The effect of nanoparticles size on photocatalytic and antimicrobial properties of Ag-Pt/TiO₂ photocatalysts

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Abstract

Ag-Pt - modified TiO₂ nanocomposites were synthesized using the sol-gel method. **Bimetallic modified TiO₂ nanoparticles** exhibited improved photocatalytic activity under visible-light irradiation, better than monometallic Ag/TiO₂ and Pt/TiO₂ nanoparticles (NPs). All modified powders showed localized surface plasmon resonance (LSPR) in visible region. The photocatalysts' characteristics by X-ray diffractometry (XRD), scanning transmission electron microscopy (STEM), diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), nitrogen adsorption (BET method for specific surface area) showed that sample with the highest photocatalytic activity had anatase structure, about 93 m²/g specific surface area, maximum plasmon absorption at ca. 420 nm and contained small NPs of silver of 6 nm and very fine platinum NPs of 3 nm. The photocatalytic activity was estimated by measuring the decomposition rate of phenol in 0.2 mM aqueous solution under Vis and UV/Vis light irradiation. It was found that size of platinum was decisive for the photocatalytic activity under visible light irradiation, i.e., the smaller Pt NPs were, the higher was photocatalytic activity. While, antimicrobial activities, estimated for bacteria *E. coli* and *St. aureus*, and pathogenic fungi belonging to

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Candida family, were only observed for photocatalysts containing silver, i.e., Ag/TiO₂ and Ag-Pt/TiO₂ nanocomposites.

Keywords: Ag-Pt/TiO₂, heterogeneous photocatalysis, plasmonic NPs, antimicrobial activity, silver nanoparticles, platinum

1. Introduction

Photocatalytic reactions at the surface of titanium dioxide have been attracting much attention in view of their practical applications to environmental cleaning, such as: self-cleaning surfaces, water, wastewater and air purification, bacteria inactivation, hydrogen generation and CO₂ photoconversion to methane and low hydrocarbons. Nevertheless, due to large band gap of pure TiO₂ (from 3.0 to 3.2 eV depending on the crystal structure), it could be activated only by UV irradiation, limiting the utilization of sunlight as an irradiation source in photocatalytic reactions. To improve the efficiency of solar-driven photocatalysis, a variety of organic [1-2] and inorganic compounds [3-4] were examined as dopants or surface modifiers. Recently, noble metal nanoparticles exhibiting plasmonic properties (localized surface plasmon resonance, LSPR) have attracted attention, since they may also activate wide bandgap semiconductors (e.g. TiO₂) towards visible-light.

An appearance of activity under visible-light after modification of titania with plasmonic nanoparticles (NPs) such as gold, silver, platinum and palladium, is caused by participation of metal in a mechanism of electron transfer. The photons are absorbed by metallic NPs through their Localized Surface Plasmon Resonance (LSPR) excitation. The electron is transferred from plasmonically excited noble metal to conduction band of titania and consecutively to adsorbed oxygen. At the same time organic molecule is oxidized either by electron-deficient metal in order to return to its metallic state or/and by O₂^{·-} [5,6]. Under UV irradiation noble metal nanoparticles deposited on TiO₂ enhance the transfer of photogenerated electrons prolonging charge carriers lifetime. The activation mechanism of

the noble metal modified TiO₂ particles in the UV range is mainly based on the formation of Schottky barrier [6].

The enhancement in reactivity was first observed by Sato et al. for the photoconversion of H₂O to H₂ using the Pt/TiO₂ system [7]. Metals (such as Pt, Au, Ag) and the semiconductor (TiO₂) have different Fermi level positions. The electron migration from the TiO₂ to the metallic nanoparticle occurs until the two Fermi levels are aligned since the metal has a work function (ϕ_m) higher than that of the TiO₂ (ϕ_s). The electrical contact has formed a space charge layer so called the Schottky barrier, which trapped electrons and suppressed electron-hole recombination [6-8]. The surface of the metal acquires an excess negative charge, while the TiO₂ exhibits an excess positive charge as a result of electron migration away from the barrier region. The height of the barrier (ϕ_b) is defined as the difference between the TiO₂ conduction band and the metal Fermi level. Electrons drawn across this barrier leaves additional positive holes in the TiO₂ matrix capable of oxidizing more organic species.

