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Review

On the Origin of Enhanced Photocatalytic Activity of Copper-Modified Titania in the Oxidative Reaction Systems

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Abstract: Modification of titania with copper is a promising way to enhance the photocatalytic performance of TiO_2. The enhancement means the significant retardation of charge carriers' recombination ratio and the introduction of visible light activity. This review focuses on two main ways of performance enhancement by copper species—i.e., originated from plasmonic properties of zero-valent copper (plasmonic photocatalysis) and heterojunctions between semiconductors (titania and copper oxides). The photocatalytic performance of copper-modified titania is discussed for oxidative reaction systems due to their importance for prospective applications in environmental purification. The review consists of the correlation between copper species and corresponding variants of photocatalytic mechanisms including novel systems of cascade heterojunctions. The problem of stability of copper species on titania, and the methods of its improvement are also discussed as important factors for future applications. As a new trend in the preparation of copper-modified titania photocatalyst, the role of particle morphology (faceted particles, core-shell structures) is also described. Finally, in the conclusion section, perspectives, challenges and recommendations for future research on copper-modified titania are formulated.

Keywords: photocatalysis; copper-modified titania; oxidative reaction systems; heterojunction

1. Introduction

Titanium dioxide (TiO_2, titania) has played a crucial role in the development of semiconductor photocatalysis over the last 40 years [1]. The applicative potential of TiO_2-photocatalysis is presently focused on the areas such as environmental remediation (water treatment [2–4] and air purification [5]), renewable energy processes—water splitting for hydrogen production [6], conversion of CO_2 to hydrocarbons [7], solar cells [8]—and self-cleaning surfaces [9]. TiO_2 is characterized by those properties that are indispensable to fulfill the requirements of efficient, stable, and green photocatalytic material (long term stability, chemical inertness, corrosion resistance, non-toxicity) [1].

Despite the above-mentioned benefits, the application of titania is still limited to regions with a high intensity of solar radiation due to its wide bandgap (ca. 3.0 to 3.2 eV). Therefore, there is a necessity to incorporate visible light absorption with TiO_2. Various strategies of titania performance improvement towards visible light responses have been proposed in recent years such as doping, modification, semiconductor coupling, and dye sensitization [10]. As a consequence of such modifications, TiO2 showed an absorption band in the visible light region and, in most cases, also photocatalytic activity under visible light irradiation for different reaction systems.

The photocatalytic activity of titania is also limited by the recombination of the photogenerated electron-hole pairs [11] as typical for all semiconducting materials. Titania exhibits only weak bandgap emission upon the recombination of conduction band electrons with valence band holes, and the irradiative recombination involving trap states is optically allowed [1,12]. Recombination is generally caused by impurities, defects or other factors, which introduce bulk or surface imperfections into the crystal and, depending on titania properties, it may occur either on the surface or in the bulk (usually a decrease in particle size results in an increase in surface recombination) [13,14]. The incorporation of species capable of promoting charge separation may reduce this phenomenon, and thus result in improvement of overall quantum efficiency of photocatalytic system. Promoted charge separation has been reported for titania modified with various modifiers, e.g., ions [14,15], noble metals [16,17], other semiconductors (heterojunction coupling) [18,19], and doped with metal ions [14].

Considering the above-mentioned limitations (vis inactivity and charge carriers' recombination), and similar ways of their removal (surface modification, doping, heterojunction), it is thought that effective materials based on TiO_2, which meet those requirements are highly designable. It must be pointed out that modification of titania towards visible light photocatalytic activity could significantly influence photocatalytic performance under UV irradiation and in some cases a decrease in photocatalytic activity has been observed since modifiers/dopants could also work as recombination centers for electrons and holes, therefore a proper selection procedure for titania modification should consider both limitation issues.

Among different metallic candidates for TiO_2 modification, copper (Cu) is a very promising material. Cu-based nanocatalysts have significant applicability in nanotechnology including catalytic organic transformations, electrocatalysis, and photocatalysis [20–22]. In comparison with other noble metals (gold, platinum and silver) recognized as very efficient co-catalysts of titania, copper—as a consequence of its abundance in the Earth's crust—is an inexpensive material, 100 times and 6000 times cheaper than silver and gold, respectively [21]. Furthermore, owing to the location in the same group of the periodic table as gold and silver, copper has similar properties due to its electronic configuration and the face centered cubic (FCC) structure of the atom's location. Therefore, one can expect the comparable potential to improve the photocatalytic activity of TiO_2, simultaneously with the higher possibility of successful application. Copper can exist in a wide range of accessible oxidation states: Cu^0, Cu^I, Cu^{II} and Cu^{III}. In this connection, the active copper species in TiO_2 photocatalytic system are copper oxides (Cu_2O, CuO) and metallic copper. Cu may also co-exist in both forms (the oxide and zero-valent) and this is the most probable case when titania is modified with metallic copper under anaerobic conditions, and thus-obtained photocatalyst is subsequently kept under aerobic conditions (surface oxidation of metallic copper deposits). The variety of copper forms can provide difficulty in understanding of their role in considered reaction systems. Therefore, a statement that the nature of Cu species in TiO_2 photocatalysis is still not clearly understood may be made. There is also some possibility of copper ions doping into TiO_2 crystal lattice. The radius of Cu^{2+} is 0.087 nm, which is larger than the 0.0745-nm radius of Ti^{4+}. Moreover, a huge difference in valence state suggests that Cu^{2+} should not replace Ti^{4+} to enable displacement doping at the crystal lattice site [23]. There is only the possibility of incorporating Cu^{2+} ions into interstitial positions in the lattice [24–27].

Various papers on copper-modified titania have been already published, including comprehensive reviews [22,28] about copper species in photocatalysis. However, these reviews are mainly focused on the photocatalytic reduction reactions, i.e., hydrogen evolution and/or CO_2 to methane conversion. Of course, the Cu/TiO_2 system is most known for the mentioned reaction systems—and the number of papers in this field is the highest—but the application of Cu/TiO_2 for the photocatalytic oxidation of organic compounds is also very promising both under ultraviolet (UV) and visible/solar irradiation, and the role of Cu species in this system needs clarification. Therefore, in the present work, an overview of papers has been carried out to compare different mechanisms resulting from an existence of various forms of copper combined with titania in relation to efficiencies of oxidative reaction systems.

2. Photocatalytic Systems Based on Cu/TiO_2

2.1. Presence of Copper Ions in the TiO_2 Suspension

The first papers about Cu/TiO_2 systems were mainly connected with photodeposition of copper on titania surface as the efficient method for Cu removal from water environments [29–32]. Cu^{II} ions were reduced to metallic copper with the participation of photogenerated electrons (e^-) and holes (h^+) according to the following Reactions (1)–(3) [29]:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$Cu^{2+} + 2e^- \rightarrow Cu \quad (2)$$

$$H_2O + 2h^+ \rightarrow 0.5O_2 + 2H^+ \quad (3)$$

In opposition to the above results of Bard's group [29], Hermann et al. suggested that Cu^{2+} ions in TiO_2 suspension were photoreduced to Cu^+ ions and that metallic copper could not be obtained [33]. However, Jacobs et al. showed that photodeposition of zero-valent Cu particles was possible and was preceded by photodeposition of Cu_2O particles [32].

Another type of study focused on the influence of the presence of copper ions on the efficiency of photocatalytic oxidation of organic compounds. It was found that addition of dissolved copper ions to TiO_2 reaction system improved significantly the rate of photocatalytic oxidation [34–39]. For example, Bard et al. observed [29] that Cu^{2+} ions retarded the electron-hole recombination by trapping of photogenerated electrons (Equation (2)). The reduced forms, in turn, could prevent the recombination by hole trapping (Equation (4)).

$$Cu + 2h^+ \rightarrow Cu^{2+} \quad (4)$$

Generally, the small concentration of Cu^{2+} ions prevents charge recombination. In the case of large amounts of Cu^{2+} ions, their influence on the reaction rate can be detrimental considering that Reactions (2) and (4) are short-circuiting. In 1985, Okamoto et al. showed that a high concentration of Cu^{2+} (50 mM) inhibited the efficiency of phenol photooxidation (the first study using copper for photocatalytic oxidation of organic compounds) [34]. The detrimental effect of a high amount of Cu^{2+} ions was also explained by absorbance of UV/vis radiation by copper species [40]. Precipitation of dissolved copper as a hydroxide could also decrease the rate of photocatalytic oxidation by reflecting UV irradiation through increased solution turbidity (shielding effect) [39]. Brezova et al. observed an inhibition effect of dissolved Cu^{2+} ions even at low concentrations (>1 mM) in the phenol oxidation system. The key point is that the observed photodeposition of metallic copper and Cu_2O on titania may significantly influence the process of charge carriers and radical intermediate generation and recombination and finally, along with Equation (2), result in the inhibition of photodegradation [40]. Butler and Davis observed negligible adsorption of copper (and other metals) on titania surface and suggested that mainly dissolved copper (and other metals) increased the reaction rate via a homogeneous pathway rather than surface reactions on copper-modified titania [39,40]. They proposed a mechanism involving formation of a ternary reactive complex between copper, organic compound or its oxidation intermediate and oxygen-containing species such as O_2, H_2O_2. Bideau et al. analyzed TiO_2 system in the presence of Cu^{2+} ions for the oxidation of three organic compounds: formic acid, acetic acid and propionic acid, and monocarboxylate complexes of Cu^{2+} were identified as important species in the reaction kinetics [35–37,41]. The observed increase in the reaction rate in the mentioned studies was explained in terms of the effects of Cu^{2+}/Cu^+ redox couple, which inhibited the electron-hole recombination and the inner sphere mechanism of Cu^{2+} ions with the organic compounds, forming organo-metallic intermediates.

