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On the mechanism of photocatalytic reactions on $Cu_xO@TiO_2$ core-shell photocatalysts

 $Cu_xO@TiO_2$ (anatase) photocatalysts, prepared by a microemulsion method, exhibit high activity and stability under long-term UV irradiation. Based on XPS analysis, it is proposed that improved photocatalytic performance under UV irradiation originates from the Z-scheme mechanism, whereas inactivity under vis irradiation (type-II heterojunction) results from the charge-carrier recombination.





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1. Introduction

The development of photocatalytic processes is still mainly connected with materials based on titanium(v) oxide (TiO₂, titania), which has been widely known as an efficient, stable and green semiconductor with photocatalytic performance and used

On the mechanism of photocatalytic reactions on $Cu_xO@TiO_2$ core-shell photocatalysts[†]

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Titania (titanium(IV) oxide) is a highly active, stable, cheap and abundant photocatalyst, and is thus commonly applied in various environmental applications. However, two main shortcomings of titania, i.e., charge carrier recombination and inactivity under visible-light (vis) irradiation, should be overcome for widespread commercialization. Accordingly, titania has been doped, surface modified and coupled with various ions/compounds, including narrower bandgap semiconductors, such as oxides of copper and silver. Unfortunately, these oxides are not as stable as titania, and thus loss of activity under longterm irradiation (photo-corrosion) has been observed. Therefore, this study has focused on the preparation of stable coupled photocatalysts, *i.e.*, Cu_xO@TiO₂ core-shell nanostructures, by the microemulsion method from commercial Cu₂O as a core and TiO₂ (ST01-fine anatase) as a shell. The photocatalysts have been characterized by DRS, SEM, TEM, XRD, XPS and reversed double-beam photoacoustic spectroscopy (RDB-PAS) methods, and activity tests under UV (anaerobic dehydrogenation of methanol and oxidative decomposition of acetic acid) and vis (phenol oxidation) irradiation. The higher activities of coupled photocatalysts than their counterparts have been found in all studied systems under UV/vis irradiation. Moreover, long-term experiments (10 h) have shown high stability of Cu_{*}O@TiO₂. However, the change of oxidation state of copper has also been observed, *i.e.*, to negative and positive values, confirming the charge transfer according to the Z-scheme under UV irradiation and type-II heterojunction under vis irradiation, respectively. The property-governed activity and the mechanism have been discussed in detail.

in water treatment, air purification, synthesis of chemical compounds, self-cleaning surfaces and renewable energy processes, such as photocurrent generation and water splitting for hydrogen production.¹⁻⁶ Although titania has been recognized as one of the best photocatalysts, two main shortcomings must be overcome for broader and commercial application, *i.e.*, charge carrier recombination (typical for all semiconductors), and inactivity under vis irradiation (due to the wide bandgap of titania, *i.e.*, *ca.* 3.0–3.2 eV).

To overcome these limitations, different strategies for the preparation of titania-based materials have been considered, *e.g.*, (i) doping with cations and anions, (ii) surface modification with various molecules and particles, (iii) formation of advanced-morphology materials (faceted, mesocrystals, and inverse opals), and (iv) coupling with other semiconductors.⁷ Accordingly, designing coupled photocatalysts, composed of TiO₂ and other metal oxides, to establish the heterojunction is an important way to enhance the charge carrier (electron-hole) separation (increasing the lifetime of charge carriers) and to obtain vis-responsive materials (in the case of oxides with a narrower bandgap than that of titania).⁸ Copper oxides (p-type semiconductors) have been considered as good candidates to

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form an efficient heterojunction with TiO2, i.e., Cu2O and CuO with bandgap energies of *ca.* 2.1 eV and 1.7 eV, respectively. In particular, among copper oxides, the selection of Cu₂O provides a promising strategy to prepare hybrid photocatalysts with high activity and good antipathogenic properties.9,10 Moreover, the Cu₂O/TiO₂ p-n heterojunction has been described as an efficient photocatalyst for degradation of organic compounds and hydrogen generation.^{8,11-14} It has been reported that even simple physical mixing of copper(I) oxide and titania (grinding) results in the formation of an efficient photocatalyst.13 The high efficiency of such material has been observed for UV/Vis-induced acetic acid oxidation, and two mechanistic variants of this heterojunction depending on the form of TiO₂ have been suggested: Z-scheme and heterojunction-type II for anatase and rutile-based samples, respectively. Furthermore, Cu₂O/TiO₂ photocatalysts have exhibited high bactericidal and fungicidal properties.13 However, loss in the activity during long-term irradiation has been observed because of the low stability of Cu₂O (photocorrosion), *i.e.*, dissolution of copper from the photocatalyst surface (e.g., $Cu^+ \rightarrow Cu^{2+}$).^{15,16} Therefore, preventing copper loss during photocatalytic reactions is the most important goal for efficient and stable Cu₂O/TiO₂ photocatalysts. For example, Wang et al. reported that a titania protective layer on Cu₂O significantly increased the stability and activity of the Cu₂O/CuO photocatalyst.17

The design of the coupled photocatalysts is also connected with the character of interactions between the two main components (metal oxides) forming the heterojunction. It has been proposed that the formation of core-shell structures is a promising strategy since such materials show the integration of individual components into a functional system that brings about an improvement in the physical and chemical properties (e.g., stability, dispersibility, and multi-functionality), which could not be achieved for the components without good and/or stable contact.18,19 Particularly, core@shell TiO2-structured materials have been recommended not only due to their enhanced activity and stability, but also improved separability, e.g., when magnetic oxides are used as a core.^{20,21} Considering Cu₂O, the main problem arises from its poor stability (photocorrosion) in an aqueous environment. Therefore, the preparation of Cu₂O(core)@TiO₂(shell) systems might allow this phenomenon to be avoided, and consequently improve the overall photocatalytic performance. Su et al. obtained stable core-shell Cu₂O/TiO₂ nanocomposites, in which the TiO₂ layer uniformly covers each Cu₂O octahedral particle.²² In other studies, Cu2O photocathodes, protected by a thin coating of Al-doped ZnO/TiO₂ or TiO₂ layer, exhibit high activity for photoelectrochemical water reduction, photoelectrocatalysis and CO2 reduction.²³⁻²⁵ In the present study, the microemulsion method, successfully applied to synthesize core-shell structured titaniabased materials (e.g., magnetic photocatalysts),²⁶ has been applied for the first time to prepare core-shell CuxO@TiO2 photocatalysts.

