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Research Article

Progress, Challenge, and Perspective of Bimetallic TiO_2-Based Photocatalysts

Anna Zielińska-Jurek

Department of Chemical Technology, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland

Correspondence should be addressed to Anna Zielińska-Jurek; annjurek@pg.gda.pl

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Bimetallic TiO_2-based photocatalysts have attracted considerable attention in recent years as a class of highly active catalysts and photocatalysts under both UV and Vis light irradiation. Bimetallic noble metal structures deposited on TiO_2 possess the ability to absorb visible light, in a wide wavelength range (broad LSPR peak), and therefore reveal the highest level of activity as a result of utilization of a large amount of incident photons. On the other hand they can enhance the rate of trapping photoexcited electrons and inhibit the recombination process due to the capability of the storage of photoexcited electrons. Based on literature two groups of bimetallic photocatalysts were distinguished. The first group includes bimetallic TiO_2 photocatalysts (BM_{OX}), highly active under UV and Vis light irradiation in a variety of oxidation reactions, and the second group presents bimetallic photocatalysts (BM_{RED}) exceptionally active in hydrogenation reactions. This review summarizes recent advances in the preparation and environmental application of bimetallic TiO_2-based photocatalysts. Moreover, the effects of various parameters such as particle shape, size, amount of metals, and calcination on the photocatalytic activity of bimetallic TiO_2-based photocatalysts are also discussed.

1. Introduction

Titanium (IV) oxide (TiO_2) is one of the most important photocatalytic materials in the area of environmental purification, hydrogen generation, and CO_2 photoconversion to methane and low hydrocarbons. The limitation in its application is resulting from low quantum yield (fast recombination of charge carriers: e^-/h^+) and necessity to use UV irradiation, which may be overcome since modified titania often possesses higher activity and ability of working under visible light irradiation. Over the past decades physical, chemical, and photocatalytic properties of TiO_2 were intensively investigated to enhance the efficiency of degradation of organic pollutants [1–7]. Among various organic and inorganic compounds used as dopants or surface modifiers, noble metal particles especially attracted attention, since they may enhance the transfer of photogenerated electrons extending the lifetime of charge carriers [8, 9]. Noble metal nanoparticles, such as gold, silver, platinum, and palladium, possess the ability to absorb visible light due to localized surface plasmon resonance (LSPR) [10–12] and therefore may also activate wide bandgap semiconductors (e.g., TiO_2) towards visible light.

Metallic nanoparticles, particularly these of silver, gold, and platinum, or a combination of these metals (Ag-Pt, Au-Pt, and Au-Ag) and various oxides (TiO_2, SiO_2) are used as templates for the creation of complex and ordered nanomaterials with tailored and tunable structural, optical, and surface properties [13].

Since the pioneering work of Haruta, Au clusters supported by oxides (Au/oxides) have perhaps become the most interesting systems in heterogeneous catalysis because of their unique catalytic properties at low temperatures for many reactions. Gold nanoparticles less than 5 nm in size are very active catalysts. However, large gold nanoparticles supported on metal oxide with diameter of about 50 nm and more exhibit photocatalytic activity for hydrogen production, environmental pollution degradation, and reduction of nitrogen oxides [11, 14].

Many reports on this subject using platinum cluster dispersions or nanoparticles have been published [15–17]. Platinum is one of the most active metals for photocatalytic

enhancement, which can produce the highest Schottky barrier among metals that facilitate electron capture and, therefore, hinders the recombination rate between electrons and holes [18, 19].

Although platinum is a very promising metal, which can increase TiO_2 activity, it is more expensive than gold [20]. Certain solution is to use bimetallic structure of platinum with another metal, which can greatly enhance the photocatalytic performance, particularly with respect to activity and selectivity [21]. Bimetallic nanoparticles revealed unique catalytic, electronic, and optical properties distinct from those of the corresponding metallic particles as used in photocatalysis, photonics, electronics, optics, drug delivery, and others [22–27]. The positive effect of metal deposits on TiO_2 surface results from the improved separation of electrons and holes on the surface of the photocatalyst. Additionally, modification of TiO_2 with noble metal nanoparticles (NPs) such as gold and silver, which exhibit plasmon absorption band at 560 nm (Au) and 410 nm (Ag), is beneficial, due to enabling the absorption of visible light in a wider range of wavelengths and thus with higher levels of activity [28]. Bimetallic NPs deposited on TiO_2 are expected to display not only the combination of the properties associated with two distinct metals, but also the new properties due to synergy between two metals.

Recently, alloying or bimetallization of platinum with gold has been reported to improve the catalytic activity of platinum clusters for visible light-induced hydrogen generation and degradation of organic dyes or phenol [15, 29]. However, the improvement of photocatalytic activity of TiO_2 modified with noble metal nanoparticles by bimetallization is observed not only between platinum and gold, but also between platinum and palladium [30, 31], palladium and gold [32, 33], platinum and copper [34], platinum and nickel [35], platinum and tin [36], platinum and iron [35], palladium and copper [37, 38], gold and silver [11, 39], and copper and silver [40].

Reports on preparation of Au/TiO_2, Pt/TiO_2, Ag/TiO_2, and Cu/TiO_2 nanocomposites with different morphological forms are progressively increasing with the focus on preparation of catalysts and photocatalysts modified with bimetallic nanoparticles of an alloy or core-shell structure. Several research targets on TiO_2 responsive to visible light or to enhance the photocatalytic efficiency in oxidation and reduction processes were reported.

The number of papers pertaining to the photocatalytic activity of modified bimetallic NPs increases, as might be expected from bimetallic nanocomposites application and their activity and selectivity, see Figure 1.

Bimetallic nanoparticles of the same size, shape, and composition show significant differences in activity when configured into different architectures. Their structure depends on distribution modes of the two elements, which can be oriented (see Figure 2):

(i) alloy or intermetallic structure,

(ii) heterostructure,

(iii) core-shell,

(iv) multishell structure,

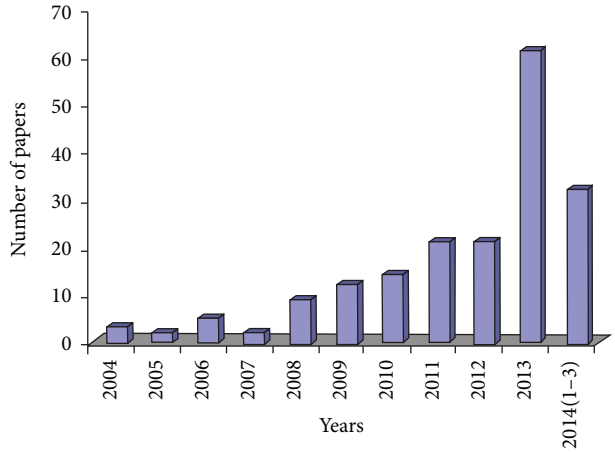

Figure 1: Number of publications concerning preparation and properties of photocatalyst modified bimetallic nanoparticles over the years 2004–2014 (till March), based on database of the ScienceDirect, with search keywords being "bimetallic photocatalyst, bimetallic modified TiO_2."

and depends on the processing parameters, miscibility, and reduction kinetics of metal ions [41]. The alloy structure represents homogenous mixture of two metals (Figure 2(a)). The heterostructure results from independent nucleation and growth of two different metal crystals (Figure 2(b)). In the core-shell structure, one metal forms a core and the other metal surrounds it in the form of a shell (Figure 2(c)). In the multishell structure, layered stable or metastable alternating shells exist (Figure 2(d)).

The structure of bimetallic nanoparticles deposited on TiO_2 depends on the particle size, the preparation procedure, the type of support (its size, porosity, BET surface, and crystallinity), and the calcination temperature of the photocatalysts [11, 33].

Among all applications of bimetallic-based nanomaterials, the degradation of environmental pollutants, especially recalcitrant organic compounds, is attracting considerable attention. From among 180 papers identified in the Science Direct database (Figure 1) referring to the catalytic activity of TiO_2 modified bimetallic NPs published over the years 2004–2014 (till March), 93 articles were published during the last year (2013 to March of 2014). In most of them, the catalytic and photocatalytic degradation of organic pollutants in gas and liquid phases, hydrogen generation reactions, and the reaction mechanism on modified TiO_2 nanoparticles were investigated.

This review focuses on three major research areas mentioned above, including crucial operating parameters such as the size of photocatalyst components, the amount of bimetallic NPs, and the extent of photocatalyst calcination.