2.2. Copper Species Deposited on TiO_2 Surface

2.2.1. Metallic Copper—Plasmonic Photocatalysis

Copper (similar to gold and silver) nanoparticles (Cu NPs)–titania couple can be a very promising photocatalytic system for both UV and visible light-induced reactions. Cu NPs as surface modifiers of TiO_2 can inhibit electron-hole recombination under UV irradiation working as an electron sink [42,43], because Fermi energy level of metallic Cu lies below the conduction band of TiO_2, and therefore photogenerated electrons in TiO_2 can be easily transferred to Cu NPs. Other important advantage of Cu NPs is that they can activate TiO_2 towards visible light due to localized surface plasmon resonance (LSPR) of Cu, thus being so-called "plasmonic photocatalysts" [44–49]. The LSPR is excited when light interacts with the free electrons of a metallic nanostructure, which results in the collective excitations (oscillations) that lead to significant improvement of the local electromagnetic fields surrounding the nanoparticles [50]. Spherical metallic nanoparticles, such as gold, silver and copper, are sufficiently small (in comparison with the wavelength of the light) to be resonant with the light coming from all directions and indicate coloration as well as a local electromagnetic field enhancement on the particle surface even without the condition of total internal reflection [44]. The existence of characteristic surface plasmon resonance band absorbing light in the visible region results in visible-light activity of noble metal-modified titania, probably due to an efficient transfer of the photoexcited electrons from metal particles to the conduction band of TiO_2 (energy transfer and plasmonic heating have been also proposed as possible reasons of vis response [51]). This would result in electron-deficiency in metal and electron-richness in TiO_2 and therefore, the direct photocatalytic oxidation occurs on the metal surface rather than on TiO_2 surfaces as shown in Figure 1 [52] or indirect oxidation proceeds by reactive oxygen species (initiated by superoxide anion radical formation).

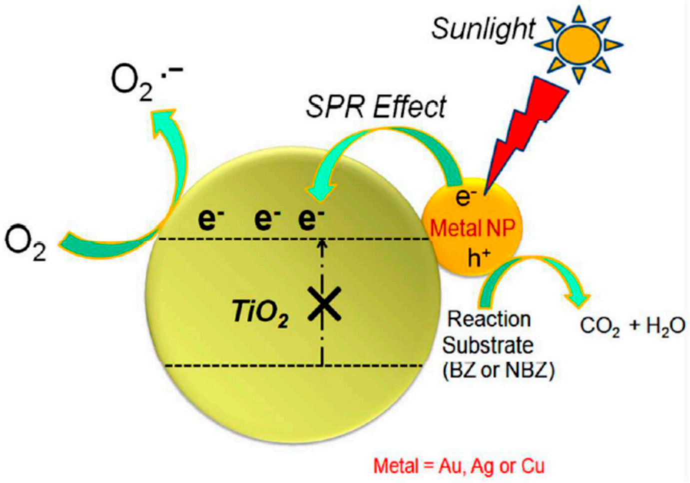

Figure 1. Surface plasmon resonance (SPR) effect of metal nanoparticles for TiO_2 photocatalysis under sunlight irradiation. Reprinted with permission from [52]. Copyright Royal Society of Chemistry, 2015.

Based on the unique properties of LSPR, many studies focused mainly on Au and Ag as plasmonic metals, which improve photocatalytic properties of TiO_2 [53]. However, very few studies have been reported about photocatalytic performance of Cu NPs in connection with titania [47–49]. The main problem with utilizing Cu NPs as a "plasmonic sensitizer" is the known fact that zero-valent copper is easily oxidized and lose plasmon resonance properties gradually under ambient conditions [54–56]. For example, (i) although, titania modification by strong radiolytic reduction of Cu^{2+} or photodeposition under anaerobic conditions resulted in formation of zero-valent copper, Cu^0 was subsequently oxidized under ambient conditions forming CuO/TiO_2 and $Cu/Cu_2O/Cu/TiO_2$, respectively [57–59] and (ii) even Cu NPs immersed in water were oxidized by dissolved oxygen [60].

The reported main solutions of this problem consider the necessity of preventing copper oxidation by maintaining Cu in anoxic environments [55,61–63] or protecting its surface with chemical corrosion inhibitors [64], polymeric layers [47,55], and by oxide encapsulation [65]. The optimal Cu NPs based plasmonic photocatalysts should work without necessity of addition of surface-obscuring chemical stabilizers and would be storable indefinitely under ambient conditions [49]. Most of these studies were focused on Cu NPs alone but not on Cu NPs-TiO_2, where it is necessary to consider interactions between Cu NPs and TiO_2 during preparation procedure [66].

Most studies about Cu NPs-TiO_2 were connected with unprotected copper under reductive, oxygen free conditions. Zhang et al. prepared TiO_2 nanotube arrays with copper NPs by pulsed electrochemical deposition method [48]. They reported visible light activity of this material for hydrogen evolution. Similarly, Kum et al. investigated the properties of the visible light active Cu/TiO_2 photocatalyst for hydrogen production [67]. This material showed high stability and photocatalytic activity in the evacuated chamber. However, it is difficult to distinguish whether the photocatalyst was activated by excitation of copper LSPR or band gap heterojunction with copper oxides since photocatalysis experiments were driven by broadband visible light irradiation.

In order to apply the Cu NPs-TiO_2 system for an oxidative system, the persistence of metallic copper to oxidative environment is necessary. Yamaguchi et al. prepared plasmonic Cu NPs deposited on TiO_2 electrode and protected by polyvinyl alcohol, which resulted in efficient photocurrent response due to LSPR [47]. In the latest research, De Sario et al. studied titania aerogels supporting ca. 5-nm Cu NPs [49]. They found that plasmonic properties of Cu NPs were preserved by offering an extended interfacial contact with reduced TiO_2 support (characteristic design issue for aerogels). An arrangement of Cu NPs at high-surface area TiO_2 (with multiple Cu-TiO_2 contacts per Cu nanoparticle) allowed the obtaining of a Cu/TiO_2 system with good stability and a high content of Cu NPs. Figure 2 shows DRS spectra of Cu/TiO_2[aerogel] (with characteristic peaks for copper LSPR at ca. 770 nm) before and after photoelectrochemical oxidation of methanol confirming high stability of this material (almost the same plasmonic properties of Cu/TiO_2).

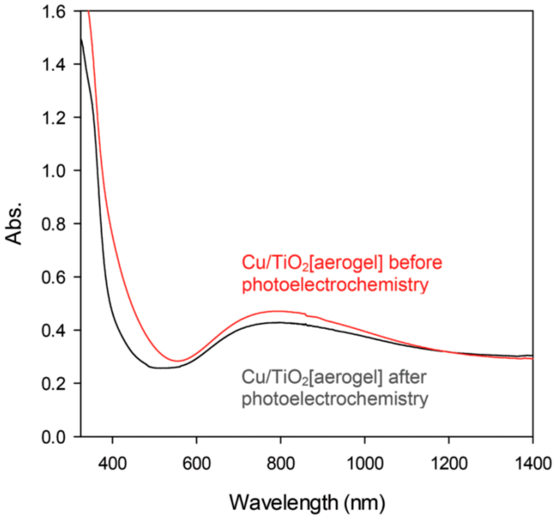

Figure 2. Diffuse-reflectance UV–visible spectroscopy of Cu nanoparticle-modified TiO_2 aerogels fabricated by photocatalytic reduction of Cu^{2+} at the TiO_2 surface before (red) and after (black) photoelectrochemical oxidation of methanol. Reprinted with permission from [49]. Copyright Royal Society of Chemistry, 2017.

2.2.2. Copper Oxides—Heterojunction Systems with TiO_2

The Concept of Heterojunction between Copper Oxides and Titania

It is well known that coupling TiO_2 with other semiconductors with different redox energy levels can lead to an increase in photocatalytic efficiency by the enhancement of the charge carrier separation process and thus an increase in the lifetime of the charge carriers. Moreover, the proper selection of coupled semiconductors can also activate the heterojunction system towards a visible light response. To create the efficient heterojunction system, both semiconductors must possess different energy levels from their corresponding conduction and valence bands. In such a configuration, several advantages can be obtained: (a) an improvement of charge carriers' separation; (b) an increase in the lifetime of the charge carrier; and (c) an enhancement of the interfacial charge transfer efficiency to adsorbed substrates [68,69].

In the case of an efficient interparticle electron transfer between the semiconductor and TiO_2, the conduction band of TiO_2 must be more anodic than the corresponding band of the sensitizer. Under visible light irradiation, only the semiconductor-sensitizer is excited and the electrons photoexited to its conduction band are injected into the TiO_2 conduction band. If the valence band of the sensitizer is more cathodic than the valence band of TiO_2, the hole generated in the semiconductor remains there (enable to migrate to TiO_2). These thermodynamic conditions favor the phenomenon of electron injections, as shown in Figure 3a. When the system of coupled semiconductors works under UV–vis irradiation, both semiconductors are excited. For heterojunction system described above, two origins of electrons in the conduction band (CB) of titania are considered: (i) injected into TiO_2 (the same as under vis excitation) from coupled semiconductor; and (ii) photoexcited electrons from titania valence band under UV irradiation, resulting in a high concentration of electrons in CB of TiO_2. Whereas, holes left in the valence band (VB) of TiO_2 may migrate to the VB of coupled semiconductor and influence a high concentration of holes in the couple semiconductor/electrolyte interface (Figure 3b) [70].