2. Materials and methods

Two commercially available TiO_2 photocatalysts, P25 (AERO-XIDE® TiO_2 P25, mixed-phase titania, specific surface area (SSA) = 52 m² g⁻¹ and crystal sizes equal to *ca.* 25 nm and 40 nm for anatase and rutile, respectively,²⁷ Nippon Aerosil, Tokyo, Japan) and ST01 (ST-01, fine anatase, SSA = 298 m² g⁻¹ and crystal size of 8 nm, Ishihara Sangyo, Osaka, Japan), have been used in this study, *i.e.*, P25 as a reference titania sample (known as one of the most active titania photocatalysts) and ST01 as a shell layer. Cuprous oxide, used as a core, was supplied by Wako Pure Chemicals, Tokyo, Japan. Other chemicals, including cyclohexane, isopropanol, acetone, hydrochloric acid, ammonia solution, methanol, acetic acid, cetyltrimethylammonium bromide (CTAB, 98%) and dioctyl sulfosuccinate sodium salt (AOT), were provided by Wako Pure Chemicals. All reagents were of analytical grade, and were thus used without further purification.

Preparation of the Cu₂O@TiO₂ core-shell heterojunction

The water-in-oil (w/o) microemulsion method was applied for the preparation of Cu_xO@TiO₂ core-shell photocatalysts. In this system, the nanodroplets of the aqueous phase have been dispersed in a continuous oil phase, stabilized by the surfactant and co-surfactant at the w/o interface. The Cu2O core was successfully covered with the titania shell layer using the changes in zeta potential of Cu₂O and TiO₂ as a function of pH value (Fig. 1), firstly proposed by Zielińska-Jurek et al. for Fe₃-O4@SiO2@TiO2 (core/interlayer/shell) particles.26 The Cux-O@TiO₂ photocatalysts were obtained via two variants of the microemulsion method, *i.e.*, under acidic (pH < 5) and basic (pH > 11) conditions. In the acidic variant, cuprous oxide was dispersed in an anionic AOT water solution and the pH was set to a value of 5 by adding of 0.1 M HCl solution. The molar ratio between water and surfactant was set at 30. The prepared solution was then dropwise added to a cyclohexane/isopropanol (100:6 volume ratio) oil phase and stirred for 2 h to stabilize the microemulsion. After stabilization, the corresponding amount of TiO₂ was added to the system and stirred for 18 h. Afterwards, the microemulsion was destabilized with acetone, washed with deionized water, dried at 80 °C for 24 h and ground in an agate mortar. A similar procedure was performed in the basic variant, but with cationic CTAB as the surfactant and at a pH value of 11, set by adding ammonia solution. The junction



Fig. 1 Zeta potential of Cu_2O and TiO_2 (ST01) suspensions as a function of pH value.

between the Cu_2O core and TiO_2 shell was promoted by their opposite surface charges, provided by the presence of anionic and cationic surfactants under acidic and basic conditions, respectively. The Cu_2O content was set to 1, 2, 5, 10 and 50 wt% of the composite.

The radius of the water in oil droplets (R_w) has been calculated, based on eqn (1),²⁸ and found to reach *ca.* 2.3 µm. Therefore, it is assumed that efficient coverage of the Cu₂O core by the TiO₂ shell inside the micelle is possible considering the sizes of their crystallites, *i.e.*, *ca.* 88 nm for Cu₂O and 8 nm for TiO₂ (and even aggregated particles, *i.e.*, 100–1000 nm and 20–60 nm, respectively, as shown in Fig. S1–S4 in the ESI†).

$$R_{\rm w} = \frac{3V_{\rm aq}}{\sigma} \frac{[\rm H_2O]}{[\rm S]} \ [\rm nm] \tag{1}$$

where $V_{\rm aq}$ is the volume of water molecules (water volume) [dm³], σ is the area per polar head [nm²], and [H₂O]/[S] is the water/surfactant ratio. For CTAB the σ value is 4.23 × 10⁻⁴ nm², according to Haq *et al.*,²⁹ and $V_{\rm aq}$ and [H₂O]/[S] have been set to 0.0108 dm³ and 30, respectively, resulting in $R_{\rm w}$ of 2.29 × 10³ nm.