2. The Importance of Charge Carriers in TiO_2-Based Photocatalysis

Titanium dioxide (TiO_2) is a semiconductor with a bandgap of 3.2 eV. The mechanism of heterogeneous photocatalytic

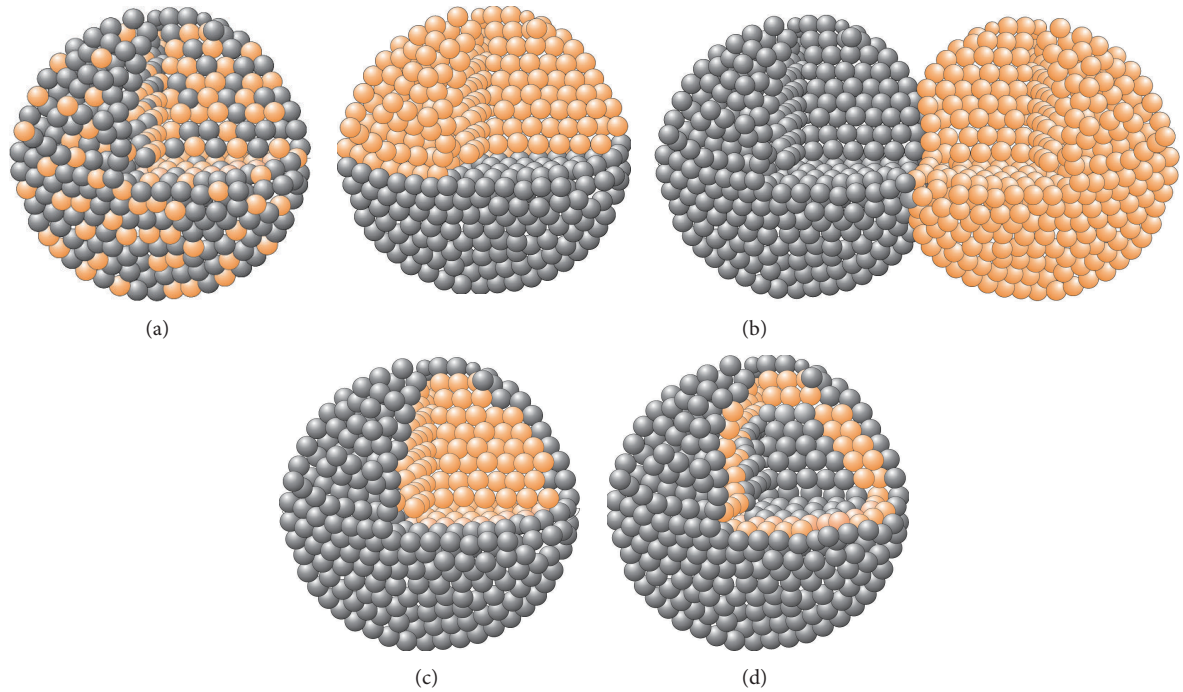

Figure 2: Schematic illustration of bimetallic NPs with different structures (a) alloy, (b) heterostructure, (c) core-shell, and (d) multishell structure.

oxidation processes has been discussed extensively in literature [42–47]. The reduction and oxidation reactions make the foundation for photocatalytic hydrogen production and photocatalytic water/air purification. Generation of excited high energy states of electron and hole pairs occurs when TiO_2 is irradiated with light of greater energy than the bandgap energy (wavelengths lower than 390 nm) as shown in Figure 3. An electron is excited (e_{CB}^-) from the valence band to the conduction band, forming a positive hole (h_{VB}^+) in the valence band. Hoffmann et al. [42] have found by laser flash photolysis studies that the characteristic time scale for this charge-carrier generation reaction is of the order of femtoseconds (fs). The charge carriers generated migrate on the TiO_2 surface and react with electron acceptor or electron donor. An important reaction that competes with the charge-carrier trapping is the electron-hole recombination reaction, which can occur either at the surface states of TiO_2 or in the core of semiconductor [48]. This is one of the most detrimental reactions in photocatalysis as it affects the interfacial charge transfer processes and hence the quantum efficiency of the photocatalytic process.

3. TiO_2 Modification Using Monometallic or Bimetallic Nanoparticles

Attempts to employ semiconductor-metal composite nanoparticles have been made to improve the charge separation efficiency. The synergy of noble metals and semiconductor photocatalysts brings in significant changes to many aspects of photocatalysis. An increase of activity under Vis light after modification of titania with plasmonic nanoparticles such as gold, silver, platinum, and palladium results from additional metal impact on the mechanism of electron transfer. The photons are absorbed by metallic particles through their localized surface plasmon resonance (LSPR) excitation [11, 49], see Figure 4. Surface plasmons of a metal are collective excitations of electrons in the conduction band and they dominate the electromagnetic responses of the metallic structure of dimensions in the order of the plasmon resonance wavelength. The surface plasmon resonance of metallic nanoparticles occurs when electromagnetic field interacts with conduction band electrons and induces the coherent oscillation of electrons. The charge oscillations of noble metals at the surface take place at optical frequencies, which depend on the dielectric constant of the material at metal surface. As shown in Figure 5(a) the electron is transferred from plasmonically excited noble metal (Ag, Au) to conduction band of titania. Another important feature is the formation of Schottky junction when noble metal nanoparticles have direct contact with the semiconductor.

The enhancement in reactivity was first observed for water splitting using the Pt/TiO_2 system [50, 51]. Under UV irradiation noble metal nanoparticles deposited on TiO_2 enhance transfer of photogenerated electrons prolonging lifetime of the charge carriers (see Figure 5(b)). Metals (such as Pt, Au, and Ag) and the semiconductor (TiO_2) have different Fermi level. Electron migration from TiO_2 to the metallic nanoparticle occurs until two Fermi levels are aligned, since the metal has a work function (ϕ_m) greater than that of TiO_2 (ϕ_s). The electrical contact resulted in a space charge layer, the Schottky barrier, which trapped electrons and suppressed electron-hole recombination [9]. Surface of metal acquires an excess negative charge, while TiO_2 exhibits an excess positive

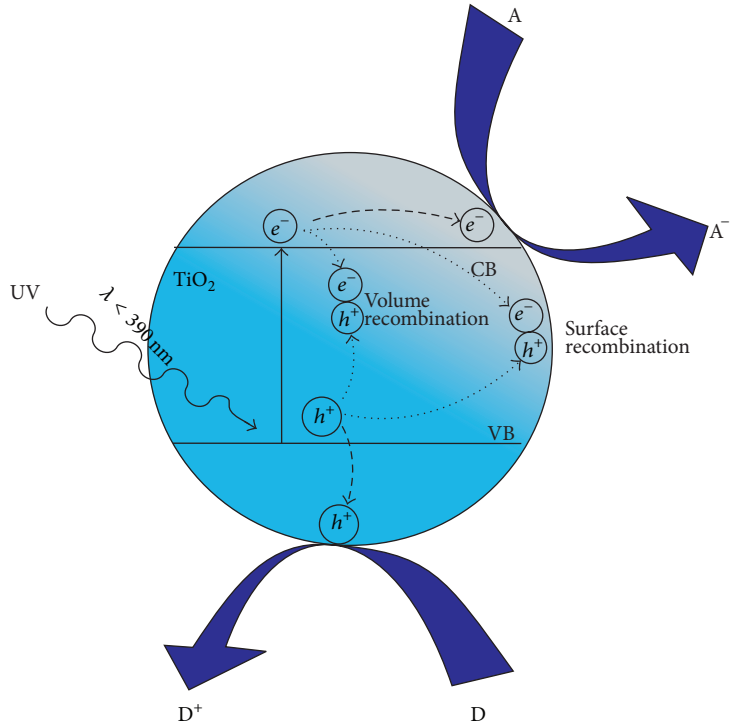

FIGURE 3: Schematic illustration of semiconductor excitation by bandgap illumination leading to the creation of "electrons" in the conduction band and "holes" in the valance band.

