Average pore size [nm]
TS	0.0212(5)	1	258(8)	3.8(3)
TS_0.05C u	0.048(2)	2.3(1)	262(8)	3.5(3)
TS_0.08C u	0.060(2)	2.8(1)	286(8)	3.4(3)
TS_0.1Cu	0.056(9)	2.6(2)	281(8)	3.5(3)
TS_0.15C u	0.0124(8)	0.58(4)	255(8)	3.6(3)
TS_0.3Cu	0.0087(9)	0.41(4)	262(8)	3.7(3)
TS_0.5Cu	0.0042(6)	0.20(3)	263(8)	3.6(3)
TS_1Cu	0.0015(5)	0.07(2)	259(8)	3.8(3)
TS_3Cu	0.0003(2)	0.014(1)	240(8)	4.1(3)

No other crystalline species were detected. For the unmodified TiO<sub>2</sub>-SiO<sub>2</sub> sample, the final quantitative analysis of crystalline phases resulted in the following crystalline phase composition: anatase - 89 %, brookite - 11 %, with the crystallite sizes equal to 3.7 nm and 10.4 nm, respectively. Cu-modified TiO2-SiO2 samples with different Cu concentrations were found to have the same crystalline structure as unmodified TiO<sub>2</sub>-SiO<sub>2</sub> composites. The addition of Cu does not change the relative ratio between anatase and brookite phase. Diffraction peaks of the (101) anatase and (121) brookite planes were used to evaluate the lattice parameters as well as the crystallite size. The obtained values are summarized in Table 2 (and Table S-1; see supporting information). There are no changes in the anatase (A) and brookite (B) crystal unit cell parameters and crystallite sizes in the Cu-modified samples, as compared to unmodified TiO<sub>2</sub>-SiO<sub>2</sub> composite.

Morphology of Cu-modified and unmodified TiO2-SiO2 photocatalysts is examined with TEM and HRTEM imaging (see supporting information, Figures S-1 and S-2). TiO<sub>2</sub> and SiO<sub>2</sub> are recognized as separate phases in the material. The SiO<sub>2</sub> phase is composed of quasi-spherical particles with the size in the range of about 10 nm to 20 nm, while TiO2 forms small crystallites with size in the range 2 nm to 6 nm. The two phases are identified with EDX elemental mapping (see supporting information, Figure S-3). HRTEM images show that SiO<sub>2</sub> nanoparticles are amorphous while TiO2 has crystalline structure, in agreement with XRD data. The same morphology is observed in Cu modified and unmodified samples. The addition of Cu does not change the morphology of TiO2-SiO2 catalyst. The CuO phase in the Cu-modified TiO2-SiO2 samples was not detected in TEM images, indicating that Cu is dispersed on TiO<sub>2</sub>-SiO<sub>2</sub> matrix in amorphous form or in the form of small nano-clusters, with a size below detection limit.



Figure 2. XRD diffractograms of TiO<sub>2</sub>-SiO<sub>2</sub> (TS) and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> samples

**Table 2.** Relative amount of Anatase crystalline phase in TiO2-SiO2 and Cu-<br/>modified TiO2-SiO2 nanocomposites, ist crystallite lattice parameters, unit cell<br/>volume, and mean crystallite size.

Sample	Anatase	Lattice para	meter [Å]		Cr. size
	[%]	a=b	С	[A ]	fund
TS	89	3.798(3)	9.327(8)	135.6(3)	3.7(9)
TS_0.05Cu	86	3.801(3)	9.324(9)	134.7(3)	3.3(9)
TS_0.08Cu	83	3.797(3)	9.332(8)	134.5(3)	3.6(9)
TS_0.1Cu	82	3.802(3)	9.329(8)	134.8(3)	3.8(9)
TS_0.15Cu	88	3.798(2)	9.331(8)	134.6(2)	3.5(9)
TS_0.3Cu	88	3.796(3)	9.332(8)	134.5(3)	3.3(9)
TS_0.5Cu	85	3.801(2)	9.328(7)	134.8(2)	3.3(9)
TS_1Cu	84	3.796(4)	9.318(8)	134.3(4)	3.7(9)
TS_3Cu	86	3.799(3)	9.321(8)	134.5(3)	3.4(9)

### Cu K-edge XANES

Cu K-edge XANES analysis was used to determine the average Cu valence state and local symmetry of Cu cations in the nanocomposite samples, where the valence is known to directly affect the shape and position of the edge features. The analysis of XANES spectra was performed with the IFEFFIT program package ATHENA.<sup>[39]</sup> The relative K-shell contribution in the absorption spectra is obtained by the standard procedure by removing the extrapolated best-fit linear function determined in the pre-edge region (-150 eV - 30 eV), and by conventional normalization extrapolating the post-edge spline background determined in the range from 150 to 600 eV in order to set the Cu K-edge jump to 1. The Cu K-edge XANES spectra of the Cu modified TiO<sub>2</sub>-SiO<sub>2</sub> samples and reference copper compounds

with different Cu cation valence state (Cu(0), Cu(I) and Cu(II)) and Cu coordination are shown on Figure 3.