Characterization of photocatalysts

The morphology of samples and distribution of elements were investigated using a scanning transmission electron microscope equipped with an energy-dispersive X-ray spectrometer (STEM-EDS, HD-2000, HITACHI, Tokyo, Japan). The specific surface area of the samples was estimated by nitrogen adsorption at 77 K using the Brunauer-Emmett-Teller (BET) equation. The photoabsorption properties of the prepared photocatalysts were analyzed by diffuse reflectance spectroscopy (DRS; JASCO V-670 equipped with a PIN-757 integrating sphere, JASCO, LTD., Pfungstadt, Germany). Barium sulfate and bare titania (ST01) were used as references for DRS analysis. Crystalline properties were analyzed by X-ray powder diffraction (XRD; Rigaku Intelligent XRD SmartLab with a Cu target, Rigaku, LTD., Tokyo, Japan). Crystallite sizes of anatase, rutile and copper were estimated using the Scherrer equation. The chemical composition of the surface (content and chemical state of elements, i.e., titanium, oxygen and copper) was determined by X-ray photoelectron spectroscopy (XPS; JEOL JPC-9010MC with MgKa Xrays, JEOL, LTD., Tokyo, Japan). The dependence of the surface charge of bare semiconductors on the pH value was measured as zeta potential. 0.1 g of semiconductor (Cu₂O or TiO₂) was dispersed in 100 mL of distilled water and continuously stirred using a magnetic stirrer. The pH value was set by adding 0.1 M HCl and 0.1 M NaOH solutions, and the changes were monitored using an Elmetron multifunction meter, CX-505, equipped with an EPS-1 14600/14 pH electrode (Elmetron, Zabrze, Poland). After the pH value was set, the sample was taken with a syringe and placed in a disposable folded capillary cell (DTS1070, Malvern Instruments Ltd., Malvern, UK). The measurement of zeta potential was performed using a Malvern Nano Zetasizer (Malvern Instruments Ltd., Malvern, UK).

The energy-resolved distribution of electron traps (ERDT) patterns and conduction band bottom (CBB) position were

analyzed by reversed double-beam photoacoustic spectroscopy (RDB-PAS) and photoacoustic spectroscopy (PAS), respectively, as described elsewhere.³⁰ In brief, for RDB-PAS measurement, the sample was filled in a stainless-steel sample holder in a home-made PAS cell equipped with an electret condenser microphone and a Pyrex window on the upper side. Methanolsaturated nitrogen was flowed through the cell for 30 min, the cell was irradiated by a 625 nm light-emitting diode beam (Luxeon LXHL-ND98, LUMILEDS, San Jose, CA, USA), modulated at 35 Hz by a function generator (DF1906, NF Corporation, Yokohama, Japan) as modulated light, and a monochromatic light beam from a Xe lamp (ASB-XE-175, Spectral Products, Putnam, CT, USA) equipped with a grating monochromator (CM110 1/8 m, Spectral Products, CT, USA) as continuous light. The continuous light was scanned from 650 to 300 nm with a 5 nm step. The RDB-PA signal was detected using a digital lock-in amplifier (LI5630, NF Corporation). The obtained spectrum was differentiated from the lower-energy side and calibrated with the reported total electron-trap density in units of μ mol g⁻¹, measured using a photochemical method³¹ to obtain an ERDT pattern. For PAS measurements, the cell window was irradiated from 650 to 300 nm by a light beam from a Xe lamp (ASB-XE-175, Spectral Products) with a grating monochromator (CM110 1/8m, Spectral Products, CT, USA) modulated at 80 Hz by a light chopper (5584A, NF Corporation, Japan) to detect the PAS signal using a digital lock-in amplifier, and then photoacoustic (PA) spectra were calibrated using the PA spectrum of graphite as a reference. The CBB, as energy from the top of the valence band (VBT), of the samples was calculated from the onset wavelength corresponding to the bandgap of the samples.

Photocatalytic activity tests

The photocatalytic activity of the samples was evaluated under UV/vis irradiation for (1) oxidative decomposition of acetic acid (CO₂ system; CO₂ evolution), and (2) anaerobic dehydrogenation of methanol (H2 system; H2 evolution), and under vis irradiation for (3) oxidation of phenol. For activity tests, (1 and 2) 50 mg and (3) 10 mg of photocatalyst was suspended in 5 mL of aqueous solution of (1) acetic acid (5 vol%), (2) methanol (50 vol%), and (3) $0.21 \text{ mmol } \text{L}^{-1}$ phenol in 35 mL Pyrex test tubes. The tubes were sealed with rubber septa, and the suspensions were continuously stirred in a thermostated water bath and irradiated by (1 and 2) Hg lamp (λ > 290 nm) and (3) Xe lamp (λ > 420 nm; water IR filter, cold mirror and cut-off filter Y-45, in a reactor shown in ref. 32). For methanol dehydrogenation, suspensions containing titania and methanol were pre-bubbled with Ar for 15 min to remove oxygen from the system. The amounts of (1) generated hydrogen, (2) liberated carbon dioxide, and (3) phenol and benzoquinone (main degradation product) were determined by chromatography: (1 and 2) GC-TCD (detection of the gas phase amount every (1) 20 min and (2) 15 min) and (3) HPLC.

Commercial titania P25 (Degussa/Evonik) was used as a reference sample since P25 has one of the highest photocatalytic activities among various titania samples in different reaction systems (oxidation and reduction^{27,33,34}), and is thus commonly used as a "standard" titania sample.

3. Results and discussion

Preparation of Cu₂O@TiO₂ core-shell particles

The zeta potential values of the suspensions of bare Cu_2O and TiO_2 samples as a function of pH value are shown in Fig. 1. The analysis is crucial for the proper selection of the microemulsion environment, particularly pH value and surfactant kind, in order to ensure efficient coverage of Cu_2O by TiO_2 . It is known that titania nanoparticles (NPs) are positively charged at pH values below 5. Indeed, in the case of the ST01 titania suspension, the isoelectric point (IEP; zeta potential equal to zero) appears at a pH value of *ca*. 6.3. The IEP of cuprous oxide occurs almost in the whole range of pH values between 8 and 9. Above and below these values, NPs are negatively and positively charged, respectively.

In the present study, Cu_xO (m_xO) TiO₂ photocatalysts have been obtained *via* two variants of the microemulsion method, *i.e.*, under acidic (pH < 5) and basic (pH > 11) conditions. For the successful covering of Cu₂O by the TiO₂ shell, it is necessary to introduce charge-changing surfactants since the substrates possess the same surface charge (both positively and negatively charged at pH values of 5 and 11, respectively).²⁶ Therefore, under acidic conditions, the anionic AOT surfactant changes the surface charge of Cu₂O in order to self-assemble with positively charged TiO₂. An analogous procedure, with the use of cationic CTAB surfactant, has been applied under basic conditions. The samples prepared under basic conditions show higher activity, and thus this manuscript presents these samples.