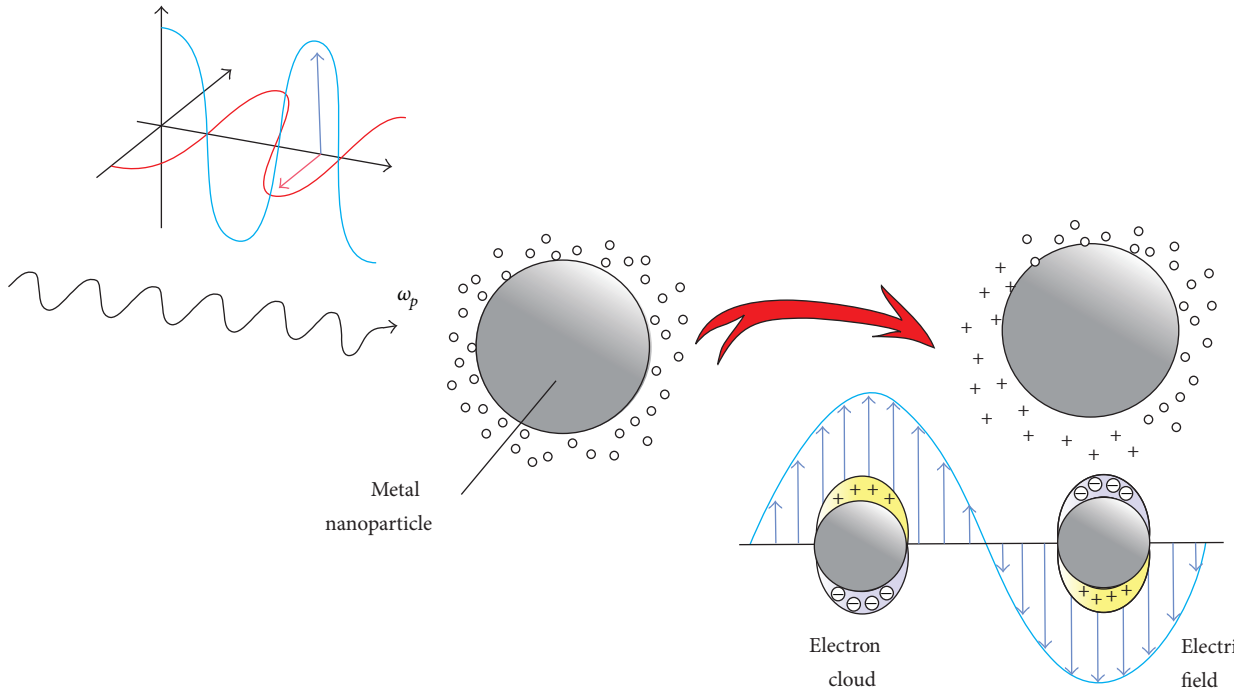

FIGURE 4: Localized surface plasmon resonance (LSPR) of noble metal (Ag, Au) nanoparticles, a collective electron density oscillation caused by the electric field component of incoming light.

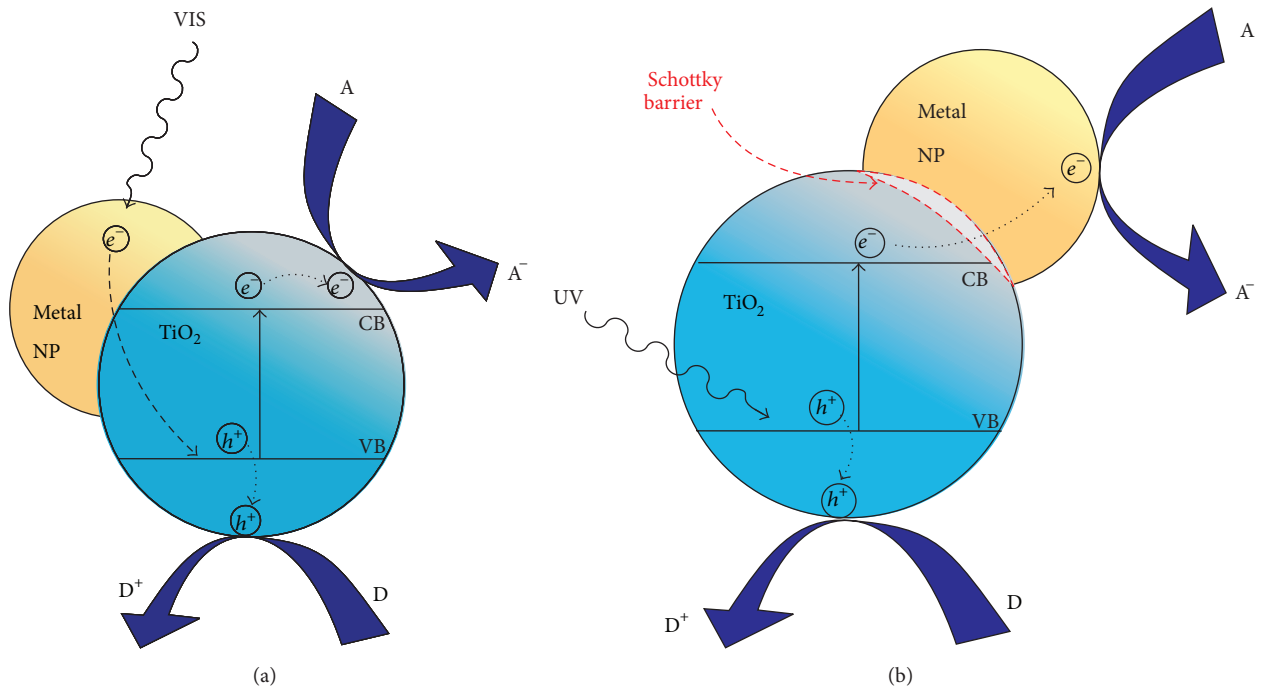

FIGURE 5: Schematic illustration of TiO_2 modified monometallic NPs mechanism of organic pollutants degradation under Vis (a) and UV light irradiation (b).

charge as a result of electron migration from the barrier region. The height of the barrier (ϕ_b) makes the difference between the TiO_2 conduction band and metal Fermi level. Electrons drawn across this barrier leave additional positive holes in TiO_2 matrix capable of oxidizing more organic species.

On the other hand, Anpo and Takeuchi [52] observed the electron transfer from TiO_2 to Pt particles, using electron spin resonance (ESR) analysis. It was found that Ti^{3+} signals increased with irradiation time, while loading of Pt reduced the amount of Ti^{3+}. They found that accumulated electrons on platinum particles can be transferred to protons adsorbed on the surface, reducing the protons to hydrogen molecules. Therefore, noble metals with suitable work function can enhance electron transfer, leading to higher photocatalytic activity [52].

For TiO_2 photocatalysts modified with bimetallic NPs the mechanism of photocatalyst excitation depends on bimetallic nanoparticles structure. Based on literature and our own work we distinguish two groups of the bimetallic photocatalysts. The first group includes bimetallic TiO_2 photocatalysts (Ag-Au, Ag-Pt, Ag-Cu, Pt-Cu, Pt-Pd, and Au-Cu) (BM_{OX}) highly active under UV and Vis light irradiation in a variety of oxidation reactions. The second group is bimetallic (Au-Pt, Au-Pd, Au-Rh, Au-Ni, Au-Co, and Pt-Ru) modified TiO_2 photocatalysts (BM_{RED}) exceptionally active in hydrogenation reactions.

For alloy structure in oxidation processes the mechanism is similar to the excitation mechanism of monometallic NPs deposited on TiO_2 as shown in Figure 6(a).

It is well known that the work function of metal decreases by alloying of other metal components with a lower work function. This suggests that alloying of other metal with Pt would decrease the work function of Pt nanoparticles. This may decrease conduction band (φB) and promote efficient e^- transfer from nanoparticles to anatase. Shiraishi et al. reported that alloy Pt-Cu particles on anatase surface activated efficiently transfer of e^- to anatase. This enhances the reduction of O_2 by e^-, resulting in enhanced aerobic oxidation [53]. The enhanced e^- transfer from the alloy particles to anatase was confirmed by electron spin resonance (ESR) analysis of the photocatalysts. It was found that the visible light irradiation of the sample creates strong signals assigned to superoxide anion stabilized on TiO_2 surface. It was concluded that the transfer of e^- to anatase was more efficient for Pt-Cu/TiO_2 than for the monometallic Pt nanoparticles deposited on TiO_2 surface [53]. Cu alloying with Pt decreases the work function of nanoparticles and decreases the height of Schottky barrier created at the nanoparticle/anatase heterojunction. This promotes efficient electron transfer from the photoactivated nanoparticles to anatase, resulting in enhanced photocatalytic activity. The Pt-Cu alloy photocatalyst is successfully activated by sunlight and enables efficient and selective aerobic oxidation of alcohols at ambient temperature.