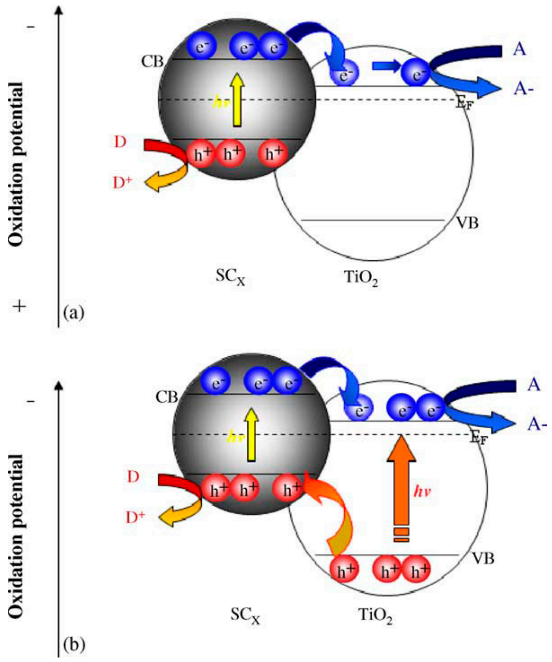

Figure 3. (**a**) Energy diagram illustrating the coupling of two semiconductors (SC) in which vectorial electron transfer occurs from the light-activated SC to the nonactivated TiO2; (**b**) Diagram depicting the coupling of SC in which vectorial movement of electrons and holes is possible. Reprinted with permission from [70]. Copyright Elsevier, 2005.

Cu_2O and CuO are *p*-type semiconductors with band gap energies of 2.1 eV and 1.7 eV, respectively. The band positions of copper oxides in relation to TiO_2 are shown in Figure 4a.

Depending on the band positions of two semiconductors forming heterojunction, three different types of heterojunction could be distinguished: I, II and III (Figure 4b). Type II, which provides the optimum band positions for efficient charge carrier separation, is considered the most probable for the Cu_xO/TiO_2 system. Photoexcited electrons are transferred from CB(B) to CB(A) and this transfer can occur directly between semiconductors due to favorable energetics of the relative positions of CBs, or due to band bending at the interface inducing and internal electric field. Whereas, holes are transferred simultaneously from VB(A) to VB(B) and as a result photogenerated electrons and holes are separated from each other, reducing the recombination probability and increasing the lifetimes of the charge carriers [71].

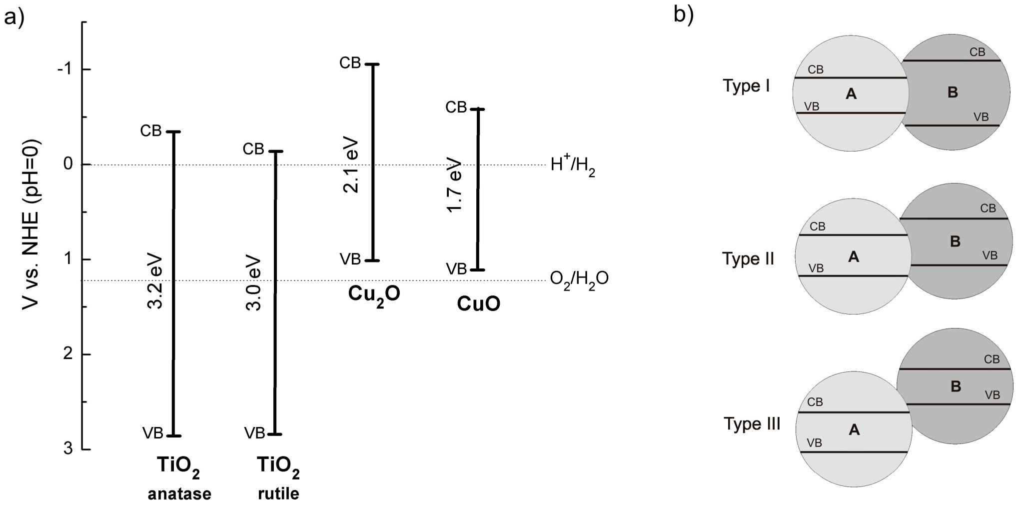

Figure 4. (**a**) Band gap energies and band positions of titania (anatase and rutile) and copper oxides—values of band positions were taken from the reference. Data collected from [71]; (**b**) Types of heterojunction system of coupled semiconductors.

Both copper oxides, especially Cu_2O, are very promising semiconductors for photocatalytic hydrogen production [72–75]. The main limitation of their application results from not good photostability, which is very important issue for oxidative photocatalytic systems. Generally, Cu_2O possesses higher photocatalytic activity than CuO for degradation of organic compounds [75,76]. Although CuO has much smaller band gap than Cu_2O, and thus is able to absorb more vis photons, the positions of CB and VB for CuO are insufficient to catalyze the production of hydroxyl and superoxide radicals, which are primary initiators for the photocatalytic oxidation of organic compounds [75]. Deng et al. found that combined CuO/Cu_2O nanostructures can be efficient photocatalysts for the photodegradation of organic compounds and possess better resistance against photocorrosion [76]. They proposed that the co-existence of CuO could inhibit the photocorrosion of Cu_2O, and furthermore the CuO/Cu_2O system can be more photocatalytically efficient than single CuO or Cu_2O.

CuO-TiO_2 Heterojunction

Taking into consideration above-mentioned issues, the heterojunction between *p*-type semiconductors–copper oxides and *n*-type one–titania could be a very promising way to improve the photocatalytic activity of titania under UV or/and visible light irradiation and to obtain more active and stable photocatalytic material than copper oxides alone. In the middle of eighties Okamoto et al. prepared Cu-deposited TiO_2 by UV-irradiation of deaerated suspension of slightly reduced (in hydrogen) anatase powder in the presence of $CuSO_4$ [34]. They assumed that only metallic copper was obtained on titania surface (but without experimental evidence). It was found that Cu-deposited TiO_2 was significantly more active in phenol photocatalytic oxidation than single TiO_2 in the presence of Cu^{2+} ions. However, the useless of this photocatalyst for wastewater treatment was suggested because of dissolution of deposited Cu into the reaction solution transforming again to Cu^+ and Cu^{2+} ions. This research expressed two main problems with the discussion on Cu/TiO_2: careful characterization of copper forms connected with titania, and the stability of prepared photocatalyst. To understand the mechanism of improvement of photocatalytic activity and to analyze perspectives of application, thorough research considering above issues is necessary.

The first research including aspects of different forms of copper in connection with titania and photooxidation activity was performed by Song et al. in 1999 [77]. They investigated the effect of oxidation state of copper loaded on titania surface on photocatalytic oxidation reaction. Cu was photodeposited on TiO_2 surface in the presence of $CuSO_4$ and ethanol as a hole scavenger. Moreover, to obtain Cu/TiO_2 photocatalysts with different oxidation states of surface-loaded copper, samples were annealed at 200 °C and 300 °C. They reported that non-annealed samples contained only metallic copper, whereas annealing at 200 °C and 300 °C resulted in copper oxidation to mainly Cu_2O and CuO, respectively. It was found that metallic copper deposited on titania improved the photocatalytic activity of TiO_2 for photooxidation of 1,4-dichlorobenzene. In contrast, the use of oxidized form of copper on titania resulted in a significant decrease in photocatalytic activity and it was proposed that copper oxide clusters on TiO_2 were not effective in the transfer of photoexited electrons [77].

Another report, which confirmed detrimental effect of CuO presence, was done by Chiang et al. for photocatalytic oxidation of cyanides in the CuO/TiO_2 system [78]. CuO/TiO_2 was prepared by photodeposition method and subsequent thermal treatment in air at 110 °C for various copper contents (0.05–10 at. % (atomic percentage) Cu). Only slight improvement of photocatalytic activity was observed for 0.1 at. % Cu, due to suggested electron trapping by CuO. It was proposed that a decrease in photocatalytic activity with a further increase in CuO content was caused by reduced photon absorption since well dispersed nanosized CuO particles covered the surface of TiO_2 (shielding effect). Moreover, it was suggested that higher concentration of CuO could promote recombination of photogenerated holes with the trapped electrons resulting in a decrease in available holes for redox reactions. Chiang et al. also examined photocatalytic activity in cyanide oxidation system under the presence of dissolved Cu^{2+} ions. The presence of copper ions was detrimental for the rate of reaction. This decrease could be explained in terms of the competition reaction of copper(I) cyanide complexes for the photogenerated hydroxyl group [78].

Shun-Xin et al. proposed another preparation method of Cu/TiO_2, i.e., impregnation of titania precursor in copper salt during sol-gel synthesis [79]. They suggested the co-existence of both copper oxides on titania surface and copper ions (Cu^{2+} and Cu^+) in the lattice of titania (doping). Authors proposed that Cu^{2+} could trap the excited electron in CB of titania, inhibiting electron-hole pair recombination, whereas Cu^+ could transfer electron to oxygen adsorbed on the surface of photocatalyst accelerating interfacial electron transfer [79].

Arana et al. studied methyl tert-butyl ether (MTBE) photocatalytic oxidation on $CuO\text{-}TiO_2$ under UV irradiation [80]. They observed a significant improvement of photocatalytic activity of copper-modified titania in comparison with pure TiO_2. Considering the reduction potential for Cu^{2+}/Cu^+ (+0.17 V vs. NHE (normal hydrogen electrode)), CuO deposits on TiO_2 surface could react with the photogenerated electrons through Reaction (5), and Cu^+ ions could be re-oxidized to Cu^{2+} by oxygen, H_2O_2 or other oxidizing species present in the Medium (6):

$$Cu^{2+} + e^-{}_{CB} \rightarrow Cu^+ \tag{5}$$

$$Cu^+ + (O_2, H_2O_2, \text{other oxidants}) \rightarrow Cu^{2+} + e^- \tag{6}$$

Therefore, the Reaction (5) of Cu^{2+} ions with the photogenerated electrons should slow down electron-hole recombination resulting in activity enhancement [80].