Different local environments of the Cu cation result in different Kedge profiles and pre-edge lines in the XANES spectra. The energy position of the absorption edge and the pre-edge features are correlated with the valence state of the absorbing atom in the sample, and can be used to determine the valence state of Cu cations.<sup>[40]</sup> The energy of the Cu K-edge and preedge features in Cu(II) compounds is shifted for about 4 eV to higher energies, compared to Cu(I) compounds.<sup>[40,41]</sup> In the reference crystalline Cu<sub>2</sub>O where monovalent Cu(I) is coordinated to four oxygen atoms, a well-defined absorption feature from the 1s-4p transition occurs at 8982 eV.[41,42] In case of Cu<sub>2</sub>O nanoparticles in the reference Cu(I)-containing MORtype zeolite (Cu(I)-MOR)<sup>[43]</sup>), the 1s-4p transition occurs at 8983 eV. In case of Cu(II) compounds the 1s-4p transition appears as pre-edge shoulder in the energy range from 8985 eV to 8989 eV. The intensity of the shoulder increases from distorted octahedral to pure planar Cu coordination.<sup>[40,44]</sup> In Cu(acac)<sub>2</sub>, Cu(II) is coordinated to four oxygen atoms at 1.92 Å, the 1s-4p transition occurs at energy between 8985-8986 eV. In the crystalline CuO. where Cu(II) cations are octahedrally coordinated to six oxygen atoms in elongated octahedron (four oxygens at 1.95 Å and two at 2.88 Å), a pre-edge 1s-4p shoulder is present at 8985 eV. In case of Cu(II) octahedrally coordinated to six oxygen atoms tetragonally distorted due to Jahn-Teller effect with four oxygens at 1.9 Å and two at 2.3 Å, the 1s-4p shoulder appears in the energy range between 8986 eV and 8989 eV (CuSO<sub>4</sub>, Cu malathion, Cu(OH)<sub>2</sub> and liquid Cu(acac)<sub>2</sub> precursor).

Judging from the energy position of the Cu K-edge and sharp pre-edge features in the XANES spectra of the catalyst samples compared to the Cu reference compounds, the oxidation state of copper is Cu(II) (Figure 3). The same conclusion can be drawn also for Cu cations in the liquid photocatalyst precursor.

The Cu K-edge profiles of all eight samples (TS\_0.05Cu, TS\_0.08Cu, TS\_0.1Cu, TS\_0.15Cu, TS\_0.3Cu, TS\_0.5Cu, TS\_1Cu, TS\_3Cu) are practically identical to one another. This qualitative observation is confirmed also by detailed quantitative analysis of the XANES spectra by Principal Component Analysis (PCA).<sup>[39]</sup> The number of eigenvectors above noise level denotes number of independent components with a physical meaning in the set of the analysed spectra. The results of PCA suggest that there is only one dominant principal component that describes all eight spectra in the set. Minor differences between spectra can be attributed to noise.



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**Figure 3.** Normalized Cu K-edge XANES spectra of the Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> samples dried in air at 150 °C for 1 h and TS\_0.08Cu\_v sample additionally dried in vacuum. Reference Cu(0), Cu(1) and Cu(11) copper compounds with different Cu cation coordination (Cu(0), Cu(0)-MOR<sup>[43]</sup>, Cu<sub>2</sub>O, Cu(1)-MOR<sup>[43]</sup>, Cu<sub>2</sub>O, Cu(0)-MOR<sup>[43]</sup>, Cu<sub>2</sub>O, C

The shape of Cu K-edge in the XANES spectra of the air-dried catalyst samples is similar to the shape of Cu K-edge of the reference Cu compounds where Cu(II) is located at the centre of Jahn-Teller distorted octahedron of six oxygen atoms. The linear combination fit (LCF) analysis<sup>[39]</sup> shows that the Cu K-edge XANES spectra of the photocatalyst samples can be almost completely described by a linear combination of two XANES reference spectra: Cu malathion (87 %) and Cu hydroxide (13 %) (Figure 4), where Cu(II) cations are coordinated with four planar oxygens at short distance of about 1.95 Å and two axial oxygens at about 2.3 Å, indicating that local symmetry and coordination of Cu(II) cations in the catalysts is similar.

The energy position of Cu K-edge of the sample additionally dried in vacuum (TS\_0.08Cu\_v) is shifted towards lower energies, indicating the reduction of Cu(II) during drying in vacuum. Results of LCF analysis (see supporting information, Figure S-4) suggest that sample contains a mixture of three

valence states of copper: 66% of Cu(0), 29% of Cu(I) and 5% of Cu(II).



Figure 4. The Cu K-edge XANES spectrum measured on TS\_0.08Cu sample. Blue solid line - experiment; red dashed line - best-fit linear combination of XANES profiles of Cu malathion (87%) and Cu(OH)<sub>2</sub> (13%). Fit components are shown below.