The promoting effect of bimetal is attributed to either the improved spatial charge separation in TiO_2 semiconductor or charge carrier transfer from metal NPs to conduction band of TiO_2. Based on catalytic, optical, and photocatalytic properties the synergy between two metals in bimetallic system is also related to the electronic and geometric effects. A bimetallic structure formed by metals with lower electronegativity and other metal with higher electronegativity seems to perform better activity in photocatalyzed oxidation reactions

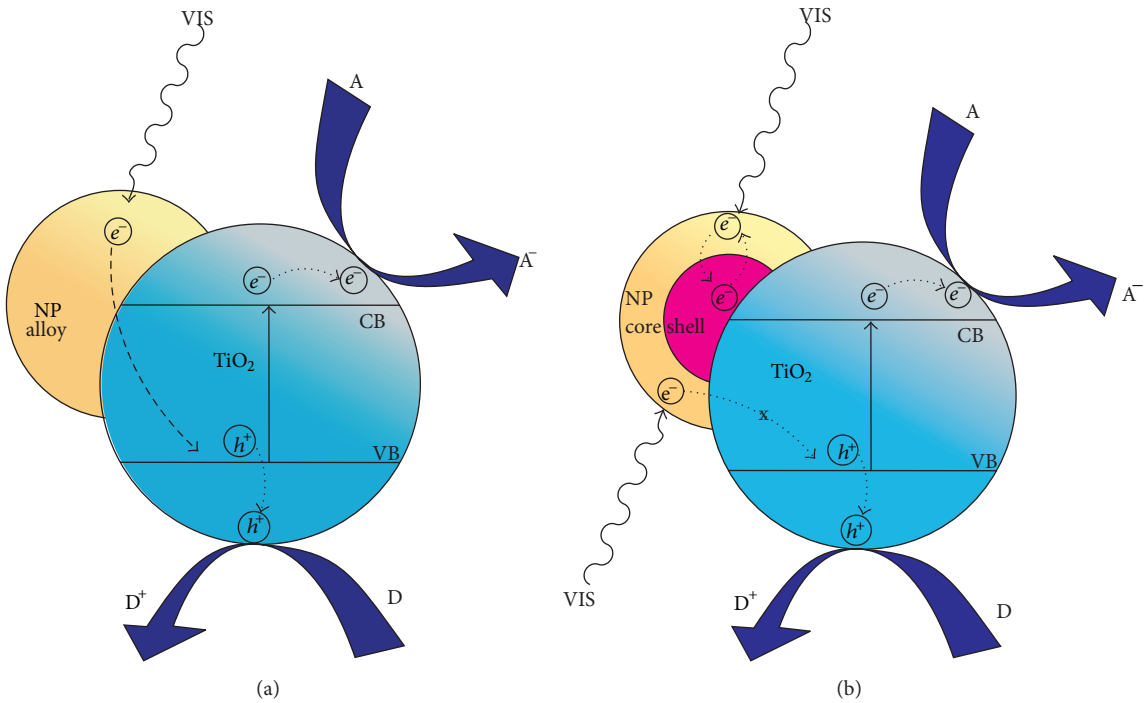

Figure 6: Schematic illustration of activation mechanism of TiO_2 modified bimetallic NPs with alloy (a) and core-shell structure (b).

[54]. The second metal is much more subject to oxidation than the other, which is enriched on the surface and may form metal oxide patches or shells on the first metal surface. The less electronegative metal can participate directly in oxidation reactions by providing reactive oxygen.

Phase segregation for the combination of two metals may occur upon treatment in an oxidizing atmosphere in either reaction or preparation process, as was reported for Ag-Au/TiO_2 nanocomposites [11, 39, 54]. In our own XPS analysis it was observed that silver as Ag_2O and gold as Au° were the dominant surface forms for Ag-Au alloy-modified TiO_2 nanoparticles [11]. The Ag-Au/TiO_2 nanocomposites showed more significant visible light photoactivity compared to monometallic Ag/TiO_2 and Au/TiO_2 nanoparticles obtained using the same preparation procedure. Important results regarding bimetallic Ag-Au NPs deposited on TiO_2 were reported by Kowalska et al. [55]. Ag-Au core-shell structure NPs on TiO_2 were obtained by the photodeposition method. Silver nanoparticles were oxidized and formed a shell on gold-rich core, while bimetallic Ag-Au nanoparticles with core-shell structure showed enhanced recombination of charge carriers. Greater ability of charge generation at the interface of a bimetallic structure does not mean better photoactivity, since in the core-shell structure plasmonic electrons instead of being transferred from silver to CB (conduction band) of titania may sink in nearby gold NP and vice versa, as shown in Figure 6(b). Plasmonic metals can be excited at visible range wavelengths via d-to-sp band transitions, recombining upon relaxation; once there is a pair of metals the relaxation is expected to be more efficient due to larger available density of electronic states.

The hydrogenation reactions are generally catalyzed by the transition metals of group VIII of the periodic table. The improvement of photocatalytic reduction processes in the presence of bimetallic-based photocatalyst is related to the enhancement of the rate of trapping photoexcited electrons and inhibition of the recombination process due to the capability of the storage of photoexcited electrons by using bimetallic nanoparticles deposited on TiO_2 surface. Gao et al. [56] found that bimetallic Ni-Cu nanoparticles on the semiconductor surface can separately trap photogenerated electrons and holes and prevent their combinations, thereby increasing their life and improving the efficiency of photocatalytic reactions [56]. Bowker et al. [57] observed enhanced photocatalytic activity, using Au-Pd random alloys on TiO_2 due to improved rate of trapping photoexcited electrons and inhibited recombination due to the capability of storage of photoexcited electrons by using alloy metal nanoparticles. The photocatalytic activity and properties of the two groups of bimetallic photocatalysts (BM_{RED}-TiO_2) and (BM_{OX}-TiO_2) active in reduction and oxidation processes are discussed in detail in the next paragraphs.

4. Bimetallic (BM_{RED}-TiO_2) Photocatalysts for Reduction Processes

Although, platinum and gold nanoparticles deposited on TiO_2 revealed the highest photocatalytic activity under Vis light irradiation, the combination of these two metals does not provide sufficient increase in photocatalytic activity in

degradation of organic pollutants. For Au-Pt/TiO_2 and Au-Pd/TiO_2 most of literature data pertains to hydrogen generation reactions. Gallo et al. [58] reported preparation procedure for bimetallic Au-Pt/TiO_2 photocatalysts in the process of hydrogen generation both under UV-A and simulated sunlight irradiation. Bimetallic-based photocatalysts were prepared by impregnation of nanosized amorphous TiO_2 with metal precursors followed by oxidation and reduction treatments. The best photocatalytic performance was obtained for sample reduced at 500°C, containing bimetallic Au-Pt nanoparticles with diameters smaller than 2 nm deposited on TiO_2 surface. It was found that the synergetic effect under simulated sunlight and the improved activity under visible light of Au-Pt/TiO_2 NPs compared to monometallic Pt/TiO_2 and Au/TiO_2 were the result of the combination of four contributing aspects [58]:

(i) the presence of Au surface plasmon band absorption at wavelengths 550–600 nm,

(ii) the presence of bimetallic Au-Pt nanoparticles which ensures prompt hydrogen evolution as for Pt nanoparticles and is different from the less active Au-based catalysts,

(iii) the low total metal loading which leaves a high fraction of TiO_2 surface available for UV light absorption,

(iv) containing both oxygen vacancies and Ti^{3+} sites.

A brief summary of recent publications on TiO_2 photocatalysts modified with bimetallic nanoparticles used in reduction processes is provided in Table 1, in which one can observe that among (BM_{RED}-TiO_2) photocatalysts Au-based bimetallic TiO_2 photocatalysts represent a significant and the most extensively studied group in a variety of catalytic and photocatalytic reactions. Many reports in literature focus on the effect of the preparation procedure and amount of metal on bimetallic structure and their effect on catalytic and photocatalytic activity. The structure of bimetallic NPs mainly depends on the nature of metals such as relative bond strengths, their surface energies, and atomic size [59]. Strong heteronuclear bonds between two different metallic species influence the formation of the alloy structure, while the strongest homonuclear bonds of one species form the core and the other metal forms the shell of the structure. Metal with lower surface energy tends to segregate on the surface of the other metal [59]. This effect is in particular described in literature for bimetallic structures of Au-Pd and Au-Pt NPs.