Characterization of Cu₂O@TiO₂ samples

The DRS spectra of all modified and bare samples are shown in Fig. 2a and b. The absorption in the UV range is due to the intrinsic interband absorption of titania (*ca.* 3.2 eV), while the absorption in the vis range is caused by the presence of copper. All $Cu_xO@TiO_2$ samples are colored, and the color intensity (from light blue to dark blue-grey) increases with the content of



Fig. 2 Properties of the samples: (a and b) DRS spectra recorded with $BaSO_4$ (a) and bare TiO_2 (b) as references; (c) photographs of the samples; (d) XRD patterns.

 Cu_2O (Fig. 2c), as confirmed by the absorption spectra (Fig. 2a and b). However, the spectra in the vis range do not resemble the shape of Cu₂O absorption (intense absorption in the range of 400-650 nm), except for that of the 50% Cu_rO@TiO₂ sample (due to the insufficient content of TiO₂ to fully cover the Cu₂O core, as shown in Fig. 3a-c and S3[†]). Interestingly, samples prepared by grinding (the same Cu₂O and TiO₂; previous study⁹) have shown a different color (pink) and DRS spectra resembling Cu₂O absorption in the vis range (a clear peak with a maximum at ca. 550 nm). Similarly, other reports on Cu₂O-modified photocatalysts have shown photoabsorption spectra correlating with Cu₂O absorption in the vis range, e.g., for Cu₂O/TiO₂ (ref. 16 and 35-38) and Cu₂O/Si³⁹ samples. Therefore, it is expected that mainly different forms of copper are responsible for vis absorption, *i.e.*, (i) in the range of 400–500 nm: mixed oxides of copper, *i.e.*, Cu^+/Cu^{40} and Cu_xO/TiO_2 (x: 1–2, due to interfacial charge transfer (IFCT) from the valence band of TiO₂ to the Cu_xO ,⁴¹ and (ii) at wavelengths longer than 500 nm: CuO,^{42,43} Cu(OH)₂ (blue samples),⁴⁴ and d-d transitions of Cu²⁺ species.⁴⁵ The most similar spectra (to data shown in Fig. 2a) have been obtained by Park et al. for CuxO/TiO2, prepared by annealing a Cu@Cu2O nanocomposite mixed with a titania precursor (TiCl₄).⁴⁶ It has been suggested that the formation of a heterojunction between Cu_xO and TiO₂ is responsible for vis absorption in the range of 400-600 nm, while absorption at 600-1000 nm is caused by the $^2E_{\rm g} \rightarrow \ ^2T_{\rm 2g}$ interband transitions in the Cu²⁺ clusters. Accordingly, it is proposed that the conditions during microemulsion might influence the properties of less stable oxides than titania, such as Cu₂O, changing their oxidation state, and thus resulting in the formation of mixedoxidation-state materials (as confirmed also by XPS data discussed in the following part).

The XRD patterns for all photocatalysts are shown in Fig. 2d, while the crystalline composition and crystallite sizes are listed



Fig. 3 STEM images of $Cu_xO@TiO_2$ samples with different Cu_2O contents: 50% (a–c) and 2% (d–f).

Table 1 The properties of the bare and composite samples⁴

		TiO ₂ (anatase)		Cu ₂ O			
Sample	Color	(%)*	Size (nm)	(%)*	Size (nm)	area $(m^2 g^{-1})$	
TiO ₂	White	100	8.6	_		310.8	
Cu ₂ O	Red	_	_	100	87.9	2.6	
1% Cu _x O@TiO ₂	Light blue	99.1	8.6	0.9	72.4	202.4	
2% Cu _x O@TiO ₂	Light blue	98.8	8.6	1.2	54.4	251.2	
5% Cu _x O@TiO ₂	Blue	95.5	8.6	4.7	68.0	238.3	
10% Cu _x O@TiO ₂	Blue/grey	88.8	8.3	11.2	60.4	231.3	
50% Cu _r O@TiO ₂	Dark blue/grey	57.9	8.2	42.1	63.6	170.4	

in Table 1. Titania (ST01) is composed of anatase, as proven by clear peaks at ca. 25°, 37-39°, 48°, 52-55°, 62-63°, 74-76° and 82-83°, with fine crystallites of ca. 8.6 nm. In the case of bare Cu₂O and 50% Cu₂O samples, clear peaks for cubic cuprous oxide could be detected at 29.63°, 36.37°, 42.45°, 61.64° and 73.75° . For the 10% Cu₂O sample, only the main {111} peak of Cu₂O could be observed in the XRD pattern. However, for the samples with lower than 10 wt% content of Cu₂O only highly enlarged patterns and Rietveld analysis could confirm the presence of copper species. It should be pointed out that the formation of core/shell structures with Cu₂O by the microemulsion method does not influence the crystalline properties of titania, as expected since titania is well known for its high chemical and thermal stability. However, a decrease in the crystalline size of Cu₂O has been observed (from 88 nm to 54 nm), probably as a result of alkaline treatment (pH value change during microemulsion). The crystalline content of titania in the coupled samples correlates well with that used for sample preparation, i.e., reaching 99.1%, 98.8%, 95.5%, 88.8% and 57.9% of TiO₂ for 1%, 2%, 5%, 10% and 50% Cu_xO@TiO₂ samples, respectively.