The mechanism for the Cu/TiO_2 system under visible light irradiation was proposed by Irie et al. for 2-propanol oxidation [81,82]. They prepared Cu(II)-grafted TiO_2 photocatalyst by impregnation method using $CuCl_2 \cdot 2H_2O$ as the source of copper. Authors suggested that Cu^{2+} ions existed in the form of amorphous CuO clusters. They proposed that visible light irradiation initiated interfacial charge transfer (IFCT): electrons in the VB of TiO_2 were directly transferred to Cu^{2+} and Cu^+, and the holes created in the VB of TiO_2 decomposed organic compounds (Figure 5) [82]. It was proposed that for efficient IFCT, Cu^{2+} ions had to be atomically isolated on the TiO_2 surface. Authors suggested that produced Cu^+ ions could reduce O_2 by a multielectron reduction, being re-oxidized to Cu^{2+}. This multi-step reduction process could be initiated by a two-electron reduction of oxygen to peroxide (Equation (7)), and the following four-electron reductions (Equations (8) and (9)).

$$2Cu^+ + O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O_2 \quad (7)$$

$$3Cu^+ + O_2 + 4H^+ \rightarrow 2Cu^{2+} + Cu^{3+} + 2H_2O \quad (8)$$

$$4Cu^+ + O_2 + 4H^+ \rightarrow 4Cu^{2+} + 2H_2O \quad (9)$$

It was concluded that Cu^{2+} ion in the amorphous form affords the smooth reversibility between Cu^{2+} and Cu^+ forms [82]. The possibility of this mechanism was also confirmed by this group for other material, i.e., Fe(III)-grafted TiO_2 [83]. Similar mechanism was proposed for CuO/WO_3 system by Arai et al. [84]. Photoexcited electrons in WO_3 were transferred to CuO and Cu^{2+} was reduced to Cu^+, and reduced surface was re-oxidized (Cu^+ to Cu^{2+}) by oxygen.

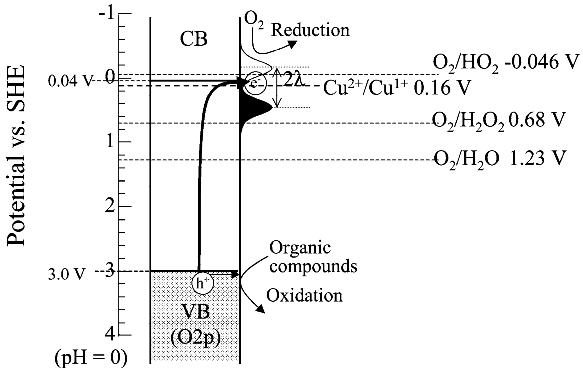

Figure 5. Mechanism for the generation of photocatalytic activity of Cu(II)/TiO_2 under visible light. Visible light irradiation induces interfacial charge transfer (IFCT) from the valence band (VB) of TiO_2 to the Cu^{2+} ion. Reprinted with permission from [82]. Copyright American Chemical Society, 2009.

The properties of photocatalytic material prepared by Irie et al. [82] were optimized in the field of crystallinity, the interfacial junction between TiO_2 and CuO nanoclusters, and the amount of CuO nanoclusters. The synthesized CuO-TiO_2 nanocomposites exhibited efficient interfacial charge transfer (IFCT) for decomposition of volatile organic compounds and strong anti-pathogenic effects under indoor conditions. The mechanism of those dual type properties is presented in Figure 6. It was proposed that Cu^+ species were very efficient for enhancing the antibacterial and anti-viral properties of TiO_2 photocatalysts (even under dark conditions), i.e., holes in the valence band (VB) of TiO_2, generated under irradiation with visible light, in combination with Cu^+ species, could attack the outer membrane, proteins, and nucleic acid (DNA and RNA) of viruses and bacteria, resulting in their death and inactivation [85].

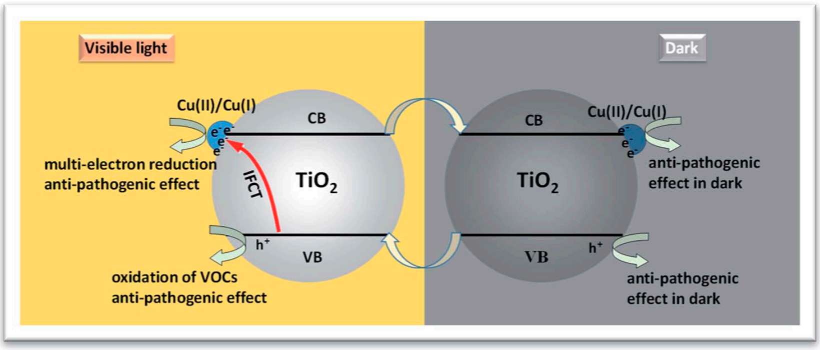

Figure 6. Proposed processes of photocatalysis and inactivation of viruses and bacteria under visible-light irradiation and dark conditions. Reprinted from [85] under CC BY-NC 3.0 license, 2009.

To understand the mechanism of coupled photocatalysts, it is necessary to know the exact positions of the valence band (VB) and conductance band (CB) of semiconductors. The ambiguity over the positions of the conduction and valence bands in CuO (and Cu_2O) results in different explanations for the mechanistic aspects of heterojunction systems. For example, Li et al. prepared CuO/TiO_2 (rutile) nanocomposites by impregnation and subsequent calcination in air [86]. They tested photocatalytic properties of this material using methylene blue as a model compound under UV/vis irradiation. The authors proposed that CuO/TiO_2 system could be classified as type I of heterojunction, as presented in the inset of Figure 7 (different CB and VB positions for CuO than presented in Figure 4a). In this system, since the band edges of TiO_2 bracketed those of CuO, coupling between CuO and TiO_2 could lead to decreased photocatalytic activity due to transfer of both electrons and holes simultaneously from TiO_2 to CuO resulting in their recombination in CuO. However, when the copper content was very low (0.1 wt %) significant improvement of photocatalytic activity was observed in comparison to unmodified titania (Figure 7). Therefore, it was proposed that copper existed in this sample as highly dispersed CuO clusters and substitional Cu^{2+} (Ti-O-Cu linkages), and UV illumination resulted in trapping of electrons in TiO_2 lattice. Photogenerated electrons were localized at Ti sites in the bulk of titania lattice and holes at interfacial sites of TiO_2-CuO (by EPR spectroscopy). However, at higher copper loadings, no photogenerated electrons were observed at titania lattice trapping sites. Slamet et al. explained this phenomenon as a "shading effect" [87] (also known as "shielding effect" or "inner filter effect" and observed for various titania surface modifications, e.g., with Au NPs [88], and Pt NPs [89]): colored CuO absorbed light and reduced the photoexcitation capacity of TiO_2 (competition about photon absorption). Li et al. concluded that efficient electron transfer from the CB of TiO_2 to CuO led to the absence of Ti^{3+} (trapped electrons) in CuO-TiO_2 at high CuO loadings. They formulated a hypothesis that the form of CuO (clusters or nanocrystallites) had a significant influence on the type of charge transfer kinetics between TiO_2 and CuO [86].

Moniz et al. prepared a CuO/TiO_2 (P25) composite using microwave co-precipitation technique [90]. It was found that 5% CuO/P25 exhibited near 1.6 times higher efficiency than pure P25 in mineralization of a model organic pollutant (2,4-dichlorophenoxyacetic acid (herbicide)) under UV/Vis. To analyze the mechanism of photocatalytic activity, the authors determined the band edge positions of CuO and TiO_2. They experimentally determined those positions by the interpretation of impedance (Mott-Schottky) plots. The difference in conduction band energies of the two materials suggested that electron transfer from TiO_2 to CuO was feasible, given the 0.34 V offset which could provide sufficient driving force for charge separation (Figure 8). It was also evidenced by the fact that pure CuO was inactive for photo-decomposition, and thus photocatalytic oxidation by CuO did not occur [90]. The concept of this junction was not connected with the increase of visible light absorption of P25 but only with more efficient charge separation. Photogenerated electrons were transferred from TiO_2 to the conductions band of CuO, followed by transfer of photoexcited holes from TiO_2 to the surface for the expected oxidation reactions.

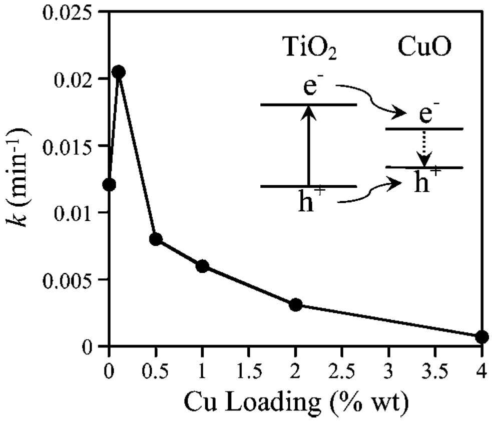

Figure 7. First-order rate constants (k in min^{-1}) as measured by methylene blue degradation under UV irradiation. Synthesized CuO-TiO_2 nanocomposites with different copper loadings were used as the photocatalysts. Inset: a schematic diagram showing the photoinduced charge separation (e^- in conduction band and h^+ in valence band) in TiO_2, charge transfer from TiO_2 to CuO and subsequent charge recombination in CuO (dotted arrow). The difference between the conduction band edges of TiO_2 and CuO is estimated to be 0.75 eV. Reprinted with permission from [86]. Copyright American Chemical Society, 2008.

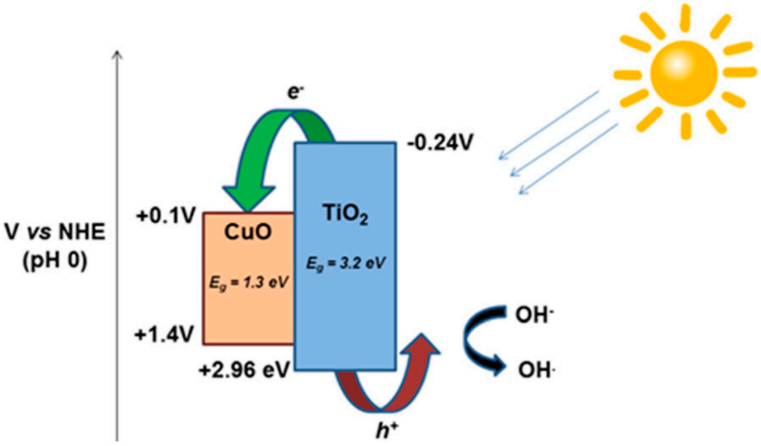

Figure 8. Mechanism of charge transfer in CuO/TiO_2 heterojunction. Reprinted with permission from [90]. Copyright John Wiley & Sons, Inc., 2015.