### Cu K-edge EXAFS

The Cu K-edge EXAFS analysis was used to determine the local structure around Cu cations in the Cu-modified TiO2-SiO2 catalysts. Fourier transforms (FT) of the  $k^2$  weighted EXAFS spectra of the samples and references compound are shown in Figure 5. The Fourier transforms spectra from the Cu modified catalysts series (Figure 5) reveal the contributions of consecutive shells of Cu neighbours of up to ~4 Å. Qualitative comparisons of the FT spectra shows that average Cu neighbourhood in the catalyst samples dried in air are similar but not the same. Small differences clearly indicate structural differences around Cu cations among the samples with different Cu loadings.

The quantitative analysis of Cu K-edge EXAFS spectra were performed with the IFEFFIT program package.<sup>[39]</sup> Structural parameters were quantitatively resolved by comparing the measured signal with the model EXAFS spectra, constructed with the FEFF6 program code<sup>[45]</sup> in which the photoelectron scattering paths are calculated ab initio from a tentative spatial distribution of neighbour atoms. We can expect a mixture of different Cu(II) species in the Cu-modified TiO2-SiO2 nanocomposites at different Cu loadings, after drying in air at 150 °C. Part of Cu(II) cations may retain the bonding to acac groups as in the liquid precursor or as in crystalline Cu(acac)<sub>2</sub>. Cu(acac)<sub>2</sub> complex may be chemisorbed on TiO<sub>2</sub> particles via coordination by surface Ti-OH groups without elimination of the acac<sup>-</sup> ligand as Jin et al. indicated.<sup>[36]</sup> Cu(II) cations may be deposited on the TiO2-SiO2 matrix as crystalline CuO nanoparticles or amorphous Cu(II) oxides<sup>[27,30,46]</sup> or bound to the surface of crystalline TiO\_2 particles.  $^{\left[ 32,36,37\right] }$ 



Figure 5. Fourier transform magnitudes of the  $k^2$ -weighted Cu EXAFS spectra of Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> calculated in the R range of 1–4 Å and in the k range of 3–11 Å<sup>-1</sup> (blue solid line – experiment, red dashed line – EXAFS model).

In the first step, FEFF models were built for local coordination of Cu(II) cations in mentioned Cu species and tested on the corresponding reference Cu compounds where available (liquid Cu(acac)<sub>2</sub> precursor, crystalline Cu(acac)<sub>2</sub> and crystalline CuO) (see supporting information, Figure S-5, Table S-2).

The Cu K-edge EXAFS spectra of the Cu-modified TiO2-SiO<sub>2</sub> catalyst samples are modelled with a combined FEFF model, composed of neighbour atoms at distances characteristic for the expected Cu(II) species that may be present in the samples. A combination of three FEFF models is used, one for Cu(II) cations bound to acac<sup>-</sup> groups as in crystalline Cu(acac)<sub>2</sub> or liquid precursor, second for Cu(II) cations in crystalline CuO nanoparticles, and third for Cu(II) cations bound to the surface of crystalline TiO<sub>2</sub> particles, taking into account the structural information obtained from EXAFS analysis of the reference Cu(II) compounds (see supporting information) and theoretical predictions for possible atomic structures of CuO nanoclusters bound to the surface of crystalline  $\text{TiO}_2$  particles.  $^{[27,30,32,36]}$ 

The FEFF model included eight single scattering paths. Six oxygen atoms were included in the first coordination shell,

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arranged in a distorted octahedron (as suggested by XANES analysis): four at 1.95 Å and two at 2.35 Å. Carbon atoms were added in the second coordination shell at about 2.9 Å, to describe the contribution of Cu-O-C connections which may be preserved in Cu(acac)<sub>2</sub> from liquid precursor after drying at 150 °C. An additional shell of Ti atoms around 3.0 Å is added to the model to test Cu-O-Ti connections (Cu atoms bonded to TiO<sub>2</sub> surface, forming Cu-O-Ti bridges).<sup>[36,37,47]</sup> The Cu–Cu (R = 3.1 Å, 3.3 Å and 3.7 Å) and Cu-O (R = 3.6 Å) single scattering paths are included to detect the presence of Cu and O neighbours characteristic for second and third coordination shell in amorphous CuO or in CuO (nano)oxides which can be expected, if a part of Cu atoms are present in the form of different nanostructured CuO species.<sup>[27,36]</sup> The EXAFS model included three variable parameters for each shell of neighbours (in total 24 parameters): the coordination number (N), the distance to the neighbour atoms ( $\Delta r$ ), and the Debye-Waller factors ( $\sigma^2$ ). The amplitude reduction factor ( $S_0^2$ ) was fixed at the value of 0.8 obtained in the model of reference compounds. A shift of energy origin  $\Delta E_0$ , common to all scattering paths, was also varied.