The morphology of the samples has been investigated by STEM microscopy with EDS mapping, and the obtained results are shown in Fig. 3, 4 and S1-S3 (ESI⁺). It should be remembered that commercial samples of TiO₂ and Cu₂O have been used for core/shell structure preparation without controlled morphology. Although, similar sizes of titania NPs could be clearly seen (9-20 nm, and aggregated NPs up to 60 nm (Fig. S4[†])), cuprous oxide is characterized by high polydispersity in size (10-1000 nm (Fig. S4[†])) and shape (including spherical and cubic particles, building-block structures and rods (Fig. S3[†])). One can distinguish two types of morphological configuration of the analysed core/shell structures. The first one is composed of fine titania NPs localized on large Cu_xO particles (Fig. 3a, e, and f and S1-S3[†]), and the covering of Cu₂O depends on the content of titania, i.e., efficient coverage for 98 wt% (Fig. 3d-f and S1[†]) and only partial coverage for 50 wt% (Fig. 3ac and S1[†]). In the case of smaller Cu_xO particles of *ca.* 10 nm (possibly the amorphous form undetected by XRD), they are also covered with fine titania, forming aggregated CurO(a)TiO₂ particles (Fig. 3d). The transmission electron (TE) image of the 1% Cu_xO@TiO₂ sample has also confirmed the coverage of Cu_2O by a thick and porous shell of titania (in the form of aggregated core/shell structures), and with fine Cu_2O NPs in the range of 3–20 nm. On the other hand, the 5% Cu_2O sample exhibits a thinner layer of titania (Fig. 4 and S2†), which is reasonable considering the lower content of TiO₂, as clearly shown by the distribution of shell thickness in Fig. S4.†

The oxidation states of elements and surface composition of samples have been investigated by XPS, and deconvoluted data are shown in Fig. 5 and Table 2 (summarized in the next section including results after photocatalytic tests). Titanium exists mainly in the form of TiO₂ (Ti⁴⁺), but a low content of reduced titanium (Ti³⁺) has also been detected, reaching *ca.* 5%. The formation of the core–shell structure results in a decrease in the content of Ti³⁺ to 0.8%. Accordingly, it is proposed that Ti³⁺ could be an active site for bonding with the Cu_xO core, similar to surface titania modification with other elements/ compounds, *e.g.*, noble metals,⁴⁷ rare-earth elements⁴⁸ and ruthenium complexes.⁴⁹ Moreover, the content of hydroxyl



Fig. 4 STEM images with EDS mapping for the 5% Cu_xO@TiO₂ sample: oxygen (red), titanium (green), and copper (yellow).



Fig. 5 XPS spectra for Ti $2p_{3/2}$, O 1s and Cu $2p_{3/2}$ of bare TiO₂ (1st line), Cu₂O (2nd line), and 1% Cu_xO@TiO₂ (3rd line) samples.

groups on the titania surface (red part in the oxygen spectrum) has decreased, which indicates that some hydroxyl groups participate in the core-shell formation. In the case of copper, the main peak at ca. 532 eV matches with that of Cu-OH, while Cu–O appears at a lower energy of *ca.* 529 eV.⁵⁰ The oxygen peak for the 1 wt% Cu_xO@TiO₂ sample could well resemble the respective counterparts, *i.e.*, Cu₂O and TiO₂, considering the low content of Cu₂O. In the case of the copper peak, four peaks might be estimated, *i.e.*, CuO, Cu(OH)₂, Cu₂O and zero-valent Cu, reaching ca. 26.7%, 59.0%, 12.5% and 1.8%, respectively. The co-existence of various forms of copper on the surface of a commercial sample is not surprising since it is well known that Cu₂O is reactive and easily oxidized. Interestingly, in the core@shell particles, the content of Cu₂O has significantly increased, reaching ca. 45%. Accordingly, it is proposed that alkaline treatment during sample preparation resulted in dissolution of the surface layer (containing Cu²⁺), leaving mainly Cu₂O as a core. Nevertheless, the mixed composition of copper forms has been confirmed (as suggested by the DRS spectra), and thus the photocatalysts have been re-named as $Cu_xO(a)TiO_2$ (instead of $Cu_2O(a)TiO_2$).

For detailed characterization of photocatalysts, reversed double-beam photo-acoustic spectroscopy (RDB-PAS) has been



Fig. 6 ERDT patterns (bars) and CBB positions (bottom of grey box) for bare TiO₂, and core–shell (a) and physically mixed (ground) (b) samples containing 1% and 5% Cu_xO; values in $\langle \ \rangle$ denote the total density of ETs in units of $\mu mol~g^{-1}.$

used. Bare and modified titania (ST01) samples, *i.e.*, with 1% and 5% Cu₂O, prepared by two methods, *i.e.*, microemulsion (this study: "(a)" samples) and physical mixing (grinding: "/" samples; previous study),13 have been investigated, and the obtained results are shown in Fig. 6. It has been proposed that the conduction band bottom (CBB), energy-resolved distribution of electron traps (ERDT) patterns and total electron-trap (ET) density might reflect the bulk structure, surface structure and bulk/surface size, respectively.⁵¹ Interestingly, only samples prepared as core@shell structures exhibit a slight narrowing of the bandgap (energy shift of the conduction band bottom (CBB)), probably due to IFCT (as discussed earlier - DRS data). The ERDT patterns of bare TiO₂, and 1% and 5% Cu_xO@ST01 clearly show that titania modification with Cu2O has induced the shift of ETs (electron traps) into the conduction band depending on Cu₂O content (Fig. 6a). On the basis of the principle of RDB-PAS measurement, in which electrons in the valence band of a sample are excited directly to ETs, and the density of electron-filled traps is measured, such high-energy shift of ERDT to the higher energy side is quite unusual and might be attributable to, at least, two phenomena. (1) Some treatment of the sample (during core/shell structure preparation) causes a change in the sample structure to induce the disappearance of lower energy traps and appearance of higher energy traps. (2) The treatment causes coverage of the sample surface to inhibit contact with methanol, used as a holetrapping agent in RDB-PAS measurement. Since, during RDB-PAS analysis, a light beam for excitation is scanned from the