Siah et al. prepared CuO photodeposited on TiO_2 [91]. Under UV irradiation, the photocatalytic activity for 2,4-dichlorophenoxyacetic acid decomposition increased by a maximum factor of 4.3 compared with unmodified TiO_2, when TiO_2 was loaded with 0.75 mol % CuO. In contrast, under visible light and solar simulator irradiation, the optimum loading of CuO was much lower (0.1 mol %), and enhancements of 22.5 and 2.4 times were observed. In the case of samples loaded with higher amounts of CuO (1–5 mol %), CuO clusters can mask the surface of titania, which prevents the light source from reaching the active sites. CuO clusters in CuO-high loaded TiO_2 may act also as recombination centers. Therefore, in addition to the increased charge separation and improved visible light absorption, the masking effect will also be considered in designing efficient heterojunctions in the copper oxides–titania system [91].

Another strategy to obtain efficient visible light active photocatalyst, based on titania–copper(II) oxide, was proposed for self-doped TiO_2 (Ti^{3+}) grafted with amorphous CuO [92]. Cu-modified self-doped TiO_2 was obtained by thermal treatment of mixture of titanium oxides (Ti_2O_3 and TiO_2 mixture) in air, and their subsequent impregnation with copper salt solution. As it was reported in earlier Irie's works [81,82], in the case of titania modified with amorphous nanoclusters of Cu^{2+} oxide, electrons in the valence band of TiO_2 could be directly excited to CuO nanoclusters, which could serve as an efficient oxygen reduction site through the multi-electron process. Significant improvement of visible light activity was achieved for CuO-modified-self-doped titania (CuO/Ti^{3+}-TiO_2) in comparison with CuO/TiO_2 in the oxidation of gaseous 2-propanol. Under visible light irradiation, induced electrons on an isolated Ti^{3+} band could be transferred to the surface CuO nanoclusters efficiently, in addition to the direct charge transfer from the titania VB to the CuO nanoclusters, as shown in Figure 9. Therefore, for CuO/Ti^{3+}-TiO_2, under visible light irradiation, there were holes in the VB decomposed 2-propanol, while photoinduced electrons were consumed (via oxygen reduction) on CuO nanoclusters. It was proposed that amorphous Cu(II) oxide nanoclusters grafted on titania surface suppressed the recombination of electron—hole pairs (at the isolated Ti^{3+} band), and acted as a co-catalyst for efficient oxygen reduction to consume the photoinduced electrons. Therefore, the photocatalytic activity of CuO/Ti^{3+}-TiO_2 under both UV and visible light irradiation was very high and stable [92].

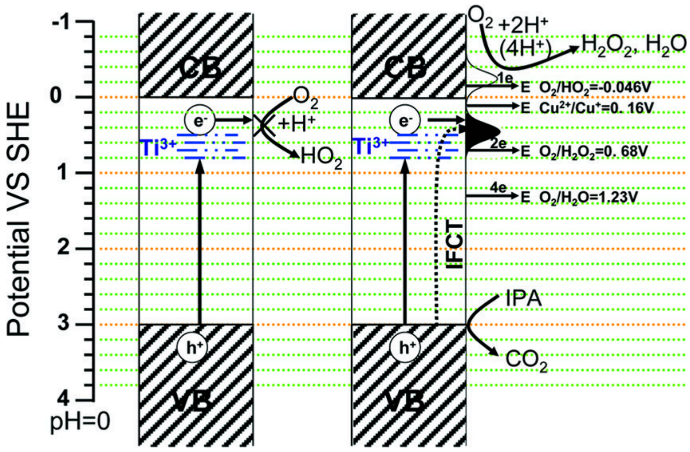

Figure 9. Proposed photocatalytic mechanism of CuO/Ti^{3+}-TiO_2 visible light activation. Reprinted with permission from [92]. Copyright American Chemical Society, 2011.

Cu_2O-TiO_2 Heterojunction

For the first time, a Cu_2O/TiO_2 heterojunction system without the presence of other forms of copper was prepared by electrochemical deposition of Cu_2O on Ti foil by Siripala et al. as a thin film heterojunction photocathode [93]. They observed a photoresponce demonstrating efficient light-induced charge carriers' separation at Cu_2O-TiO_2 junction. Moreover, it was proposed that TiO_2 film successfully protected the Cu_2O layer against photocorrosion. In the next study, Li et al. prepared composites of Cu_2O-TiO_2 (P25) by electrochemical method for UV-decomposition of dye brilliant red [94]. Prepared material was more active than pure P25, but unfortunately the mechanism was not discussed.

Bessekhouad et al. studied photocatalytic efficiency of Cu_2O/TiO_2, prepared by direct mixing of both semiconductors [70]. The activity of this heterojunction system was checked by using model organic pollutant Orange II under both UV and visible light irradiation. It was assumed that Brownian motion sufficed to permit charge transfers between the particles of the two solids. They observed that the amount of Cu_2O in the heterojunction played an important role, since vis photocatalytic efficiency increased with an increase in Cu_2O amount reaching saturation at ca. 30% (Figure 10a). It was proposed that under visible light irradiation, electrons from Cu_2O could be injected into the CB of TiO_2, and at titania surface react with dissolved oxygen molecules and induce a formation of oxygen peroxide radicals ($O_2^{\bullet-}$). Similarly, in the case of the UV system, an increase in content of Cu_2O resulted in enhanced efficiency, but resultant activities at high content of Cu_2O were only slightly higher than that of pure TiO_2, whereas for low content of Cu_2O a significant deactivation of TiO_2 was noticed (Figure 10b). This fact was attributed to the increase of charge trapping mechanism contributions when both semiconductors are excited. According to the authors, the CB of Cu_2O was more negative than the CB of TiO_2 favoring the electron transfer from Cu_2O to TiO_2. Other conditions, such as the kinetics of reactions occurring at each surface, should be also considered. For example, the holes generated in Cu_2O had to react faster to induce an efficient charge separation [70]. Moreover, it should be reminded that lack of holes' consumption (oxidation reaction by holes) could result in photocorrosion of the sensitizer (here Cu_2O) [69].

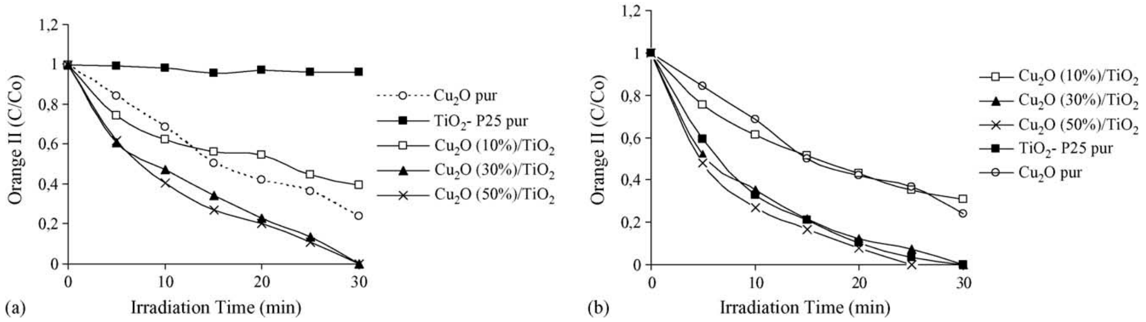

Figure 10. Photocatalytic degradation of Orange II in Cu_2O/TiO_2 system under: (**a**) visible irradiation and (**b**) UV–vis irradiation. Reprinted with permission from [70]. Copyright Elsevier, 2005.

Huang et al. performed similar investigations on Cu_2O/TiO_2 system under UV and visible light irradiation for decomposition of Orange II [95]. They used titania P25, $Cu(CH_3COO)_2 \cdot H_2O$ as a copper source and alcohol-aqueous based chemical precipitation method to prepare heterojunction photocatalysts, in which copper was present in only one form-Cu_2O (2–3-nm particle size). Similar to Bessekhouad work, it was found, that an increase in content of Cu_2O resulted in higher photocatalytic activity (70%-Cu_2O content with highest activity). They reported 6 and 27 times higher photocatalytic activity for Cu_2O/TiO_2 system than that for pure P25 for UV–Vis and visible light irradiation, respectively. The weak point of this and Bessekhouad's research under visible light irradiation is the fact that vis-response should not be tested for dyes due to possibility of semiconductor sensitization [96,97]. Although Huang et al. justified that the excited electrons could not migrate from Orange II to Cu_2O, since the reduction potential of Acid Orange II was lower (−1.25 V) than CB of Cu_2O (−1.5 V), the possibility of electron migration to CB of titania could not be omitted. According to Figure 11, under UV light irradiation, both Cu_2O and TiO_2 could be excited (process (1) and (3) corresponding to Equations (10) and (11), respectively), the generated electrons in Cu_2O and holes in TiO_2 could migrate to CB of TiO_2 (process (2)) and VB of Cu2O (process (4)), respectively. This transfer process is thermodynamic favorable since both CB and VB of Cu_2O lie above that of TiO_2 (heterojunction type II), which results in prolongation of the lifetime of excited electrons and holes, inducing higher quantum efficiency. Meanwhile, the generated electrons react with dissolved oxygen molecules and produce $O_2^{\bullet-}$ (Equations (12) and (13)) to decompose organic pollutants (Equation (14)), while the holes could induce some oxidation process directly (Equation (15)). Under visible light irradiation, process (1) can also occur due to the narrow band gap of Cu_2O (2.0 eV), and thus Orange II still can be photocatalytically decomposed by the redox reactions (Equations (11)–(14)), where Equation (12) is possible due to the transfer of electrons from Cu_2O (process (2)):

$$Cu_2O + h\nu \rightarrow Cu_2O(e^-) + Cu_2O(h^+) \tag{10}$$

$$TiO_2 + h\nu \rightarrow TiO_2(e^-) + TiO_2(h^+) \tag{11}$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \tag{12}$$

$$Cu_2O(e^-) + O_2 \rightarrow Cu_2O + O_2^{\bullet-} \tag{13}$$

$$OII^*_{ads} + O_2^{\bullet-} \rightarrow \text{products} \tag{14}$$

$$OII^*_{ads} + TiO_2(h^+) \rightarrow \text{products} \tag{15}$$

Similar conclusions were proposed by Zhang et al., who prepared TiO_2 film covered by a Cu_2O microgrid by the microsphere lithography method [98]. The underlying TiO_2 film was composed of nanosized particles covered by microgrids of Cu_2O, which were composed of particles smaller than 20 nm. By comparison of three types of thin films—TiO_2, Cu_2O and TiO_2-Cu_2O for methylene blue degradation—it was found that under both UV and visible light irradiation the heterojunction system was the most active. The authors suggested the same mechanism of heterojunction as that explained above (Figure 11).