Edwards et al. [60] observed the effect of catalyst calcination and reduction on the optimum composition of Au-Pd modified TiO_2 nanoparticles. Under heat treatment, smaller pure-Au particles sinter and combine with palladium forming large alloy particles [60]. Cybula et al. [33] observed a similar effect of the calcination temperature (from 350 to 700°C) and segregation of metals (Au, Pd) on TiO_2 surface depending on the annealing temperature. Microscopic analysis revealed that for the sample calcinated at 350°C three main fractions of Au-Pd NPs could be distinguished: small particles in the range of 1 to 6 nm, anisotropic particles from 15 to 50 nm, and spherical ones with the diameter of about 50 nm. For the sample treated at 450°C particles smaller than 10 nm were not found. Au-Pd particles in the range from 10 to 50 nm remained spherical, while bigger ones (from 70 to 360 nm) had irregular shape. Calcination at 700°C resulted in bimodal distribution of 15–20 nm particles and 65–330 nm particles, both irregular, as shown in Figure 7. With respect to sample calcinated at 350°C, it could be observed that the core of bimetallic NPs was rich in gold, but the shell contained mostly palladium. Rising the calcination temperature from 350 to 700°C led to alloying of the metals and increased the size of nanoparticles [33]. The photoactivity of Au-Pd/TiO_2 nanoparticles was studied in oxidation of phenol. Therefore, no spectacular synergistic effect of bimetallic Au-Pd NPs immobilized on TiO_2 surface was observed. Regarding the effect of the calcination temperature for 0.5Pd_1.25Au_TiO_2 sample, it was found that for UV-mediated photoactivity increasing the calcination temperature resulted in improvement of phenol degradation rate from 5.8 to 7.1 and 6.2 $\mu mol \cdot dm^{-3} min^{-1}$ for the photocatalyst calcinated at 350, 400, and 450°C, respectively. The highest photoactivity under UV light was observed for sample calcinated at 500°C. Annealing temperature of 700°C resulted in the drop of photoactivity to 5.7 $\mu mol \cdot dm^{-3} min^{-1}$. The visible light activity was suppressed for the samples treated at an elevated temperature. Thus, phenol degradation rate under visible light decreased from 3.8 and 3.4 $\mu mol \cdot dm^{-3} min^{-1}$ for the sample calcinated at 350 and 400°C, respectively, to 0.7 $\mu mol \cdot dm^{-3} min^{-1}$ after calcination at 700°C. Samples calcinated at 350 and 400°C had much higher activity than those calcinated at 450 and 700°C.

Previously reported inhibitory effect of a core-shell structure of bimetallic NPs immobilized on TiO_2 photocatalysts on photoactivity under visible light irradiation in oxidation processes was not observed in the reduction processes. Moreover, the authors reported a promotional effect of a core-shell structure on photocatalytic activity in reaction of hydrogen generation.

Yu et al. [61] obtained Au-Pd alloy-modified TiO_2 nanotube film by photodeposition of Au and Pd precursors on self-organized TiO_2 nanotubes. The photoactivity of bimetallic photocatalysts was evaluated under reducing and oxidation conditions. Compared with TiO_2 having immobilized mixture of Au and Pd monometallic nanoparticles, a synergistic effect was observed in photocatalytic hydrogen evolution when TiO_2 was immobilized with Au-Pd bimetallic nanoparticles. In case of organophosphorus pesticide malathion, using Au-Pd comodified TiO_2 nanotube film, higher photocatalytic degradation rate was observed for Au-Pd alloy NPs deposited on TiO_2. The improvement of photocatalytic activity resulted from the presence of small metal clusters on TiO_2, which promotes the separation of photogenerated charges, and thus more holes could be involved in the malathion oxidation reactions [61]. Whereas the oxidation processes require a high content of the second metal in the bimetallic structure for efficient degradation of organic pollutants, in hydrogen generation processes the basis metal (generally Au) acts as promotor of the other metal to prevent its poisoning by intermediates or byproducts. Therefore, in hydrogen generation only a small amount of the second metal is required for synergistic effect and improvement of photocatalytic activity of nanocomposites.

Table 1: Recent publications of TiO_2 photocatalysts modified bimetallic nanoparticles used in reduction processes.

Bimetallic NPs	Range particle size [nm]	Irradiation source	Degradation effect and comments	Reference
Au-Pd alloy	n.m. 32 nm-anatase	450 W high-pressure mercury lamp	The amount of H_2O_2 obtained on Au-Pd/TiO_2 film (44.0 μM) in 60 min was about 3 times higher than on pristine TiO_2 (15.2 μM).	[61]
Au-Pd alloy	Au—5 Pd—7 Au/Pd—3 to 5	400 W Xe arc lamp	Pd yielded more than Au in photoreforming, especially at low loadings	[57]
Au-Pd random alloy Au-Pd core (shell) structure	4 to 5	300 W Xe arc lamp	Studying photochemical evolution of H_2 from ethanol occurred only from illuminated catalyst. The core/shell structure performed better under Vis, while alloy structure (after calcination) performed better under UV	[32]
Au-Pd alloy Au-Pd-core (shell)	Bimodal size distribution 1 to 8 (Au) and 40 to 70 (Au-Pd)	n.d.	Two types of catalysts were synthesized and investigated. The active catalysts contained relatively large alloy particles with Au core surrounded by a Pd-rich shell. The photocatalytic activity was not studied	[60]
Au/Pt clusters	32	n.d.	Oxygen vacancies produced by electron irradiation stimulated the growth of Au crystals, while the nucleation behavior of Pt was less affected	[76]
Au-Pt structure not identified	<2 nm	Medium pressure Hg lamp with a cut-off filter at $\lambda > 400$ nm	Synergetic effect of Au-Pt/TiO_2 NPs under simulated sunlight compared to monometallic Pt-TiO_2 and Au-TiO_2 was reported. Higher activity of Au0.5-Pt0.5/TiO_2 results from interaction between Au and Pt which can induce a decrease in metal-hydrogen bond strength and improve the electron trapping ability of NPs	[58]
Pd-Cu alloy	n.m.	125 W high-pressure mercury lamp	The role of Pd was to split H_2 into absorbed Pd–H atoms, which can reduce nitrite to other nitric species, but also reduce the adjacent copper oxides into metal copper. The highest activity was achieved by using Pd-Cu/TiO_2 (Pd : Cu = 2 : 1, 3 wt.%) catalyst	[37]
Cu-Ni/TiO_2	20 to 40	500 W halogen lamp	The addition of a small amount of Ni onto Cu/TiO_2 (10 wt.%, Cu : Ni mass composition of 9 : 1) enhanced the performance of photocatalyst from producing 5.0 cm^3 to 6.1 cm^3 of hydrogen	[65]
Ni-Cu/TiO_2	20 to 30	125 W high-pressure mercury lamp	Cu-Ni/TiO_2 nanoparticles revealed about 1.2 times and 2.6 times higher photoactivity than bimetallic photocatalysts Pt-Cu/TiO_2 and Pd-Cu/TiO_2 obtained using the same preparation procedure	[37]
Pt-Ru/TiO_2	50 to 100	n.d.	Among the prepared TiO_2 supported bimetallic (Pt-Pd/TiO_2 and Pt-Ru/TiO_2 and Pt-Au/TiO_2) nanocatalysts Pt-Ru/TiO_2 showed the best overall conversion and selectivity towards geraniol and nerol	[77]
Pt-Ru clusters	Pt—2.3 Ru—2.2 Pt/Ru—2.0	500 W high-pressure mercury lamp	The present platinum/ruthenium systems were much more active than gold/platinum bimetallic clusters in the reaction of hydrogen generation	[29]