The fits of individual spectra reveal similar structures around Cu cations in all the samples. Cu EXAFS results show that Cu atoms in all eight samples are coordinated to six oxygen atoms in a distorted octahedron: four oxygen atoms in the equatorial plane are at shorter Cu-O distance (1.94 Å -1.97 Å) and two oxygen atoms on axial positions at longer distance (2.35 Å). The second shell of neighbours consists of Ti and C atoms at 2.85 Å and 2.9 Å, respectively and Cu neighbours distributed from 3.0 Å to 3.9 Å. The presence of Cu-O-C connections indicate that Cu coordination to two acac groups, as found in in the liquid precursor, are partially preserved after drying at 150 °C, however, a part of Cu cations is bound to TiO<sub>2</sub> surface forming Cu-O-Ti connections and part of Cu cations are present in the form of CuO nanoparticles as indicated by Cu-O-Cu connections. In the fitting of the second coordination shell, the contributions of silicon backscattering were ruled out, judging from the unfavourable fit results (absence of Cu-O-Si connections).

To detect small structural differences between the samples in the local Cu neighbourhood and to minimize uncertainties of fitting parameters due to high correlations between them in the fit of individual spectra, a parallel fit of the spectra (divided in the groups of three) was performed, where some parameters for all spectra were constrained to common values and some parameters were fixed at the values obtained in the fit of reference spectra. The coordination number of nearest oxygen neighbours and their distances to Cu atom in the first coordination shell is varied for each sample. Debye-Waller factors of all paths except the first were fixed to common values for the same type of atoms (Ti, Cu and O). For all spectra, Cu-Ti distance was constrained to a common value. Number of axial O atoms and their distance to Cu atom is fixed to the known values based on the liquid Cu precursor model (two O at 2.35 Å). Number of C atoms was varied at fixed distance of 2.8 Å. At larger distances, fixed number of Cu and O atoms that belong to CuO oxide nanoparticles found in crystalline CuO. There were in total 42 independent points and 27 independent variables in the parallel fit of three spectra within the fitting range in the k interval from 3 Å<sup>-1</sup> to 11 Å<sup>-1</sup> and the *R* range of 1 Å up to 4 Å. A very good fit is obtained for all spectra (Figure 5). A complete list of the best fit parameters for all of the samples is given in the Table 3.



**Figure 7.** Histogram of relative photocatalytic activity of unmodified  $TiO_2$ - $SiO_2$  and Cu-modified  $TiO_2$ - $SiO_2$  samples dried at 150 °C, relative amount of Cu-O-Ti bonds (Red line – experiment, dashed green line – model), Cu-O-Cu bonds (blue line), and specific surface area of a given catalysts.

The most important structural difference between the Cu modified TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposites at different Cu loadings detected by EXAFS analysis is the average coordination number of Ti neighbours found in the second Cu coordination shell at 2.85 Å. Average number of Cu-O-Ti connections changes with Cu concentration (Figure 7). At low Cu loadings (from 0.05 to 0.1 mol% Cu), we found highest number of Cu-O-Ti connections (Cu is adsorbed on TiO<sub>2</sub> surface). Those samples are also most photocatalytically active. At increased Cu loadings (from 0.1 to 3 mol%), we observed drop in the average number of Cu-O-Ti connections. Average number of Cu neighbours in more distant coordination shells is almost constant, independent of Cu loading.

The presence of Cu-O-C connections clearly indicate that part of Cu(II) cations remain in the form of Cu(acac)<sub>2</sub> preserved from liquid precursor after drying. Relative number of Cu connections to organic acac<sup>-</sup> group is also independent of Cu loading. We can estimate that about 20% to 30% of Cu remains bonded to acac<sup>-</sup> groups after drying at 150 °C at all Cu concentrations. The Cu(acac)<sub>2</sub> is chemisorbed on the surface of TiO<sub>2</sub> via coordination by surface Ti–OH groups without elimination of the acac<sup>-</sup> ligands.<sup>[36]</sup>

We can explain the observed decrease of average number of Ti neighbours at higher Cu loadings (from 0.1 to 3 mol%), if

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we assume that at Cu concentrations above 0.1 mol% absolute amount of Cu directly bonded to  $TiO_2$  surface remains the same as at the concentration of 0.1mol%, independent of the Cu loading, and the remaining Cu forms CuO nanoparticles or remains attached to acac groups. The theoretical prediction of a decrease of an average number of Ti neighbours at higher Cu loadings, based on above assumption, matches with the observed measured trend (Figure 7).

The fact that average number of Cu neighbours in more distant coordination shells, attributed to Cu cations bounded in CuO nanoparticles, is approximately constant and independent of Cu loading, suggests that CuO nanoparticles do not grow to form larger particles, but rather that at higher Cu loadings, smaller CuO nanoparticles are dispersed on the surface of TiO<sub>2</sub>-SiO<sub>2</sub> matrix.