Table 2 Surface composition of samples after deconvolution of XPS peaks													
	Ti		0			Cu							
Samples	Ti ³⁺	${\rm Ti}^{4^+}$	О-Н	М-ОН/С=О	Metal oxide	Cu(OH) ₂	CuO	Cu ₂ O	Cu				
TiO ₂	5.1	94.9	5.3	34.2	60.5	—	_	_	_				
Cu ₂ O	—	_	7.5	61.9	30.6	26.7	59.0	12.5	1.8				
1% Cu _x O@TiO ₂ initial	0.8	99.2	1.7	54.1	44.2	10.2	40.5	45.4	3.9				
1% Cu_xO (UV) H_2 (UV)	3.3	96.7	4.4	25.1	70.5	—	—	71.2	28.8				
1% Cu ₂ O@TiO ₂ 8 h CO ₂ (UV)	3.4	96.6	4.5	21.5	74.0	—	2.9	89.7	7.4				
1% $Cu_x O$ (a) TiO ₂ 8 h (vis)	49.7	50.3	15.2	23.4	61.4	16.4	68.3	1.5	13.8				

Nevertheless, the total ET density of the 1% Cu_rO(a)TiO₂ sample is much higher (almost double) than that of other samples. It should be noted that it has been proposed that shallow ETs with high energy might be responsible for high photocatalytic activity.52,53 In addition, it must be remembered that the total ET density might reflect the specific surface area (SSA),⁵¹ and thus an increase in specific surface area should result in enhanced photocatalytic activity.³⁰ Interestingly, the physically mixed (ground) samples (1% and 5% Cu₂O/TiO₂) show similar tendencies (Fig. 6b), i.e., the higher the content of Cu₂O, the deeper the ET distribution inside the CB. Moreover, the 5% Cu_2O/TiO_2 sample with the highest total ET density (83 μ mol g⁻¹) and the deepest ET distribution inside the CB has shown the highest activity in both reaction systems under UV/ vis irradiation, *i.e.*, H₂ and CO₂ evolution.¹³ In the present study, the most active samples for H₂ and CO₂ evolution (discussed in the next section) are 1% Cu_xO@TiO₂ and 5% Cu_x-O@TiO2 samples, respectively. Accordingly, it might be proposed that the total ET density (in the case of high energy traps) and the shift of the ERDT peak to higher energy might result in efficient reduction and oxidation reactions, respectively.

Activity of Cu₂O@TiO₂ samples

The photocatalytic activities of the samples have been tested under UV/vis irradiation in two systems, *i.e.*, oxidative decomposition of acetic acid with CO_2 evolution (CO_2 system) and dehydrogenation of methanol with H_2 evolution (H_2 system), and the obtained data are shown in Fig. 7.

The low activity of bare titania (ST01 and P25) in the H_2 system (black bars) is not surprising since titania needs a cocatalyst for efficient H_2 evolution. Although usually zero-valent noble metals (NPs or nanoclusters) have been used as co-catalysts,^{47,51,54} other compounds have also been successfully applied, *e.g.*, graphene,⁵³ Cu₂O¹³ and Cu_xO.^{14,55} Similarly, the Cu_xO @TiO₂ core/shell photocatalysts exhibit high photocatalytic activity for H₂ evolution, and the sample with the lowest content of Cu_xO has been the most active. Interestingly, the samples prepared by grinding (previous study)¹³ have also shown high activity enhancement after Cu_2O addition, but the best performance has been obtained for larger content of Cu_2O , *i.e.*, 5%. It should be pointed out that in ground samples, Cu_2O was the predominant form of copper (pink sample) and an irregular mixed-oxide structure has been formed. Here, the formation of a core/shell structure with a porous titania layer is highly beneficial for photocatalytic performance, reaching *ca*. 1.5 times higher activity that that by the most active ground sample.

Two possible mechanisms for the enhanced activity of the Cu₂O(a)TiO₂ photocatalysts have been proposed, *i.e.*, electron transfer via type-II heterojunction and charge separation in the Z-scheme mechanism. In the case of heterojunction type II (Fig. 8a), the electron transfer from the CB of Cu_xO into the CB of TiO₂, and reverse hole transfer (*i.e.*, from the VB of TiO₂ into the VB of Cu₂O) might result in efficient charge carrier separation, but also in lower redox ability (electrons in a less negative CB and holes in a less positive VB). Therefore, the Z-scheme mechanism with recombination of electrons from TiO₂ and holes from Cu2O (Fig. 8b) is preferable for efficient redox reactions. It should be remembered that CurO has been used as a core, and thus the change of oxidation state of copper might confirm the mechanism of action, *i.e.*, oxidation and reduction of copper should indicate heterojunction type II and Z-scheme, respectively. Indeed, XPS analysis (Fig. 9 and Table 2) performed after prolonged irradiation (8 h; stability study discussed in the following part; Fig. 11) suggests that copper has been reduced, resulting in the formation of a sample with a high content of zero-valent copper (an increase from *ca.* 4 to 28%), as shown by the color change of samples (Fig. 7b) and schematic drawings in Fig. 8c and d. Wang et al. have found similar reduction of copper (XAFS analysis) even for copper NPs deposited on the titania surface during H₂ generation under UV irradiation, *i.e.*,



Fig. 7 Photocatalytic activity of samples under UV-vis irradiation in a H_2 system and CO_2 system (a), and photographs of the samples' color changes (b) during irradiation (from the top: 0, 15, 30 and 45 min of irradiation) in the H_2 system.