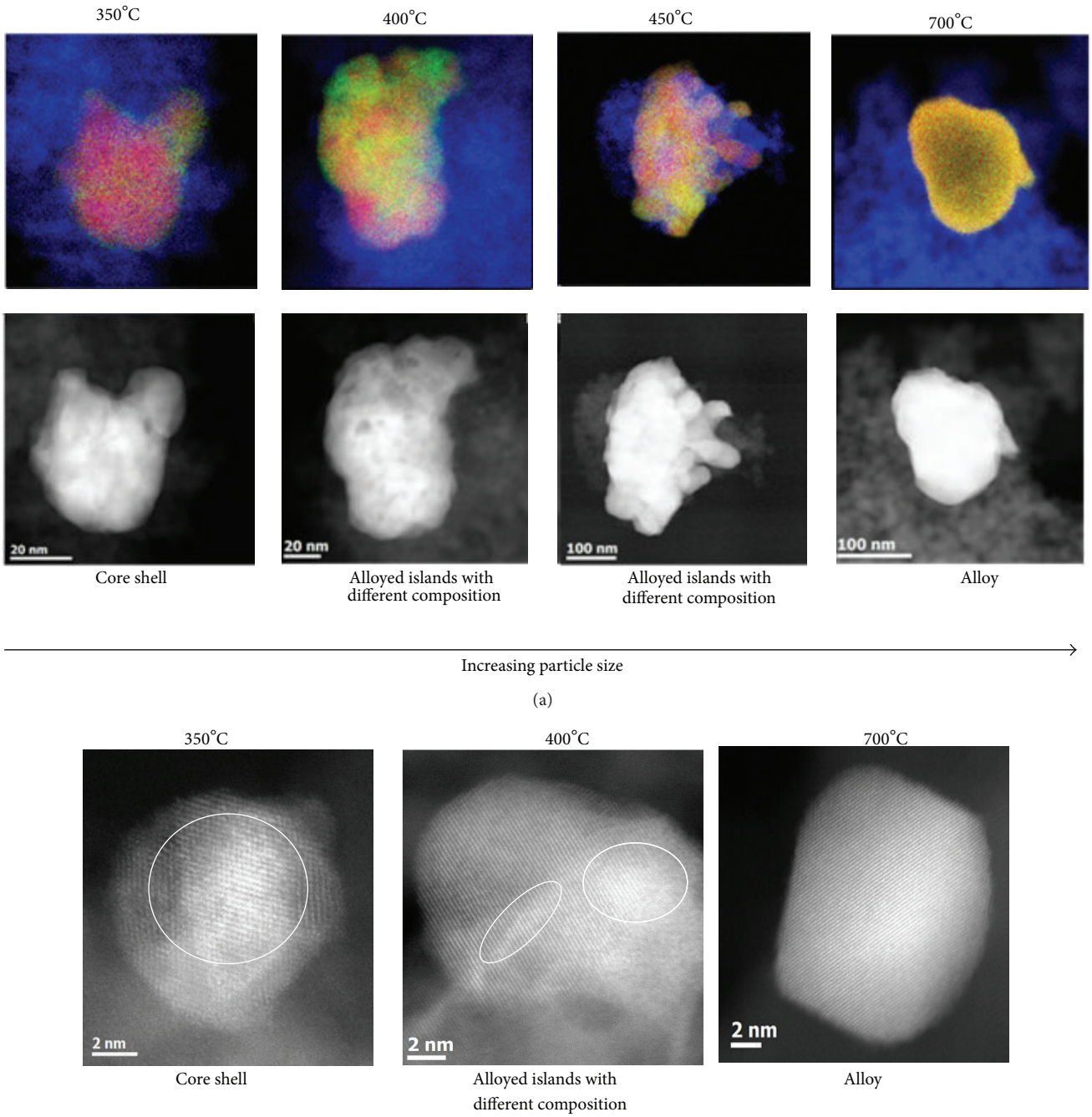

Figure 7: The effect of calcination temperature on the structure of Au/Pd bimetallic nanoparticles. (a) High resolution HAADF images with z-contrast for Au/Pd nanoparticles calcined at 350°C, 400°C, and 700°C. (b) The yellow circles show gold-rich areas (palladium gives a light contrast than gold as a lighter element) [33].

Mizukoshi et al. [32] reported the dependence of the nanostructure of Au-Pd NPs on photocatalytic activity of the Au-Pd/TiO_2 nanoparticles obtained by ultrasonication. The effect of metal amount in bimetallic structure was investigated. The authors observed that the best photocatalytic performance of hydrogen generation could be attributed to sample containing 75 mol% of Pd and 25 mol% of Au in bimetallic core-shell structure. The average diameter of the particles was from 4 to 5 nm. In hydrogen generation process the core/shell immobilized photocatalyst exhibits the highest performance under Vis illumination, whereas the alloy-modified TiO_2 sample exhibits the highest performance of the photocatalysts under UV irradiation. This effect could be explained based on palladium and gold efficiency in the reaction of hydrogen generation. It was observed that Pd produces better yields of hydrogen, and, indeed, the peak

rate of the production (as a function of weight loading) is higher for palladium than for gold [32]. It was stated that bimetallic nanoparticles containing large amounts of Pd can accept electrons more effectively, as Pd has a larger work function than Au [62, 63]. However, it was observed that the amount of H_2 did not increase linearly with the increase of Pd amount in the structure. On the other hand Lee et al. [64] reported that the alloy structure bimetallic photocatalysts had better photocatalytic efficiency in the reactions of organic compounds degradation. Au shell-Pd core/TiO_2 18–25 nm NPs were obtained by thermal reduction of metal ions in citrate solution. The core-shell structure of bimetallic photocatalysts was less selective in the reaction of crotyl alcohol oxidation. The photoactivity increased with the increasing temperature, because elevated temperatures promote alloying of Au-Pd nanoparticles. The maximum oxidation rate occurred for 700°C annealed Au (shell)-Pd (core)/TiO_2 NPs, which possess a surface alloy composition (Au40Pd60) [64].

Kait et al. [65] obtained copper-nickel bimetallic photocatalysts active in hydrogen production under visible light from glycerol-water mixture. It was found that bimetallic photocatalyst calcinated at 200°C for 1 h produced the highest amount of H_2 similar to that produced by monometallic Cu/TiO_2. The addition of a second metal enhanced the performance of Ni/TiO_2 but was not so efficient compared to Cu/TiO_2 NPs [65].

Xu et al. [34] reported preparation of Pt-Cu/TiO_2 photocatalysts for nitrate reduction in water. Compared to monometallic Pt/TiO_2 or Cu/TiO_2, which were active in the reaction of nitrate reduction to ammonia or nitrite, the obtained bimetallic photocatalyst exhibited a considerable N_2 selectivity for photocatalytic nitrate reduction. The photocatalytic activity and N_2 selectivity of the supported bimetallic photocatalyst were dependent on TiO_2 calcination temperature, Pt-Cu ratio, and metal loading amount. It was found that high Pt-Cu alloy dispersion as well as small metal particle size can be achieved over TiO_2 calcinated at 300°C, which favors the selective nitrate reduction. Increasing Cu content in the bimetallic photocatalyst leads to the increased Cu content in Pt-Cu alloy and enhances nitrate reduction to nitrite, while high Cu content in Pt-Cu alloy is detrimental to N_2 selectivity of the bimetallic photocatalysts [34].

Gao et al. [37] reported application of Ni-Cu/TiO_2 in photocatalytic reduction of nitrates. It was found that bimetallic photocatalyst Ni-Cu/TiO_2 showed higher photocatalytic activity compared with corresponding monometallic Ni/TiO_2 and Cu/TiO_2 nanoparticles. The photoactivity of Ni-Cu/TiO_2 photocatalyst with 3 : 1 metal weight ratio and 4 wt.% total metal content was about 2.5 times and 3.5 times higher compared to monometallic Cu/TiO_2 and Ni/TiO_2 photocatalytic activity, respectively. Compared to other bimetallic photocatalysts, Cu-Ni/TiO_2 nanoparticles revealed about 1.2 times and 2.6 times higher photoactivity than bimetallic photocatalysts Pt-Cu/TiO_2 and Pd-Cu/TiO_2 obtained using the same preparation procedure.

Oros-Ruiz et al. proposed [66] photocatalytic hydrogen production using Au-Cu_2O/TiO_2, Au-Ag_2O/TiO_2, and Au-NiO/TiO_2 photocatalysts. It was found that the presence of gold and metal oxides like Cu_2O or NiO as cocatalysts on TiO_2 surface increased significantly the production of hydrogen by avoiding the recombination of the hole electron. The combination of Au-Cu_2O/TiO_2 and Au-NiO/TiO_2 effectively increased hydrogen production (2064 and 1636 $\mu mol \cdot h^{-1} \cdot g^{-1}$) compared to Au/$TiO_2$ (1204 $\mu mol \cdot h^{-1} \cdot g^{-1}$). On the other hand Au-$Ag_2O$ system had a detrimental effect compared to Au/TiO_2 photocatalyst, inhibiting hydrogen production. Higher photoactivities of Au-Cu_2O and Au-NiO nanoparticles deposited on TiO_2 were apparently caused by enhancement of the electron charge transfer from TiO_2 to Au-M_xO_y systems and the effect of surface plasmon resonance of gold nanoparticles [66].

5. Bimetallic Photocatalysts (BM_{OX}-TiO_2) for Oxidation Reactions

The structure of bimetallic catalysts depends on the preparation conditions, miscibility, and kinetics of the reduction of metal ions. Silver and gold have almost identical lattice constants (0.408 for Au and 0.409 for Ag) and are completely miscible over the entire composition range, which leads to a strong tendency toward alloy formation [66]. Thus Ag-Au bimetallic NPs with homogenous composition can be expected.