To examine the stability of the nanocomposites after drying at 150 °C, one Cu-modified photocatalyst (TS 0.08Cu) was additionally dried in vacuum (TS 0.08Cu v). The results (see supplementary information) reveal that by exposing Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst nanocomposites to vacuum Cu(II) cations in the sample are reduced to Cu(0) metal nanoparticles with fcc crystal structure and Cu(I) nanooxide particles, while Cu-O-C connections are preserved. As we already showed in our previous work<sup>[37]</sup> additional calcination of the dried Cumodified TiO2-SiO2 photocatalysts at 500 °C also induces significant structural changes of the nanocomposite: Cu-O-Ti connections are lost, Cu partially incorporates into the SiO<sub>2</sub> matrix, and amorphous copper oxides are formed. In this way the photocatalytic activity of the material is lost, so Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts is unstable if calcined or exposed to vacuum.

XRD results showed that Cu modification of TiO<sub>2</sub>-SiO<sub>2</sub> matrix, did not change anatase and brookite crystal unit cell parameters and crystallite size of the unmodified TiO<sub>2</sub>-SiO<sub>2</sub> composite, and the specific surface area of all Cu modified photocatalysts is the same or very similar as that of unmodified TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite. Also TEM and HRTEM images show that the addition of Cu does not change the morphology of TiO<sub>2</sub>-SiO<sub>2</sub> catalyst. From the observed difference in Cu local structure, we can conclude that the key feature influencing the photocatalytic activity of Cu modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts is the relative number of direct connections of Cu(II) cations to the surface of TiO<sub>2</sub> nanoparticles, distinguishing high active from low active and inactive samples.

The observed dependence of photocatalyst activity at different Cu loadings indicates a presence of two competitive mechanisms responsible for improvement or reduction of photocatalytic activity of the Cu modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts: one mechanism responsible for promoting photocatalytic activity at low Cu concentrations (from 0.05 to 0.1 mol% Cu) and inhibition mechanism strongly expressed at high Cu loadings (higher than 0.1 mol% Cu).

To understand the nature of the photocatalytic improvement/inhibition, we need to elucidate the photo-reaction mechanism of TiO<sub>2</sub>. The basic mechanism of photoinitiated oxidative transformations of organic pollutants on the TiO<sub>2</sub> surface is well-known. Water or the hydroxyl ion (OH<sup>-</sup>) is the possible trap for the valence band hole, which leads to the formation of the hydroxyl radical ('OH). Oxygen over the TiO<sub>2</sub> surface traps the covalent band electron and generates the superoxide radical anion. After charge separation, electrons and

holes migrate to the catalyst surface and participate in redox reactions.

The experimental findings of Li et al.<sup>[30]</sup> and Xin et al.<sup>[31]</sup> showed that modification of TiO<sub>2</sub> surface with Cu(II) cations may increase the photocatalytic activity at low Cu concentrations. They explained that metal to metal charge transfer in Ti-O-Cu complexes at TiO<sub>2</sub> surfaces enhance photoactivity through charge carrier separation. Our results strongly support mentioned findings of Li et al.<sup>[30]</sup> and Xin et al.<sup>[31]</sup>. We also found that that interfacial Ti-O-Cu linkages exist in a Cu modified TiO<sub>2</sub>– SiO<sub>2</sub> nanocomposite at low copper loadings and we can ascribe the enhancement of photocatalytic activity to the metal to metal charge transfer across Ti-O-Cu bridges at TiO<sub>2</sub> surfaces.

At higher Cu loadings Cu forms CuO nanoparticles or remains attached to acac groups and consequently, relative amount of Cu-O-Ti bridges is reduced. Decrease of photocatalytic activity at higher Cu concentrations can be ascribed to the shielding effect<sup>[48]</sup> of CuO on the TiO<sub>2</sub> surface that prevents the access of pollutants to the photoactive surface of TiO<sub>2</sub> and hinders its photocatalytic activity. The mechanism of inhibition of TiO<sub>2</sub> photocatalytic activity by CuO nanoclusters on its surface is additionally supported by findings of G. Li et al.<sup>[30]</sup>, who showed that CuO nanoparticles on TiO<sub>2</sub> surface decrease photocatalytic activity due to charge transfer from TiO<sub>2</sub> to CuO and subsequent charge recombination in CuO nanoparticles.

## Conclusions

In this research we have shown that modification of TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts with low amount of copper, synthesized by low temperature sol-gel synthesis based on organic Si, Ti, and Cu precursors leads to increased photocatalytic activity under UV/Vis irradiation. Photocatalytic activity measurements showed up to three times increase in photocatalytic activity of air dried photocatalysts when TiO<sub>2</sub>-SiO<sub>2</sub> matrix is modified with Cu in a narrow concentration range from 0.05 to 0.1 mol%. At higher Cu concentrations dried samples exhibit smaller photocatalytic activity compared to the unmodified reference TiO2-SiO2 photocatalyst. All samples exhibit predominantly nanocrystalline anatase crystal structure of TiO2 with a smaller amount of brookite phase, with the same crystal unit cell parameters and same crystal sizes as in unmodified TiO2-SiO2 photocatalyst, independent of the relative amount of Cu in the TiO2-SiO2 matrix. SiO<sub>2</sub> is in the form of glass-like amorphous silicate nanoparticles. Cu-modified samples containing low amount of copper (from 0.05 to 0.1 mol%) showed largest number of Cu-O-Ti connections, and consequentially increased photocatalytic activity. Metal to metal charge transfer in Ti-O-Cu complexes at TiO<sub>2</sub> surfaces enhances photoactivity through charge carrier separation. At higher Cu loadings (more than 0.1 mol% Cu), average number of Cu-O-Ti connections decreases, major part of Cu cations formed amorphous or nanocrystalline Cu(II) oxide nanoparticles on the surface of TiO<sub>2</sub> and photocatalytic activity of the material is hindered.