Fig. 8 The schematic drawings of (a) heterojunction type II between Cu_xO and TiO_2 , (b) basic Z-scheme mechanism of charge transfer between Cu_xO and TiO_2 , (c) modified Z-scheme mechanism of charge transfer between Cu_xO and TiO_2 with participation of zero-valent Cu, (d) oxidative decomposition of acetic acid on a porous $Cu_xO@TiO_2$ photocatalyst, and (e) methanol dehydrogenation of zero-valent Cu.



Fig. 9 XPS spectra for Ti $2p_{3/2}$, O 1s and Cu $2p_{3/2}$ of the 1% Cu_xO@TiO₂ sample before (1st line; same data as that in Fig. 3) and after 8 h irradiation during methanol dehydrogenation under UV irradiation (2nd line), acetic acid oxidation under UV irradiation (3rd line) and phenol oxidation under vis irradiation (4th line).

from Cu^{2+} via Cu^+ to $Cu^{0.56}$ Additionally, it should be pointed out that zero-valent copper is not stable (due to fast oxidation), and the obtained XPS data have confirmed that the core@shell structure has been formed, keeping metallic copper safely inside the titania porous layer. However, it is also expected that proton reduction might be impossible on the surface of copper when it is inside the titania shell. Therefore, it has been proposed that the titania layer is not compact, but rather composed of fine NPs, resulting in the formation of a highly porous layer that is permeable to small atoms/molecules (e.g., H^{+}/H_{2}), as shown in Fig. 8e. Additionally, considering the dark coloration of the samples during irradiation (the formation of zero-valent copper), the highest activity of the sample with the lowest content of copper should be caused by the less dark color. It is clear that light transmittance through such dark suspensions is hindered (due to the shielding effect; similarly for Pt/TiO₂),⁵¹ and thus only a part of the sample is photoactivated by the incident light.

In the case of the CO_2 system, the photocatalytic activity of almost all coupled samples (except the 50% sample) has been significantly increased after titania modification with Cu_2O ,

reaching almost three times higher activity (for 1-5% Cu_xO samples) than that of bare titania. It should be pointed out that the color of the samples has not changed significantly during short (60 min) irradiation under aerobic conditions, and thus the photocatalytic activity might mainly correlate with the specific surface area (SSA). It is well known that a larger SSA results in more efficient adsorption of reagents, and thus faster reactions, especially in the CO₂ system, which has already been confirmed by systematic studies performed on more than 40 titania samples in different reaction systems.³⁰ Indeed, a significant activity drop has been obtained for the sample with reduced SSA, *i.e.*, containing 50% Cu_xO. Like in the H₂ system, both mechanisms (Z-scheme and type-II heterojunction; Fig. 8a and b) should be considered in the CO₂ system. XPS data (Fig. 9) have confirmed that also in the case of oxidation reaction, copper has been reduced. Accordingly, the Z-scheme has been proven in both reaction systems under UV irradiation, confirming efficient formation of the core@shell structure, which prevents the photo-corrosion of Cu_xO and its leakage.

For the CO₂ system, oxidation of acetic acid might proceed by two pathways, *i.e.*, via (i) photo-generated holes in TiO₂ and/ or (ii) the superoxide ion (O_2^{-}) formed from O_2 reduction by electrons from Cu_xO. Since the photocatalysts show high stability (Fig. 11b and 12b; discussed later), it is expected that oxidation should also proceed via O2. (if not the activity should stop since for an efficient Z-scheme both an electron acceptor on the Cu_xO core and an electron donor on the TiO₂ shell are necessary). In the case of O_2 ., two possibilities should be considered, *i.e.*, (i) the penetration of O_2 inside the TiO₂ shell or (ii) an electron transfer *via* the TiO_2 network to the adsorbed oxygen on the shell surface. It is proposed that the latter is more possible since oxygen is probably too large to penetrate via the titania shell and due to negligible activity of the samples under vis irradiation (lack of electron donor inside the titania shell, as discussed in the next section). Accordingly, the electron transfer via the titania shell has been proposed for efficient activity of core@shell photocatalysts in the CO2 system, as shown in Fig. 8e. This mechanism might also explain the increase in activity with an increase in CuxO content from 1% to 5% (99 wt% and 95 wt% titania, respectively), resulting from the formation of core@shell particles with a thinner titania shell, thus allowing fast electron transfer via the TiO₂ network. Moreover, the experiments in the presence of different scavengers (Fig. S5 in the ESI[†]) have confirmed that O₂^{•-} radicals are mainly responsible for oxidative decomposition of acetic acid, i.e., activity has dropped by ca. 50% in the presence of 4hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL). It should be mentioned that isopropanol as a HO' scavenger also decreases activity significantly (by ca. 30%), which might also indirectly confirm the Z-scheme mechanism.

Since all coupled samples are coloured, the photocatalytic activity under vis irradiation has also been tested for oxidative decomposition of phenol as a model compound. It must be pointed out that the disappearance of phenol (concentration decrease in an aqueous phase) does not necessarily imply its degradation, but could also be caused by its adsorption on the photocatalyst surface (as confirmed by 30 min pre-stirring in the



Fig. 10 Vis-activity of the bare samples and coupled photocatalysts in terms of the rate of phenol disappearance (a), and the rate of benzoquinone generation (b), and the possible mechanism under vis irradiation (c).