Efficiency of (photo)catalytic process depends strongly on particle size and shape of noble metal deposits, therefore control of structural properties of metallic nanoparticles is critical to photocatalytic and antimicrobial activity. It was reported that small and monodispersed silver nanoparticles ranging from 5 to 10 nm exhibited the highest photocatalytic and antimicrobial activity [9]. However, for gold nanoparticles deposited on titania an increase in gold NPs size resulted in enhancement of photocatalytic activity, probably due to the ability of photoabsorption of more photons by larger and rod-like gold nanoparticles of broad plasmonic absorption band [5, 10]. In contrary, a considerable increase of photocatalytic activity was observed for small bimetallic NPs of Ag-Au and Pt-Pd (2 to 5 nm) deposited on TiO₂, e.g., bimetallic modified titania (1.5 mol% Ag and 0.5 mol% Au) decomposed phenol three and two times faster than titania single modified with

Au and Ag, respectively [10, 11]. Therefore, nano-architecture arrangement (shape and size of noble metal) as well as selection of noble metal and titania form may allow preparing the photoactive catalysts under overall solar spectrum [12].

In the present study we have examined the effect of surface properties of Ag-Pt/TiO₂ photocatalysts on the antimicrobial activity and efficiency of phenol degradation under UV/Vis and Vis ($\lambda > 420$ nm) light irradiation. Platinum is one of the most active metals for photocatalytic enhancement under UV irradiation, which can produce the highest Schottky barrier among metals facilitating electron capture, and therefore hindering the recombination between electrons and holes [13]. While, Ag particles dispersed on the surface of TiO₂ could greatly enhance photocatalytic and antimicrobial activity.

The effect of properties of noble metal and titania, i.e., amount and size of noble metal, specific surface area, particle size and polymorphic form of titania, on the efficiency of removal of model organic compound and model microorganisms from aqueous phase have been systematically investigated.

2. Experimental

2.1. Materials and instruments

Titanium isopropoxide (pure p.a.) was purchased from Aldrich and used as titanium source for the preparation of TiO₂ NPs. Such obtained titania and commercial TiO₂: ST-01 anatase (particle size: 8 nm, $S_{\text{BET}} = 250 \text{ m}^2 \text{ g}^{-1}$, supplier: Ishihara Sangyo Ltd., Japan), P25 (a mixture of the crystalline phases: anatase (73-85%), rutile (14-17%), and amorphous titania (0-13%) [14], $S_{\text{BET}} = 50 \text{ m}^2 \text{ g}^{-1}$ supplier: Evonik, Germany) were used for the preparation of Ag-Pt - modified TiO₂ photocatalysts. Silver nitrate and chloroplatinic acid hexahydrate were provided by Aldrich and used as starting materials for the preparation of silver and platinum NPs.

XRD analysis were performed using a Rigaku Intelligent X-ray diffraction system SmartLab equipped with a sealed tube X-ray generator (a copper target; operated at 40 kV and 30 mA), a D/teX high-speed position sensitive detector system and an ASC-10 automatic sample changer. Data acquisition conditions were as follows; 2θ range: $10\text{--}90^\circ$, scan speed: $1.00^\circ \text{ min}^{-1}$ and scan step 0.008° . The obtained XRD patterns were analyzed by Rigaku PDXL, a crystal structure analysis package including Rietveld analysis, installed in a computer controlling the diffractometer.

The atomic composition was examined by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS, JEOL JSM-6360LA). Powdered samples were attached to conductive carbon paint on aluminum and a copper holder for XPS and SEM/EDS analysis, respectively, and dried overnight under vacuum. All XPS spectra were recorded on JEOL, JPC-9010MC spectrometer using Mg $K\alpha$ X-rays, 50 scans were carried out for Ag and Pt ranges and average data were used for analysis. For SEM/EDS measurements, average data taken from three different regions for accelerating voltage higher than 15 kV and the working distance of 10 mm were used for analyses.

To characterize the light-absorption properties of modified photocatalysts, diffuse reflectance spectra (DRS) were recorded, and data were converted to obtain absorption spectra. The measurements were carried out on Jasco V-670 spectrophotometer equipped with a PIN-757 integrating sphere where the baseline was recorded using pure TiO_2 as a reference.

Nitrogen adsorption–desorption isotherms were recorded at liquid nitrogen temperature (77 K) on a Micromeritics Gemini V (model 2365) and the specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method.

High-resolution transmission electron microscopic (HRTEM) measurement was performed using an electron microscope (TEM, FEI Europe, Tecnai F20 X-Twin). To obtain a suitable sample for TEM characterization Ag-Pt/TiO₂ powder was dispersed in ethanol in an ultrasound bath for a few minutes. Some drops of suspension were deposited on carbon covered microgrid.

2.2. Preparation of Pt/TiO₂ and Ag-Pt/TiO₂ photocatalysts

Anatase nanoparticles were prepared by hydrolysis of titanium (IV) isopropoxide (TIP). In this regard TIP was added to ethanol and the mixture was stirred for 5 min using a magnetic stirrer operating at 500 rpm. After stirring, 5.71 cm³ of water was added to the alkoxide solution by burette and white thick precipitate was formed which gradually peptized for 2 h to form clear sol. The rate of water addition was kept at 0.5 cm³·min⁻¹. The molar ratio of H₂O/TIP was 12.