It was previously reported by Zielińska-Jurek et al. [11] that bimetallic silver- and gold-modified TiO_2 nanoparticles exhibited improved photocatalytic activity in the oxidation reactions under visible light irradiation, better than monometallic Ag and Au nanoparticles, respectively. Ag-Au/TiO_2 samples obtained using microemulsion method show higher photodegradation rate in visible region than Ag/TiO_2 and Au/TiO_2 photocatalysts. Greater silver amount was more beneficial to the photocatalytic activity of the obtained Ag-Au/TiO_2 nanoparticles than that of gold. XPS analysis of the surface layer indicated that both Au clusters and nanoparticles were produced at TiO_2 surface. However, for the most active Ag-Au/TiO_2 sample, the dominant surface form of silver was Ag_2O and gold occurred in the form of Au° but the presence of metallic Ag° as well as gold in the form of $Au^{\delta+}$ and $Au^{\delta-}$ was also confirmed. Under UV irradiation silver acts as a promoter to provide reactive oxygen in variety oxidation reactions as well as facilitates electron-hole separation and promotes interfacial electron transfer. In addition, bimetallic Ag-Au alloy nanoparticles possess the ability to absorb visible light in a wide wavelength range (broad LSPR peak) and, therefore, reveal the highest level of activity as a result of utilization of a large amount of incident photons. The photoactivity efficiency of Ag-Au/TiO_2 photocatalyst was measured during the reaction of phenol degradation under Vis light irradiation ($\lambda > 420$ nm). The sample modified with 1.5 mol% of Ag and 0.5 mol% of Au exhibited 3.0 and 2.0 times faster degradation rate (3.57 $\mu mol \cdot dm^{-3} \cdot min^{-1}$) compared to Au/$TiO_2$ and Ag/TiO_2 nanoparticles, respectively [11]. A brief summary of recent publications on TiO_2 photocatalysts modified with bimetallic nanoparticles used in oxidation processes is provided in Table 2. Ji et al. [39] reported that the structure of bimetallic NPs on TiO_2 depends on the preparation procedure. Bimetallic Ag-Au nanoparticles (NPs) with

Table 2: Recent publications of TiO_2 photocatalysts modified bimetallic nanoparticles used in oxidation processes.

Bimetallic NPs	Average particle size [nm]	Irradiation source	Degradation effect and comments	Reference
Ag-Au alloy Ag (shell)-Au (core)	17	n.d.	Structure depends on the molar ratio between Ag and Au. Higher Ag ratios result in an increase in silver shell on the surface of Ag/Au alloy core, while lower Ag ratios tend to the formation of alloy particles	[39]
Ag-Cu alloy	5 to 6	1000 W Xe arc lamp	The photodegradation efficiency under visible light increased with the increase in copper loading up to 0.5 mol% and then decreased	[69]
Au-Cu alloy	3 to 5	300 W Xe arc lamp	Modification of Cu leads to better enhancement in the photocatalytic properties compared to modification of Au. The best photocatalyst is Au-Cu/P25 with Au-Cu 1 : 3	[70]
Au-Cu alloy	3	n.d.	The bimetallic Au-Cu/TiO_2 catalysts showed higher activity in terms of methanol conversion and hydrogen selectivity than the monometallic Au/TiO_2 and Cu/TiO_2 catalysts	[71]
Pt-Cu alloy	2 to 6	Xe arc lamp cut-off filter ($\lambda > 450$ nm)	Bimetallic alloy nanoparticles consisting of 80 mol% of Pt and 20 mol% of Cu, supported on anatase TiO_2, successfully promote aerobic oxidation of alcohols under sunlight irradiation at ambient temperature	[53]
Pt-Pd alloy	1 to 12 depending on metal precursors amount	1000 W Xe arc lamp cut-off filter ($\lambda > 420$ nm)	The best photocatalytic activity was observed for the sample Pt-Pd/TiO_2 modified with 0.5 mol% of platinum and 0.5 mol% of palladium. Average degradation rate of 6.84 μmol $dm^{-3}min^{-1}$ for phenol was about 19 times greater than for pure TiO_2 obtained using the same preparation procedure	[30]
Pt-Pd alloy	2 to 4	100 W high pressure mercury lamp	The optimum loading of platinum around 0.5–1.0% was observed for the photocatalytic oxidation of methyl orange dye. The photocatalytic activity of Pd/TiO_2 decreased with the increase of palladium loading	[78]

alloyed and core-shell structures were obtained at temperature (75°C) from gold and silver NPs precursors in aqueous solution. Based on microscopic and spectroscopic analyses they stated that both the digestive ripening and Ostwald ripening were responsible for the formation of alloy or core-shell structures during the heating process. The structure of bimetallic NPs depended on Ag and Au molar ratio. Higher Ag contribution increases silver shell on the surface of Ag-Au alloy core, while lower Ag amount leads to the formation of alloy particles [39]. Kowalska et al. [55] proposed two mechanisms for plasmonic titania photocatalysts under visible light irradiation: (1) charge carrier transfer (electron transfer from plasmonic metal NPs to CB of titania) and (2) energy transfer (from plasmonic NPs to titania). Basing on the obtained results for core/Au-shell/Ag structures immobilized on TiO_2, which exhibited enhanced field at the interface between titania and metallic nanoparticles, it was stated that the electronic mechanism for plasmonic photocatalysts under visible light irradiation is responsible for the enhanced or reduced visible light activity. Recently, it was reported for TiO_2 modified monometallic NPs that nanoparticles size and shape are critical to the photocatalytic activity [30, 67, 68].

A series of Ag-Cu modified TiO_2 photocatalysts were obtained using the microemulsion method [69]. As it was previously reported for Ag-Au/TiO_2 photocatalysts microemulsion method allows obtaining monodisperse alloy NPs deposited on TiO_2 surface. For Ag-Cu/TiO_2 a maximum in the photocatalytic activity under visible light was observed for the sample containing 0.5 mol % of Cu and 1.5 mol% of Ag. Average rate of phenol decomposition was 2.41 μmol/min and it was higher than for Ag/TiO_2 and Cu/TiO_2 NPs. The photocatalytic activity increased with silver loading up to 4.5 mol% and then decreased. Silver presence was more beneficial for visible light activation of modified TiO_2 photocatalysts than more copper amount. Hai et al. [70] observed similar relation as was previously described for the Ag-Cu/TiO_2 system, regarding metal amount and composition in the bimetallic structure assessed for wastewater treatment. Modification with Cu leads to better enhancement in the photocatalytic properties compared to modification with Au. TRMC signals show that bimetallic nanoparticles are better electron scavengers than Cu and Au NPs [70].

Ou et al. [71] studied the effect of Au/TiO_2 (2 wt.% Au), Cu/TiO_2 (2 wt.% Cu), and Au-Cu/TiO_2 (1 wt.% Au-1 wt.% Cu) catalysts on partial oxidation of methanol (POM) to produce H_2. The antisintering effect in Au-Cu alloy-modified TiO_2 NPs was observed. Copper nanoparticles acted as a stabilizer and prevented gold NPs from aggregation or sintering during calcination. The bimetallic Au-Cu/TiO_2 catalysts showed higher activity in terms of methanol conversion and hydrogen selectivity than the monometallic Au/TiO_2 and Cu/TiO_2 catalysts. Bimetallic Au-Cu/TiO_2 catalysts were more active and stable and exhibited better hydrogen selectivity with a smaller amount of CO compared to monometallic Au/TiO_2 and Cu/TiO_2 catalysts. The enhanced activity, selectivity, and stability of bimetallic catalysts are due to the Au-Cu interaction that creates smaller metal particles, which consequently stabilize the active component for POM to produce hydrogen. XPS analysis revealed that this interaction is caused by the redox properties of Cu, which leads to stabilization of active $Au^{\delta+}$ and also stabilizes Au particle size [71].

A considerable increase of the photocatalytic activity in the reaction of phenol degradation was observed for 1 to 5 nm NPs of Pt-Pd deposited on TiO_2 [30]. The effect of the crystallite size of TiO_2 anatase and Pt-Pd bimetallic nanoparticles led to observation that sample of Pt-Pd/ TiO_2 with anatase crystallite size of about 30 nm and 8–15 nm bimetallic particles deposited on TiO_2 was 2.3 times less photoactive than Pt-Pd alloy immobilized on TiO_2 containing 5 to 9 nm Pt-Pd nanoparticles aggregated with smaller TiO_2 (~9 nm) nanoparticles. The results indicate that the rate of phenol decomposition in the presence of Pt-Pd/TiO_2 under Vis light is comparable to the data for commercial TiO_2 photocatalysts exposed to UV light. Thus, remarkable step forward in visible light photocatalysis for Pt-Pd alloy NPs on TiO_2 was reported [30]. The average degradation rate of 6.84 μmol·dm^{-3} min^{-1} for phenol was about 19 times greater than for pure TiO_2 obtained using the same preparation procedure and about 4 times higher compared to Pd/TiO_2. However, monometallic Pt/TiO_2 photocatalyst revealed only slightly lower photodegradation rate of 6.20 μmol·dm^{-3} min^{-1}. Thus other less expensive platinum-based bimetallic structures in photocatalytic processes need investigation.