 $\sigma^2$  [Å<sup>2</sup>]

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R-factor

# **FULL PAPER**

Table 3. Parameters of the nearest coordination shells around Cu atoms in Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub>: N - the number of neighbour atoms, R - distance,  $\sigma^2$  -

is obtained wi	th the amplitude	e reduction facto	$r S_0^2 = 0.8 \text{ eV}.$	neter. The best			TS_0.3Cu		
Cu	N	<i>R</i> [Å]	σ² [Ų]	R-factor	0	3.8(3)	1.956(6)	0.004(1)	
neighbour					0	2	2.35	0.02	
		TS_0.05Cu			С	1.0(5)	2.8	0.008	
0	4.7(5)	1.943(8)	0.006(2)		Ti	0.2(3)	2.80(3)	0.009	0.0068
0	2	2.35	0.02		Cu	1.3(4)	3.15(4)	0.009	
С	1.0(5)	2.8	0.008		Cu	2	3.37(4)	0.009	
Ti	0.8(5)	2.80(3)	0.009	0.0063	0	2	3.8(1)	0.01	
Cu	1.4(6)	2.93(6)	0.009		Cu	1	3.9(1)	0.01	
Cu	2	3.12(5)	0.009				TS_0.5Cu		
0	2	3.71(9)	0.01		0	3.9(5)	1.956(6)	0.004(2)	
Cu	1	3.94(7)	0.01		0	2	2.35	0.02	
		TS_0.08Cu			С	1.0(5)	2.8	0.008	
)	4.0(5)	1.974(8)	0.005(2)		Ti	0.3(4)	2.80(3)	0.009	0.0068
)	2	2.35	0.02		Cu	0.5(7)	3.2(1)	0.009	
	1.0(5)	2.8	0.008		Cu	2	3.48(3)	0.009	
ï	1.0(4)	2.80(3)	0.009	0.0063	о	2	3.6(1)	0.01	
Cu	1.4(6)	3.03(2)	0.009		Cu	1	3.7(1)	0.01	
Cu	2	3.25(3)	0.009				TS_1Cu		
)	2	3.8(1)	0.01		0	3.8(3)	1.962(6)	0.003(1)	
Cu	1	3.91(7)	0.01		0	2	2.35	0.02	
		TS_0.1Cu			с	1.0(5)	2.8	0.008	
)	3.7(5)	1.974(8)	0.004(2)		ті	<0.1	2.85	0.009	0.0075
)	2	2.35	0.02		Cu	0.8(9)	3.3(1)	0.009	
;	1.0(5)	2.8	0.008		Cu	2	3.50(7)	0.009	
1	0.6(5)	2.80(3)	0.009	0.0063	0	2	3.6(1)	0.01	
Cu	2.3(9)	3.03(2)	0.009		Cu	1	3.79(5)	0.01	
Cu	2	3.28(4)	0.009			· ·	TS_3Cu		
)	2	3.8(1)	0.01		0	3 6(3)	1,958(6)	0.004(1)	
u	1	3.9(1)	0.01	Y	0	2	2.35	0.02	
_		TS_0.15Cu			С	-	2.8	0.008	
)	4.1(4)	1.956(6)	0.006(1)		Ti	<0.1	2.85	0.000	0.0075
)	2	2.35	0.02		Cu	1 2(6)	3 12(3)	0.000	
	1.0(5)	2.8	0.008		Cu	۰. <u>در</u> ن) م	3 35(1)	0.009	
ï	0.4(3)	2.80(3)	0.009	0.0068	0	2	3.50(0)	0.009	
Cu	2.6(4)	3.03(2)	0.009		Cu	∠ 1	3.02(5)	0.01	
)u	2	3.25(3)	0.009			1	J.93(0)	0.01	
	2	3.85(7)	0.01						
Cu	1	3.80(5)	0.01						

Cu

N

R [Å]

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## **Experimental Section**

Synthesis of Cu-modified TiO2-SiO2 photocatalysts



Figure 8. Diagram of sol-gel synthesis of Cu-modified  $\text{TiO}_2\text{-}\text{SiO}_2$  photocatalysts.