Such obtained titania and two commercial TiO₂: ST-01 and P25 were used for the preparation of Pt/TiO₂ and Ag-Pt/TiO₂ nanoparticles.

The Pt/TiO₂ samples were obtained by addition of a certain amount of H₂PtCl₆ for different nominal amounts of deposited Pt (0.1 or 0.5 mol% calculated to TiO₂) into TiO₂ gel or TiO₂ slurry dispersed in ethanol. The Ag/TiO₂ samples containing from 2.5 to 6.5 mol% of Ag were prepared by adding silver precursor (AgNO₃) aqueous solution at room temperature into TiO₂ dispersed in ethanol. After 30 min of mixing, reduction of metal cations by 5-cm³ NaBH₄ aqueous solution was performed and obtained NPs were 1-hour aging. The molar ratio of NaBH₄ to metal ions equaled to 3.

All Ag-Pt - modified TiO₂ samples were obtained by the sequential addition of H₂PtCl₆ and then AgNO₃ into TiO₂. Samples Ag-Pt/TiO₂_T1-T5 were obtained without using reducing agent. Precipitated Ag-Pt/TiO₂ particles were centrifuged (2000 rpm for 5 min), dried at 70°C for 48 h and calcinated at 400°C for 3 h. For Ag-Pt/TiO₂_R1-R3 samples,

sodium borohydride was used as a reducing agent with the molar ratio of NaBH₄ to silver and platinum ions equaled to 3:1.

2.3. Measurements of photocatalytic activity

The photocatalytic activity of Ag/TiO₂, Pt/TiO₂ and Ag-Pt/TiO₂ powders was estimated by measuring the decomposition rate of phenol aqueous solution in the presence of visible and UV/Vis irradiation. Phenol was selected as a model pollutant since it is a non-volatile and common contaminant frequently present in industrial wastewaters. The mechanism of phenol decomposition is also well established [15, 16]. 25 cm³ of 2.1·10⁻⁴ M phenol solution containing 125 mg suspended photocatalyst was stirred using a magnetic stirrer and was continuously aerated (5 dm³/h) prior and during the photocatalytic process. The suspension was irradiated using a Xenon lamp (6271H, Oriel) emitting both UV and Vis light. The light flux at UV range (310-380 nm) was 85 mW/cm². The 25-cm³ photoreactor of 3-cm thickness of exposure layer was equipped with a quartz window. The optical path included a water filter and a cut-off glass filter (GG 420, λ>420 nm). The temperature of the aqueous phase during irradiation was kept at 10°C using a water bath. Aliquots of 1 cm³ of the aqueous suspension were collected at regular time periods during irradiation and filtered through syringe filters (Ø = 0.2 µm) to remove the photocatalyst particles. Phenol concentration was estimated by colorimetric method using a UV–Vis spectrophotometer (DU-7, Beckman). Photocatalytic degradation runs were preceded by blind test in the absence of a photocatalyst or illumination. No degradation of phenol was observed in the absence of either the photocatalyst or illumination.

2.4. Measurements of bioactivity (antibacterial and antifungal)

MIC (minimal inhibitory concentration)

Antibacterial and antifungal activity was determined by the microtiter plate method of serial twofold dilutions, in Mueller Hinton Broth 2 medium (MHB2, Sigma) and in

RPMI 1640 medium (with L - glutamine and phenol red, without bicarbonate) buffered with MOPS (Sigma) and supplemented with D-glucose to a final concentration of 2%, respectively. Plates containing serially diluted compounds (suspended Ag/TiO₂, Pt/TiO₂ and Ag-Pt/TiO₂) and compound-free control were inoculated with overnight cultures of tested strains to the final concentration of 10⁴ cfu/cm³ for *C. albicans* and 10⁶ cfu/cm³ for both bacterial strains. Then, plates were incubated for 24 h at 37°C and 30°C for antibacterial and antifungal activity determination, respectively. Microbial growth was quantified in each well by the measurement of an optical density at $\lambda = 531\text{nm}$ using the microplate reader (Victor³V, PerkinElmer). The antimicrobial activity of TiO₂ nanocomposites was estimated using *Escherichia coli* ATCC 10536, *Staphylococcus aureus* ATCC 6538 and *Candida albicans*.

Zones of inhibition

The solid RPMI (Sigma) (RPMI broth supplemented with bacteriological agar to a final concentration of 2%) or Tryptic Soy Agar (BTL) was liquefied by warming at 100°C and then chilled to 40°C. The semi-liquid medium was inoculated with 3x10⁵ cells·cm⁻³ of an overnight culture of microbial cells, poured into Petri plates and left for solidification. The photocatalysts were suspended in dimethyl sulfoxide (DMSO) to create a concentration of 4 mg·cm⁻³. Suspension (0.02 cm³) was spotted onto the agar medium surface (diameter of each spot ~ 5 mm, five spots on each plate). Plates were incubated for 24 h at 37° C (antibacterial activity determination) or at 30°C (antifungal activity determination). Growth inhibition zones appearing around the spots were measured.