Shiraishi et al. [31] reported preparation of Pt-Cu/TiO_2 photocatalysts highly active for aerobic oxidation driven by visible light. The effect of alloy particle size on photocatalytic activity in the reaction of benzyl alcohol oxidation was investigated. The photocatalytic activity of the photocatalysts with larger alloy particles was much lower than that prepared at 673 K which contain alloy particles 2 to 6 nm of diameter. Bimetallic Pt-Au/anatase, Pt-Ag/anatase, Pt-Pd/anatase, and Au-Cu/anatase alloy particles, often used for aerobic oxidation, showed activity much lower than that of the Pt-Cu/anatase alloy.

6. Challenges and Prospects

Significant progress has been achieved in recent years in the field of heterogeneous photocatalysis, particularly in noble metal nanoparticles as surface modifiers, which enhanced photocatalytic activity in visible light. Alloying a parent metal with a second metal can lead to efficient charge separation by trapping or removing electrons from TiO_2. Although significant progress has been made in the application of TiO_2 modified bimetallic NPs the development of bimetallic is still an attractive research aim. The most challenging problems are expected physicochemical properties such as monosize, uniform size, and even distribution of metal nanoparticles over the photocatalyst support. The photocatalytic and optical properties of bimetallic modified TiO_2 photocatalysts directly depend on the preparation procedure. Different preparation methods may result in different defect structures, surface morphology, and bimetallic NPs structure. Table 3 represents the bimetallic photocatalyst prepared via different preparation methods and their application for photocatalytic processes. Most of TiO_2 modified bimetallic NPs reported in literature were prepared by the coprecipitation and impregnation method. However, most commonly used inexpensive

Table 3: Recent publications of preparation of bimetallic photocatalysts and their application in reduction and oxidation processes.

Bimetallic NPs	Preparation procedure	Average particle size [nm]	Pollutant	Reference
Ag-Au	Deposition-precipitation method	3 to 4	The catalysts were examined in reaction of CO oxidation. Au-Ag/TiO_2 catalysts activated in H_2 at high temperature (550°C) exhibit higher activity than monometallic gold catalysts containing particles of the same size. Monometallic silver catalyst was inactive	[79]
Ag-Au	Sol-gel	Metals n.m. TiO_2 crystallite size 7 to 9	The photocatalytic activity was determined in the reaction of degradation of 4-chlorophenol. The presence of the 0.05% and 0.1% Au/TiO_2 rapidly degraded hydroquinone (HQ) to hydroxyhydroquinone (HHQ) (i.e., intermediates from 4-chlorophenol degradation)	[80]
Ag-Au	Photodeposition	Bimodal size distribution 1 to 2 (silver NPs) and 20 (Ag-Au)	The photocatalytic activity was examined during methanol dehydrogenation (50% MeOH, argon) under UV irradiation (Hg lamp) and 2-propanol oxidation (5 vol%) under visible light irradiation (Xe lamp, $\lambda > 450$ nm)	[55]
Ag-Au	Microemulsion	5 to 10	The photocatalytic activity of noble metals modified TiO_2 powders under visible light irradiation was estimated by measuring the decomposition rate of phenol in an aqueous solution. Bimetallic alloy samples (AgAu/TiO_2) showed a higher photodegradation rate in visible region than monometallic photocatalysts	[11]
Ag-Au	Precipitation-decomposition method	4 to 100	It was found that Ag-Au-ZnO is more efficient than Ag-ZnO, Au-ZnO, bare ZnO, commercial ZnO, TiO_2-P25,and TiO_2 (Aldrich) for degradation of MB under UV-A light	[81]
Pt-Ir	Coimpregnation method by chemical vapor deposition. The reduction of both metallic salts was carried out under inert atmosphere at 400°C	0.9	The addition of iridium to platinum catalysts could affect directly the dispersion and size of metal particle because of synergetic and electronic effects and consequently cause an improvement in the catalytic development	[82]
Pt-Ir	Impregnation/precipitation method	1 to 2	The activity was studied in the reaction of cyclohexane dehydrogenation and cyclopentane hydrogenolysis. For both bimetallic catalyst series decalin conversion increases as Ir loading and temperature level increase	[83]
Cu-Ni	Precipitation method	11 to 35	The decolorization of Orange II was studied under visible light using bimetallic Cu-Ni/TiO_2 nanoparticles. The best performing Cu-Ni/TiO_2 photocatalyst has 9 : 1 Cu : Ni mass composition and calcined at 180°C giving 100% Orange II removal with 16.1 ppm TOC value	[84]
Cu-Ni	Electrodeposition	bimodal size distribution 20 to 30 (Ni NPs) and 100	Nickel nanoparticles possess a ball-flower structure, leading to a large specific surface area. In addition, copper interlayer enhanced the conductivity of substrate and showed a synergistic effect with Ni, which enhanced the rate of electron transfer process	[85]
Cu-Ni	Incipient wetness technique/precipitation	1 to 10	The properties of bimetallic alloy particles were investigated. It was found that the presence of Cu greatly enhanced the reducibility of the Ni species and about 85% of the particles were metallic. After initial reduction, many nanoparticles quickly nucleated on the grain boundaries or surface defects of the titania supports. The nanoparticles grew rapidly via the Ostwald ripening or short-range particle-particle coalescence mechanisms	[86]

methods allow to obtain metallic NPs with particles size from 5 to10 nm. It is well known that smaller monodispersed silver nanoparticles ranging from 5 to 10 nm exhibit the best photocatalytic and antimicrobial activity. Recently it was also reported that fine platinum nanoparticles in the size range 0.8 to 2 nm revealed the highest activity under visible light irradiation among all monometallic plasmonic nanoparticles. Therefore, preparation of monodisperse and very small monometallic and bimetallic NPs is a very important task. Another challenge regarding bimetallic modified TiO_2 is preparation of bimetallic-based nanomaterials with a well-controlled shape [72]. It was reported that the shape of bimetallic NPs determines surface atomic arrangement and the optical properties. In this regard, nanoarchitecture arrangement (shape and size of metals) as well as the selection of noble metal and titania form may allow to prepare photoactive catalysts under overall solar spectrum. A photocatalyst with very high efficiency is not practical if the cost of its modification with metals is too high.

Although platinum is a very promising catalyst which can increase TiO_2 activity its amount in the photocatalyst need to be lowered by orders of magnitude to keep it economical. The presence of more abundant second metal could contribute to decreasing the overall costs. Therefore, more research is needed to identify low-cost metals with acceptable enhancement of photocatalytic activity.

Recently, preparation of Pt-Fe or Pt-Co nanoparticles [73, 74] for catalytic processes was reported. Moreover, preparation of Pt-shell and Co (Fe)-core NPs with fine particle size allows to enhance charge separation and facilitates separation and recycling of the photocatalyst. Hsieh et al. [35] reported preparation of bimetallic Pt-M (M = Fe, Co, and Ni) catalysts active in electrooxidation of methanol, using oxidized CNTs as the catalyst support. The particle size of Pt-Co NPs was within 5 to 10 nm. The Pt-Co/CNT catalyst exhibited the best electrochemical activity, CO tolerance, and long-term cycle ability [35]. Chen et al. [75] obtained Fe-Pt nanoparticles with controlled composition and the particle size below 9 nm. The size of the particles was controlled by the molar ratio of stabilizers to platinum acetylacetonate and the heating conditions. In the first step of particle formation mechanism Pt-rich nuclei were formed by reduction of platinum acetylacetonate. In the next step more Fe atoms coat over the existing Pt-rich nuclei, forming larger clusters. Exposition of clusters to the air leads to the formation of Pt-rich Fe-Pt/Fe_3O_4 followed by heating the clusters to 300°C, which leads to atomic diffusion and formation of fcc-structured Fe-Pt nanoparticles [75].

Another embodiment in the preparation of active photocatalysts under visible light may be combination of large plasmonic particles of gold or palladium with fine (1 to 2 nm) particles of platinum, silver, or copper which allows to absorb light in a wider wavelengths range.

Summarizing, although intensive development has led to preparation of highly active bimetallic photocatalysts in the reactions, the number of papers dealing with bimetallic NPs applications in catalysis is still greater than the number of publications in the area of photocatalysis. Many aspects are not fully covered yet, particularly a low-cost preparation methods, the control of particle size, and increased absorption of visible light which seems to be crucial for technological application of photocatalysts.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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