Low temperature sol-gel method was used to synthesize Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts with different copper concentrations (0.05, 0.08, 0.1, 0.15, 0.3, 0.5, 1 and 3 mol%). We have revised a formerly proposed synthesis method<sup>[49]</sup>, as described in detail in our previous publication.<sup>[37]</sup> The chemicals used for synthesis were titanium tetraisopropoxide (TTIP), tetraethyl ortosilicate (TEOS) and colloidal SiO<sub>2</sub>, and copper acetlyacetonate (Cu(acac)<sub>2</sub>) as Ti, Si and Cu sources (Figure 8). For the TiO<sub>2</sub>-SiO<sub>2</sub> colloidal solution we prepared silica binder from tetraethyl orthosilicate (TEOS), colloidal SiO<sub>2</sub> Levasil 200/30% aqueous solution, HCl to catalyse TEOS hydrolysis and after 1h of mixing 1-propanol was added. The  $TiO_2$  sol was prepared by dissolving titanium tetraisopropoxide (TTIP) in absolute ethanol. In the first step, double deionized water and perchloric acid were mixed separately. This solution was then added to the TTIP solution drop-wise, under reflux and heating, where exothermic reaction of uncontrolled hydrolysis and condensation of TTIP took place, gaining white precipitate of hydrated amorphous TiO2. After heating and refluxing for 48 h, a stable translucent TiO<sub>2</sub> sol was obtained. The TiO<sub>2</sub>-SiO<sub>2</sub> sol (denoted TS) was obtained by adding silica binder solution to TiO<sub>2</sub> sol. The sol was further diluted with double deionized water and organic solvents (1-propanol and 2-propoxyethanol). Copper cations were added by direct incorporation during the sol-gel synthesis. Cu(acac)<sub>2</sub> dissolved in 2-propoxyethanol, used as a source of copper, was added into the TiO2-SiO2 sol. All TiO2-SiO2 sols (unmodified and Cu-modified) were dried at 150 °C for 1 h, to obtain unmodified TiO2-SiO<sub>2</sub> and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> catalysts with different copper concentrations (0.05, 0.08, 0.1, 0.15, 0.3, 0.5, 1 and 3 mol%), denoted as TS, TS\_0.05Cu, TS\_0.08Cu, TS\_0.1Cu, TS\_0.15Cu, TS\_0.3Cu, TS\_0.5Cu, TS\_1Cu, TS\_3Cu, respectively. One Cu modified photocatalyst (TS\_0.08Cu) was additionally dried in vacuum at room temperature (sample denoted as TS\_0.08Cu\_v) to examine the stability of the Cu species, present in the Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> nanocomposite photocatalysts after drying at 150 °C in air, if the photocatalyst is additionaly dried in vacuum.

### Characterization

### Photocatalytic activity tests

The photocatalytic activity of the unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> catalysts in the powder form was determined using a fluorescence-based method of terephthalic acid decomposition. The stock solution of TPA was prepared by mixing together TPA<sup>[50]</sup> (130 mg) and aqueous solution of NaOH (1L, 2.10-3 M).<sup>[38]</sup> Working solution of TPA (100 mL, 83 mg/L) was freshly made prior to photocatalytic experiments. 25 mL of TPA working solution and 10 mg of photocatalyst were mixed in 25 mL of double deionized water and stirred under sunlight irradiation. Samples (1 mL) of the aqueous solution were taken from the 100 mL glass beaker at different UV irradiation times (0 min, 5 min, 10 min, 15 min, 20 min, 30 min, and 45 min) and centrifuged (1300 min<sup>-1</sup>) for 3 min. A fixed volume (159 µL) of the solution was then sampled with an automatic pipette, and transferred into microtiter plate wells (microtiter plate with 96 wells, flat bottom, black) for fluorescence measurements. Photocatalytic tests were carried out in solar simulator (Suntest XLS+, Atlas, USA) chamber with a simulated solar irradiation source (Xenon lamp), using daylight filter (300-800 nm), at UV light flux of 750 W/m<sup>2</sup>. During irradiation in the presence of the photocatalyst, TPA is decomposed and highly fluorescent 2-hydroxyterephthalic acid (HTPA) is formed as an intermediate oxidation product. Fluorescence measurements were performed using a microplate reader in the fluorescence mode (Infinite F200 Microplate reader, Tecan, Switzerland). The wavelength of the excitation light was 320 nm (filter bandwidth: 25 nm) and emission was measured at 430 nm (filter bandwidth: 35 nm). The instrument was operating in top mode with 25 reads per well, with 20 µs integration time. The amplification factor for the photomultiplier tube was 56. For each irradiation time, at least four parallel photocatalytic tests were done. Measurements of HTPA concentrations were performed in the time interval from 0 to 45 minutes.

### XRD

The crystal structures of unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> samples were investigated by X-ray diffraction (MiniFlex Benchtop 300/600, 150) using Cu K $\alpha$  irradiation from 10 to 80° at a scan rate of 2°/min. Quantitative phase composition analysis was performed using Rietveld refinement method by the High Score Plus software. The crystallite size was determined from XRD pattern, using Scherrer formula:

d =	(0.9λ/β	cos	θ)
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where *d* is the crystallite size in nm,  $\lambda$  is the wavelength of X-ray in Å (1.5418 Å),  $\beta$  is the full width of diffraction peaks at half maxima (FWHM) in radians, and  $\theta$  is the Bragg angle.