dark), and thus the determination of oxidation products is highly recommended. Consequently, activity data are presented for both (i) a decrease in the phenol concentration (Fig. 10a) and (ii) formation of the main intermediate, *i.e.*, benzoquinone (Fig. 10b). In the case of vis activity, only Cu_xO could be excited, and thus the mechanism of the type-II heterojunction with only Cu_xO excitation should be considered, *i.e.*, an electron transfer from the CB of Cu_xO into the CB of TiO₂. Accordingly, oxidation of organic compounds (here phenol) could proceed on the titania surface. However, for efficient and stable photocatalytic performance of Cu_rO, both redox reactions should take place, *i.e.*, reduction and oxidation. In the case of the Cu_xO core, there is no hole acceptor inside the titania shell, and thus the photogenerated holes first self-oxidize the Cu_xO core, as confirmed by the change of oxidation state of copper ($Cu^+ \rightarrow Cu^{2+}$; Fig. 9 and Table 2), and then no further reaction might occur. Interestingly, an electron transfer from Cu_xO into TiO₂ has also been confirmed by XPS data for titanium since a significant reduction of Ti⁴⁺ has been noticed (Ti³⁺ content increases from *ca.* 1 to 50%). Indeed, the obtained data have confirmed the negligible vis-response of the Cu_xO@TiO₂ core/shell photocatalysts. Interestingly, bare commercial TiO₂ (P25) exhibits an even higher vis response than core@shell photocatalysts, which might be cause by the presence of ETs inside the bandgap. A slight vis-response for commercial and faceted titania samples with shallow ETs has already been reported,⁵⁷ and the defectrich titania ("self-doped") has been proposed as an efficient vis-responsive material.58

In order to check the stability of samples, long-term photocatalytic activity has been investigated, and the results are shown in Fig. 11. Since high accumulation of gas products (H_2 and CO_2) inside the test tubes during 8 h irradiation and insufficiency of dissolved oxygen in the CO_2 system were observed, the test tubes were re-opened, purged with Ar or air (in the case of H_2 and CO_2 systems, respectively) and once more irradiated for 120 min and 180 min, respectively.



Fig. 11 Long-term photocatalytic activity of samples in (a) the CO₂ system for 1% and 5% Cu_xO@TiO₂ samples, and (b) the H₂ system for 1% Cu_xO@TiO₂, and (c and d) photographs of the samples during irradiation in the H₂ system: (c) first irradiation (after 0, 1, 2, 3, 4, 5, 6, 7 and 8 h of irradiation (from the top)), (d) second irradiation (after 0, 15 min, 30 min, 45 min, 1 h and 2 h of irradiation (from the top)).

Stable activity has been observed in the CO₂ system during 4 h of irradiation for fresh and pre-irradiated samples (Fig. 11a). Extended irradiation (>4 h) caused a slight decrease in reaction rate, because of insufficient content of dissolved oxygen, which has been confirmed by the increase in reaction rate during the subsequent irradiation of air-bubbled samples. Accordingly, it is proposed that even when the surface state of copper changes during irradiation from Cu²⁺ into mainly Cu⁺, stable activity without sample discoloration is achieved. In the case of the H₂ system, although stable activity is observed during 8 h irradiation (Fig. 11b), opening of the test tube and Ar-bubbling cause a decrease in reaction rate by about half. Therefore, it is proposed that small amounts of copper (e.g., as Cu^+ or Cu^0) clusters) could also penetrate through the titania layer, acting as a co-catalyst on its surface for H₂ evolution. However, postbubbling could cause their detachment from the photocatalyst surface, and thus the re-irradiated sample shows lower activity, resulting from a smaller number of active sites for H₂ evolution. This hypothesis could be confirmed by the slight colour change of samples during irradiation, i.e., (i) slight discoloration during the first irradiation (loss of copper species; Fig. 11c), and (ii) stable colour during re-irradiation (no more copper leakage from the photocatalyst surface; Fig. 11d). Accordingly, it is proposed that even if a slight loss of activity in the initial stage of the photocatalytic process is observed (due to imperfect Cu_xO coverage by the TiO₂ layer), the coupled photocatalysts are quite stable, and could be successfully applied for photocatalytic reactions under UV irradiation. It should be pointed out that samples prepared by grinding are not stable at all with complete discoloration during longer irradiation.13



Fig. 12 Long-term photocatalytic activity of a thermally treated (2 h, 180 °C) 1% Cu_xO@TiO_2 sample in (a) the CO_2 system, and (b) the H_2 system.

To further improve the stability of core@shell particles and to avoid any possibility of copper leakage, thermal treatment was applied. At first, the annealing conditions were optimized, *i.e.*, 2 h at 180 °C, for the bare Cu_2O sample to avoid oxidation of cuprous oxide to cupric oxide. Accordingly, the 1% $Cu_xO@TiO_2$ core@shell sample was heated and then tested during three photocatalytic cycles in both reaction systems, and the obtained data are shown in Fig. 12. It might be concluded that posttreatment by annealing results in successful preparation of stable photocatalysts during long-term irradiation and recycling.

4. Conclusions

The microemulsion method has proven to be an efficient strategy for the preparation of Cu_xO @TiO₂ core/shell photocatalysts. However, the alkaline conditions during sample preparation result in the change of oxidation state of copper (mixed-oxidation states) and in a decrease in Cu_xO size. Nevertheless, the core@shell structure guarantees high stability under UV irradiation (especially after annealing), in contrast to simply mixed oxides (Cu_2O/TiO_2), independent of the kind of redox reaction (both for oxidation and reduction). Moreover, the change of surface charges of the copper core indicates the Z-scheme mechanism, which is the main reason for the high efficiency of the Cu_xO@TiO₂ photocatalyst. The core@shell particles have only one, but quite serious, shortcoming, *i.e.*, negligible activity under vis irradiation. However, efficient reduction of copper oxides inside the titania layer under UV irradiation might enable the formation of a stable and efficient vis-responsive material, *i.e.*, plasmonic photocatalyst (Cu⁰@TiO₂). The above results unequivocally show that coupled Cu_xO@TiO₂ with a core@shell nanostructure has significant potential to be an efficient and stable photocatalyst dedicated to various reaction systems.

Conflicts of interest

There are no conflicts to declare.

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