A modified explanation of the enhanced photocatalytic activity of Cu_2O/TiO_2 heterojunction system considering the role of Ti^{3+} was proposed by Xiong et al. [99]. TiO_2 and Cu_2O were prepared separately and final coupled photocatalyst was obtained by suspension mixing. It was reported that Cu_2O/TiO_2 photocatalyst had much better vis activity in degradation of brilliant red X-3B and photocatalytic hydrogen evolution than TiO_2 and Cu_2O alone. It was proposed that photogenerated electrons from Cu_2O were captured by Ti^{4+} ions in TiO_2 and thus being reduced to Ti^{3+} ions, as shown in Figure 12. Whereas, left holes in the valence band of Cu_2O formed "hole centers" hampering the charge carriers' recombination. Therefore, trapped electrons (in Ti^{3+} ions with prolonged lifetime) could be transferred to the interface between the composite and solution, resulting in retarded recombination between electrons in TiO^2 (Ti^{3+}) and holes in Cu_2O [99].

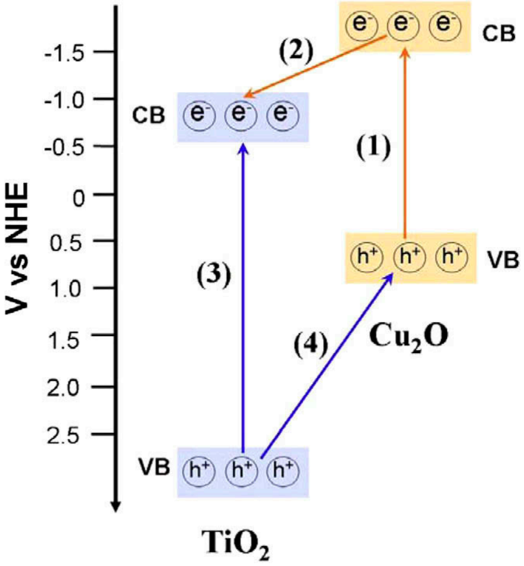

Figure 11. The scheme of excitation and separation of electrons and holes for Cu_2O/TiO_2 heterostructures under irradiation. Transformations (1) and (3) represent the excitation process in Cu_2O and TiO_2, respectively; process (2) and (4) stand for the transfer of electrons and holes between Cu_2O and TiO_2). Transformations (1) and (2) occur both under UV and visible light, while process (3) and (4) under UV light. Reprinted with permission from [95]. Copyright Elsevier, 2009.

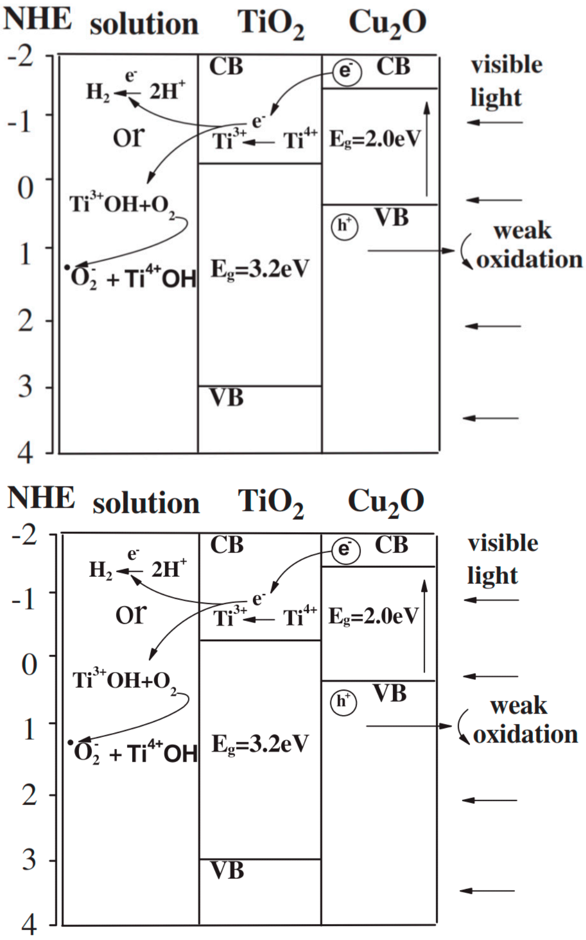

Figure 12. Interfacial electron transfer in Cu_2O/TiO_2 composite in the presence of Ti^{3+}. Reprinted with permission from [99]. Copyright Elsevier, 2011.

Wang et al. prepared Cu_2O-loaded TiO_2 nanotube arrays (NTAs) by electrochemical anodization of Ti foil and subsequent Cu_2O deposition by an ultrasonication-assisted sequential chemical bath deposition (S-CBD) method [100]. They check both visible light photocatalytic (Rhodamine B as model pollutant) and photoelectrocatalytic activities of Cu_2O/TiO_2 NTAs. The photocatalysts with small content of Cu_2O exhibited the largest photocurrent and photoconversion efficiency under visible light irradiation, as well as the highest visible light photocatalytic degradation rate of RhB. In particular, when 0.5 V bias potential was applied, Cu_2O/TiO_2 NTA photoelectrodes were found to possess superior photoelectrocatalytic efficiency, due to a synergistic effect of electricity and visible light irradiation [100].

However, in the case of heterojunctions for photocatalysts obtained according to standard methods an improved charge separation was observed, some limitations were also suggested, due to the incompact contact and small interface between two semiconductors. Therefore, the preparation of interconnected heterostructures with a large interface between two semiconductors was proposed for improvement of the charge transfer efficiency. For example, $Cu_2O@TiO_2$ core-shell photocatalyst was prepared by in situ hydrolysis and crystallization method (Figure 13), and tested under solar radiation for 4-nitrophenol degradation [101]. It was found that $Cu_2O@TiO_2$ had absorption properties similar to pure Cu_2O: strong visible light absorption in the range of 400–600 nm (Figure 14a), and was the most active among other coupled photocatalysts, e.g., prepared by physical mixing $Cu_2O/TiO_{2(PM)}$ and by chemical method denoted to Cu_2O/TiO_2 (Figure 14b). Moreover, weaker photoluminescence signals for $Cu_2O@TiO_2$ sample than for pure Cu_2O suggested retardation of charge carriers' recombination, probably because introduction of TiO_2 shell could reduce the surface oxygen vacancies and defect in Cu_2O core [101].

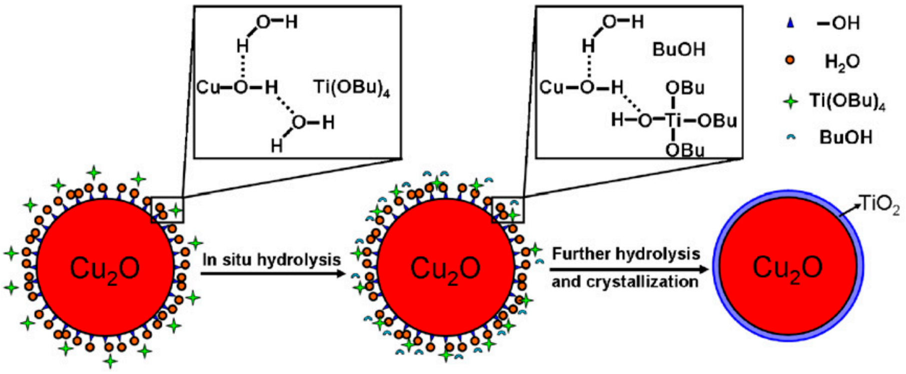

Figure 13. The formation of compact interface between two components ascribed as in situ hydrolysis and crystallization synthetic method of core-shell $Cu_2O@TiO_2$. Reprinted with permission from [101]. Copyright Elsevier, 2011.

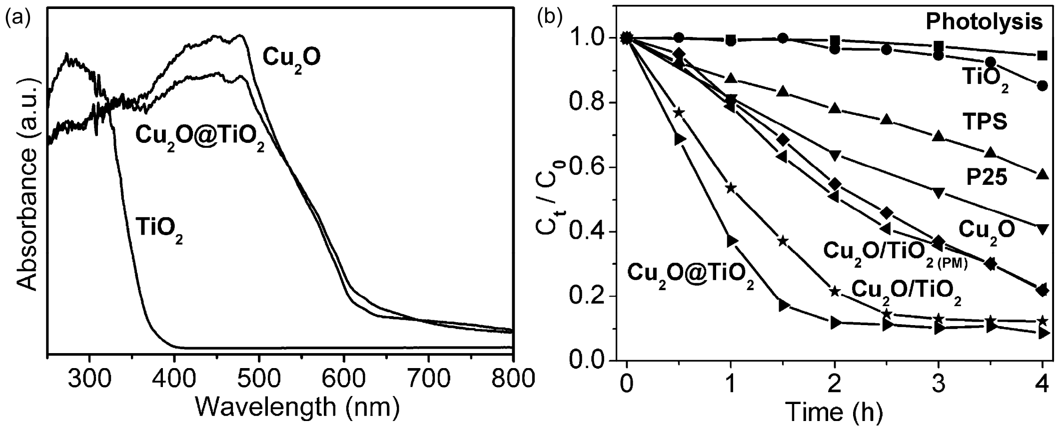

Figure 14. (**a**) UV–Vis diffuse reflection spectra of pure Cu_2O and $Cu_2O@TiO_2$ sample; (**b**) comparison of photocatalytic degradation of 4-nitrophenol under solar light in the absence of the photocatalyst and over different photocatalytic systems. Reprinted with permission from [101]. Copyright Elsevier, 2011.