#### N<sub>2</sub>-physisorption

The specific surface area of the unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst samples was evaluated from N<sub>2</sub> sorption isotherms obtained at 77 K using a Tristar 3000 Micromeritics volumetric adsorption analyser. The BET specific surface area<sup>[51]</sup> was calculated from adsorption data in a relative pressure range from 0.05 to 0.25. The pore size distributions (PSDs) were calculated from nitrogen adsorption data using the Barrett-Joyner-Halenda (BJH) method.<sup>[52]</sup>

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### TEM /STEM/EDX

Unmodified and Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalyst samples for TEM/STEM/EDX characterization have been prepared by immersing a Lacey-carbon TEM grid in a water suspension and air-dried at room temperature. The electron microscopy analysis has been performed by means of a Field-Emission Transmission Electron Microscope (JEM-2100F, JEOL) operated at 200 kV. The microscope is equipped with a STEM unit and a detector for EDX mapping and spectroscopy (X-MAX80, Oxford).

#### X-ray absorption spectroscopy

The local atomic structure and the chemical state of copper cations in Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts were analysed by X-ray absorption spectroscopy methods XANES and EXAFS. Cu K-edge absorption spectra of the prepared photocatalyst samples were recorded at room temperature in transmission and fluorescence detection mode at the XAFS beamline of the ELETTRA synchrotron radiation facility in Trieste, Italy, and at P65 beamline of PETRA III, DESY, Hamburg, Germany. The Cu-modified TiO2-SiO2 samples were prepared in the form of homogenous pellets, pressed from micronized powder mixed with BN. In all cases the total absorption thickness (µd) of the sample was about 2 above the Cu K-edge. A Si (111) double crystal monochromator was used with energy resolution of 1 eV at Cu K-edge. The intensity of the monochromatic X-ray beam was measured by three consecutive ionization detectors (XAFS beamline: 30 cm long ionisation chambers filled with gas mixtures: (first) 1250 mbar N2, 750 mbar He; (second) 250 mbar Ar, 1000 mbar  $N_2$  750 mbar He; (third) 1000 mbar  $N_2$ , 300 mbar He, 700 mbar Ar; P65 beamline: 5 cm long ionisation chambers filled with: (first) 1000 mbar N<sub>2</sub>, (second) 1000 mbar Ar, (third) 1000 mbar Kr). The samples were mounted on the sample holder placed after the first ionization detector. For fluorescence detection, the samples were rotated 45° with respect to the X-ray beam. The absorption spectra were measured in the energy region from -150 eV to +1000 eV relative to the Cu K-edge. In the XANES region equidistant energy steps of 0.25 eV were used, while for the EXAFS region equidistant k steps of 0.03  $Å^{-1}$ were adopted, with an integration time of 2s/step for transmission measurements. For samples with low Cu concentration, fluorescence detection mode was used, with SDD fluorescence detector at XAFS beamline, and 7-pixel Ge detector at P65 beamline, to measure the intensity of Cu K-alpha emission line. At both beamlines we used 100micron thick aluminium foil as a filter to reduce Ti K-alpha signal from the sample. Three to eight repetitions of the scans with integration time of 5s/step, were superimposed to improve signal-to-noise ratio. The exact energy calibration was established with simultaneous absorption measurement on a 5-micron thick Cu metal foil placed between the second and the third ionization chamber. The first inflection point in the spectrum of the copper K-edge in the Cu metal with fcc crystal structure is at 8979.0 eV Absolute energy reproducibility of the measured spectra was ±0.03 eV. The quantitative analysis of EXAFS spectra is performed with the IFEFFIT program package<sup>[39]</sup> in combination with FEFF6 program code<sup>[45]</sup> for ab initio calculation of photoelectron scattering paths.

## Acknowledgements

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**Keywords:** titanium dioxide, Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts, photocatalytic activity, Cu K-edge XANES, EXAFS.

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## Layout 1:

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**Optimal Cu loading:** Cu-modified TiO<sub>2</sub>-SiO<sub>2</sub> is synthesized using lowtemperature sol-gel method, with Cu concentrations from 0.05 to 3 mol%. Photocatalytic activity is increased up to three times for Cu concentrations from 0.05 to 0.1 mol%, due to metal to metal charge transfer in Ti-O-Cu complexes at TiO<sub>2</sub> surfaces. At higher Cu loadings CuO nanoparticles on the surface of TiO<sub>2</sub> hinder photocatalytic activity of the material.



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## Page No. – Page No.

Effects of different Cu loadings on photocatalytic activity of TiO<sub>2</sub>-SiO<sub>2</sub> prepared at low temperature for oxidation of organic pollutants in water