Another strategy for obtaining efficient copper oxide–titania coupled photocatalyst is based on consideration of the morphology of copper oxide and titania. For example, Liu et al. synthesized Cu_2O nanospheres decorated with TiO_2 nanoislands (Cu_2O-NS/TiO_2-NI) by a facile hydrolyzation reaction followed by a solvent-thermal process. [102]. It was found that Cu_2O-NS/TiO_2-NI demonstrated superior photocatalytic performance under visible light illumination for methyl orange degradation, *E. coli* bacteria disinfection, and also a better stability during the photocatalysis process from their specific structure. The design of a partial coverage of Cu_2O nanosphere with TiO_2 nano-islands enabled the reaction between photo-generated holes and water to produce hydroxyl radicals or directly with organic pollutants/microorganisms in water. Therefore, the accumulation of holes on the underlying Cu_2O films prevented photocorrosion, and subsequently made this photocatalyst stable during the photocatalysis process (Figure 15). It was shown that part of Ti^{4+} was reduced to Ti^{3+} in Cu_2O-NS/TiO_2-NI, suggesting that under visible light irradiation photo-generated electrons in Cu_2O were transferred to TiO_2 and trapped there. After shutting off the irradiation, these trapped electrons could be gradually released from TiO_2 to react with O_2 producing reactive radicals, which imparted the photocatalytic memory effect to Cu_2O-NS/TiO_2-NI photocatalyst (Figure 15) [102].

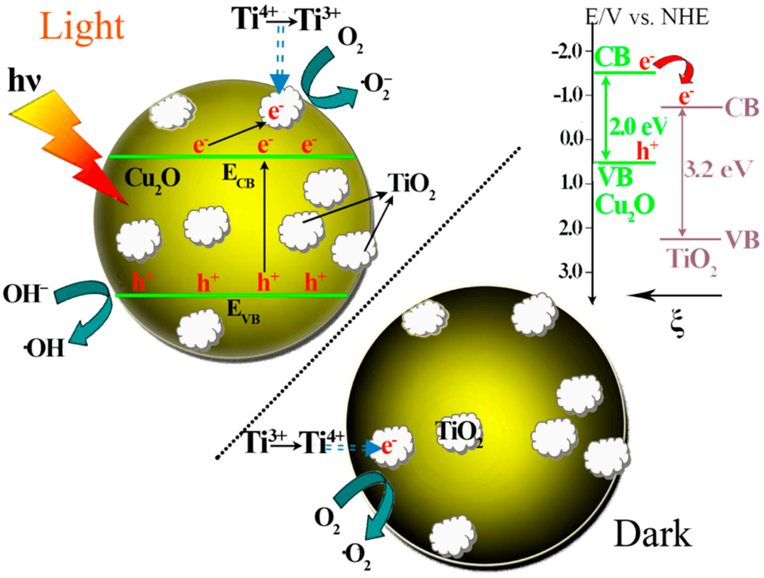

Figure 15. Proposed energy band structure of the Cu2O/TiO2 *p*-*n* heterojunction, the photocatalytic activity enhancement mechanism under visible light illumination, and the post-illumination catalytic memory mechanism in the dark. Reprinted with permission from [102]. Copyright American Chemical Society, 2014.

It is well known that controlled morphology by application of exposed facets (faceted semiconductors) significantly enhances photocatalytic performance, due to excellent crystallinity and low content of defects, e.g., octahedral and decahedral anatase particles [103,104]. Therefore, it is not surprising that similar concept was applied for copper oxide–titania heterojunction systems. For example, Liu et al. prepared $Cu_2O@TiO_2$ photocatalysts using Cu_2O with exposed facets [105]. First, Cu_2O nanocrystals with different types of morphology: cubes, cuboctahedra and octahedra were synthesized, and then $Cu_2O@TiO_2$ core-shell polyhedral nanostructures were prepared by hydrothermal reaction. It was proven then the morphology of Cu_2O cores was well preserved during hydrothermal process (Figure 16A). Well-crystallized anatase nanoparticles created a uniform and rough layer covering the smooth surface of Cu_2O core. The photocatalytic activity of $Cu_2O@TiO_2$ in the visible light was checked in relation to methylene blue and 4-nitrophenol. The activity of all coupled samples was higher than that of single Cu_2O and TiO_2, and increased with the following order regarding Cu_2O morphology: cubes < cuboctahedra < octahedra. The surface photovoltage spectroscopy (SPS) was used to analyze photoinduced carrier separation and charge transfer behavior, where the magnitude of SPS response peak depended on the amount of net charge accumulated on the material surface. It was shown that SPS response correlated with the type of facet configuration, and $Cu_2O@TiO_2$ octahedra had the strongest SPS response, $Cu_2O@TiO_2$ cuboctahedra—medium, whereas $Cu_2O@TiO_2$ cubes—the lowest (Figure 16B), showing the same tendency as the photocatalytic activity. Moreover, it was found that $Cu_2O@TiO_2$ core-shell photocatalysts had different band offset values (Figure 16C), demonstrating a clear facet-dependent activity. The photocatalytic performance of $Cu_2O@TiO_2$ polyhedra was different with that of pure Cu_2O polyhedra without TiO_2 shells, which could be attributed to the different driving forces for the charge carrier separation [105].

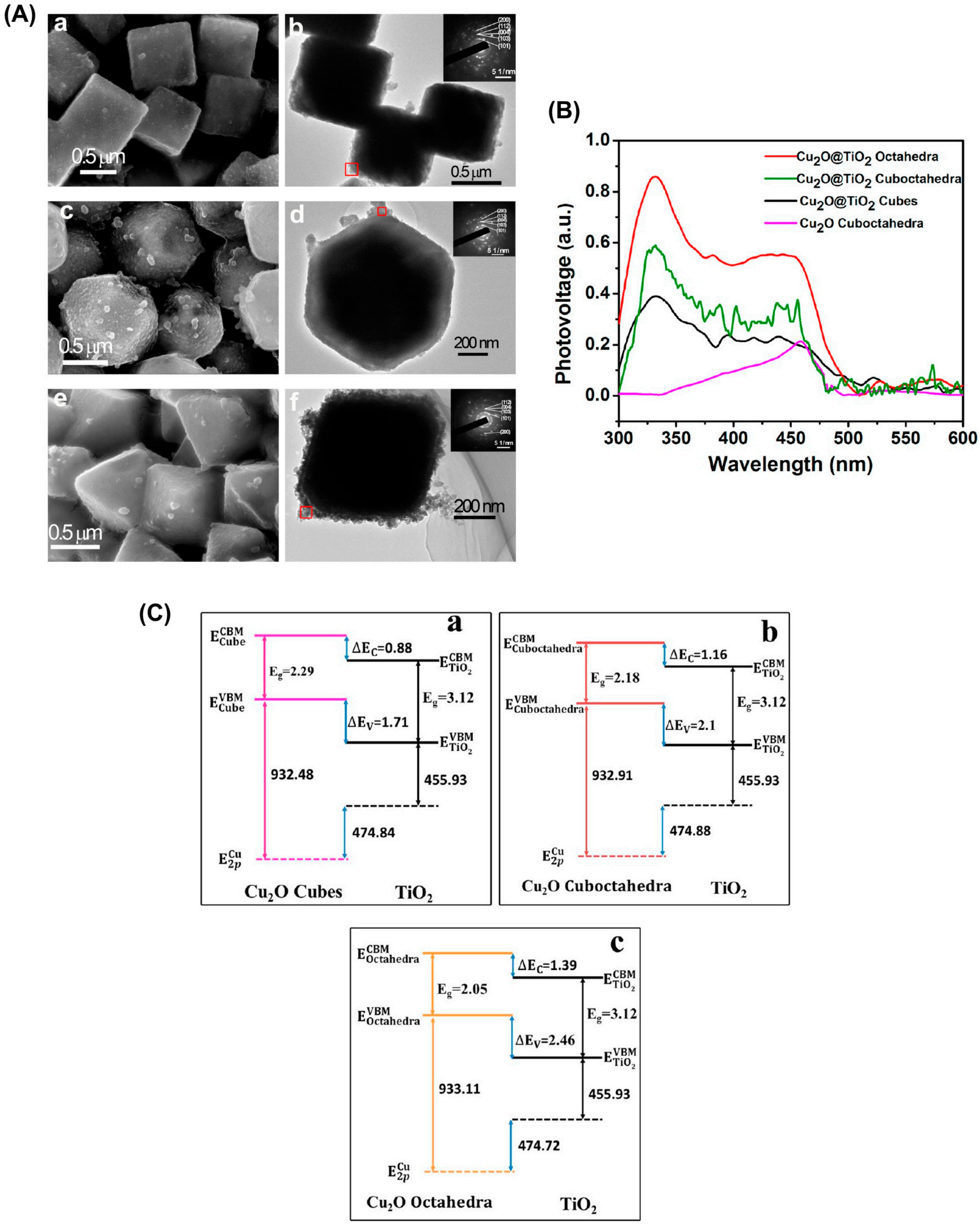

Figure 16. (**A**) SEM and TEM images of $Cu_2O@TiO_2$, Cu_2O nanocrystals in the shape of cubes—(**a**,**b**) and, cuboctahedra—(**c**,**d**), and octahedra—(**e**,**f**); (**B**) Surface photovoltage spectroscopy (SPS) spectra of $Cu_2O@TiO_2$ core-shell polyhedra, compared with that of the as-synthesized Cu_2O cuboctahedra; (**C**) Energy band diagrams for different types of morphology. Reprinted with permission from [105]. Copyright American Chemical Society, 2015.

Mixed Copper Species Deposited on Titania Surface

Frequently, during preparation of copper-modified TiO_2, a mixture of copper species is obtained [58,59], and such systems are named as "cascade heterojunction systems." For example, Helaili et al. prepared Cu_2O/TiO_2, $Cu/Cu_2O/TiO_2$ and $Cu/Cu_2O/CuO/TiO_2$ heterojunctions using chemical methods, and examined their potential application as photocatalysts for oxidative reactions

(Orange II as a model dye pollutant) under visible light irradiation [106]. The obtained results suggested the following rules, which could govern the electrons transfer mechanism: (a) metallic Cu improved the photocatalytic activity of single semiconductor by the formation of apparent Ohmic junction enhancing the charges transfer kinetics; (b) electromotive forces developed from semiconductor/semiconductor heterojunction suppressed the effect of metallic Cu due to the formation of an apparent Schottky type junction; (c) diffusion potential developed from multiple steps electrons transfer had more impact for improving the efficiency than that developed from one step transition; and (d) heterojunction cascade obtained from monobloc of photosensitizers was more efficient than that obtained from direct mixture of the semiconductors [106]. Xing et al. prepared Cu/Cu_2O/TiO_2 photocatalyst as an efficient heterojunction system for terephthalic acid degradation under UV/Vis irradiation [107]. According to the mechanism presented in Figure 17, under UV/vis irradiation electrons and holes are photogenerated on both Cu_2O and TiO_2. Because the Fermi energy level of Cu is lower than that of $_p$-type Cu_2O, electrons from the CB of Cu_2O migrate to Cu until the two Fermi levels are aligned. Holes in the VB of Cu_2O recombine with electrons in the CB of TiO_2. Therefore, holes in the VB of TiO_2 are efficiently separated from electrons, and engage in hydroxyl radicals' formation. In the case of visible light irradiation, only Cu_2O is photoexcited. Electrons in the CB of Cu_2O are trapped by highly conductive Cu, whereas migration of holes from the VB of Cu_2O to VB of TiO_2 is impossible, and thus, the negligible amount of hydroxyl radicals can be detected. This transmission pathway (under UV) is analogous to that of the Z-scheme system instead of a type II heterojunction system. It means that Cu/Cu_2O/TiO_2 system with very intensive charge separation is much more efficient in the case of UV/vis system than for visible light system, where Z-scheme model dominates [107].

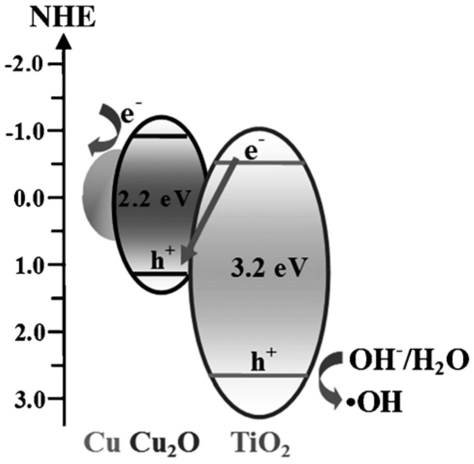

Figure 17. Reaction pathway for photoexcited e–h pairs in Cu/Cu_2O/TiO_2 nanojunctions. Reprinted with permission from [107]. Copyright John Wiley & Sons, Inc., 2013.

Analogically, it is thought that the morphology of titania should be also important issue for the efficiency of copper species–titania heterojunction system. Janczarek et al. prepared copper-modified titania based on decahedral anatase particles (DAP) with eight equivalent (101) facets and two (001) facets [58]. Copper species were photodeposited on DAP surface. It was estimated that Cu_2O was a predominant form of copper (82.0%), whereas other copper species existed in minority, CuO (12.8%) and Cu(0) (5.2%). Copper species formed small nanoclusters of ca. 2 nm, which were uniformly distributed on all facets of DAP. This material Cu/Cu_2O/CuO/TiO_2(DAP) was especially active in UV/vis system for acetic acid oxidation but very low improvement of activity for 2-propanol oxidation was observed under visible light irradiation, confirming mechanistic issues described in the previously mentioned studies [58].

Qiu et al. prepared Cu_xO-TiO_2 nanocomposites dedicated to indoor environments for degradation of volatile organic compounds and pathogens [108]. The structure of copper species deposited on titania surface was nanocluster mixture of Cu_2O and CuO. The balance between Cu(I) and Cu(II) states in Cu_xO was critical to achieving efficient VOC decomposition and antipathogenic activity. It was found that the optimum Cu(I)/Cu(II) ratio in Cu_xO nanoclusters was 1.3. This material had also good antiviral and antibacterial activity under dark conditions. The ratio of Cu(I)/Cu(II) did not markedly change after long-term visible-light irradiation, indicating that the multielectron reduction reaction was catalytic in air with a turnover number greater than 22 [108]. Luna et al. studied Cu_2O-CuO-TiO_2(P25) semiconductors for gallic acid oxidation under UV/vis LEDs irradiation [109]. By using UV light, CuO addition to TiO_2 did not enhance the photoactivity and acted like an impurity or a defect at the surface, favoring the fast recombination of charge carriers, or like an electron fast scavenger. In the case of visible light system (Figure 18), CuO addition evidenced the injection of charge carriers from Cu_2O to TiO_2 and CuO, as suggested by TRMC study. Gallic acid degradation proceeded by a sequence of reactions involving the formation of intermediates such as, maleic, fumaric, oxalic and formic acids, before reaching its mineralization [109].

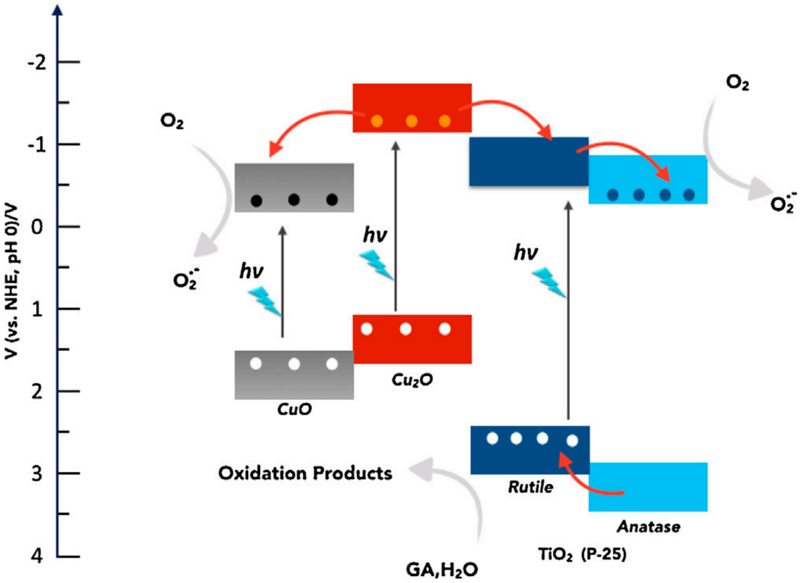

Figure 18. A proposed scheme showing the photoredox processes during degradation of gallic acid (GA) in presence of Cu_2O–CuO–TiO_2 (P25) photocatalysts, air and visible light (LEDs). Reprinted with permission from [109]. Copyright Elsevier, 2016.

3. Conclusions

The design of an efficient and stable photocatalyst for oxidative reaction systems with high activity under UV and visible light is still a challenge. Among various metals considered as titania modifiers, copper is one of the most promising because of its abundancy, low cost and similar properties to expensive noble metals such as gold and silver. The enhancement of TiO_2 photocatalytic activity with copper modification can be realized by two main mechanistic concepts: preparation of plasmonic photocatalyst with metallic copper on titania surface and formation of heterojunctions between titania and copper oxides. Direct doping of titania lattice by copper ions is rather difficult because of different sizes of Cu^{2+} and Ti^{4+}. The chemical stability of copper species is a very important issue for copper-modified TiO_2. This issue should be always considered in design thinking about copper-modified titania, primarily for metallic copper. In this review, the successful attempts to obtain stable metallic Cu were presented, and this breakthrough research may cause an increase in the number of research in the copper-focused, visible light-oriented plasmonic photocatalysis.

This review also highlights various heterojunction concepts according to different copper oxides–titania configurations. Owing to the authors' knowledge there is still no comprehensive research paper considering all main variants of copper oxides–titania heterojunctions to perform a comparable study. To analyze the mechanism of heterojunction, it is necessary to calculate exact positions of VB and CB of semiconductors. The problem is that these values for copper oxides can significantly differ in various papers, resulting in change of the possible type of heterojunction. Therefore, an accurate photoelectrochemical characterization of each component of heterojunction system is required. Among copper oxides in relation to heterojunction with titania, Cu_2O has the promising application potential to wastewater treatment including its very good antipathogenic properties, even better that metallic copper [108]. For oxidative reaction systems, cascade heterojunction with different forms of copper is also a perspective option. Additional presence of metallic copper in such heterojunction system is beneficial under UV irradiation, but is detrimental in the case of visible light irradiation. The presence of Ti^{3+} ions can also positively influence the efficiency of heterojunction system. Moreover, the content of copper oxides (Cu_2O/CuO) in cascade heterojunction system is a very significant parameter influencing photocatalytic activity. The new research areas are opening with the development of methods, which allow to obtain copper oxides and titania with specific particle morphology. The influence of different types of crystal facets of Cu_2O on the efficiency of Cu_2O/TiO_2 system has been confirmed and is still under debate. Furthermore, the core-shell configurations for copper oxide–titania heterojunctions can increase a photocatalytic efficiency and stability of whole photocatalytic system. Additionally, the post-illumination catalytic memory phenomenon, observed in Cu_2O(nanospheres)/TiO_2(nanoislands) can be important extension for photocatalytic properties under dark conditions.

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