3. Results and discussion

3.1. Absorption properties

The modified photocatalysts were light yellow, yellow and grey as shown in Table 1. The optical properties of Ag-Pt/TiO₂ nanoparticles were studied by DRS and obtained data are

shown in Fig. 1. Ag and Pt nanoparticles exhibited plasmon bands with maxima at around 395 nm and 400 nm, respectively. For Ag-Pt/TiO₂ nanoparticles it should be pointed out that depending on TiO₂ source (ST-01, P25 or TiO₂ from TIP hydrolysis) Ag-Pt/TiO₂ exhibited absorption extended into the visible region over the range of 360 ~ 600 nm. The maximal absorption for the Ag-Pt/TiO₂ nanoparticles appeared mainly at 400 - 410 nm. However, due to overlapping of LSPR peaks for Ag and Pt nanoparticles it was difficult to match unequivocally LSPR peaks as an alloy, composite nanostructure or individual NPs. Samples Ag-Pt/TiO₂_T1 and Ag-Pt/TiO₂_T2 revealed a relatively narrow absorption between 395 and 400 nm, while Ag-Pt/TiO₂_T3, Ag-Pt/TiO₂_R2 and Ag-Pt/TiO₂_R3 exhibited a more substantial and broader absorption shoulder up to 800 nm. The broad LSPR peak indicates the variety of size of deposited metallic NPs. The most intense absorption of light in the visible spectrum revealed the samples Ag-Pt/TiO₂_T3 and Ag-Pt/TiO₂_T4. Nanocomposites of Ag-Pt/TiO₂_T3 and Ag-Pt/TiO₂_R2 showed two absorption peaks at 370 nm (less intense) and at 420 nm (main peak). These samples were obtained by deposition of metal nanoparticles on commercial TiO₂ (P25, Evonik). The absorption shoulder at the shortest wavelengths corroborated presence of smaller nanoparticles, though, the main absorption/extinction spectral features were dominated by the largest volume nanoparticles. Larger particles exhibit increased scattering and have peaks that broaden significantly and shift towards longer wavelengths. It was previously reported, e.g., for Au-Cu/TiO₂ nanocomposites, that plasmon band was sensitive to the environment and could be shifted depending on the stabilizer and on the substrate [17].

3.2. BET surface area analysis

The BET surface areas of Ag-Pt/TiO₂ powders are given in Table 1. The surface area and average crystalline size for self-obtained pure TiO₂ were 81 m²·g⁻¹ and 10 nm, respectively. The deposition of Ag-Pt metal nanoparticles at the self-obtained TiO₂ reduced

the surface area from $81 \text{ m}^2\cdot\text{g}^{-1}$ to about $68 \text{ m}^2\cdot\text{g}^{-1}$ indicating the presence of larger metallic nanoparticles on TiO_2 . The surface area of the samples based on ST-01 varied from 109 to $188 \text{ m}^2\cdot\text{g}^{-1}$, while for pure ST-01 equaled to $250 \text{ m}^2\cdot\text{g}^{-1}$. Comparison between specific surface area and obtained photocatalytic activity (shown also in Table 1) indicates that rather other factor than specific surface area governs photocatalytic activity, e.g., crystalline size of metallic nanoparticles as will be discussed later.

3.3. XRD analysis

Exemplary XRD patterns of bare and modified TIP titania are shown in Figure 2. Self-prepared titania was mainly composed of anatase and small amount of brookite. The metal was hardly detected in the case of modification with only one metal, which indicates either small amount of deposited metal or small size of metallic NPs. In the case of deposition of both metals on the titania surface the presence of silver and metallic platinum was easily detected. For some samples, e.g., Pt/ TiO_2 _1 and Ag-Pt/ TiO_2 _T2 the disappearance of brookite phase was noticed.

The determined crystalline sizes of metallic NPs (shown in Table 1) correspond well with change of specific surface area, e.g., the existence of larger metallic NPs than size of titania (8 nm), e.g., 69-nm Ag_2O , resulted in decrease of specific surface area of Ag-Pt/ TiO_2 _T1 from 81 to $68 \text{ m}^2\cdot\text{g}^{-1}$. While, the presence of small NPs of silver of 6 nm and very fine platinum of 3 nm resulted in an increase of specific surface area of Ag-Pt/ TiO_2 _T2 to $93 \text{ m}^2\cdot\text{g}^{-1}$. The difference between samples with deposited larger and smaller metallic NPs than size of titania was also easy noticed by broader and narrower LSPR peaks, respectively, as shown in Figure 1. For example, Ag-Pt/ TiO_2 _T2 containing higher amount of platinum than Ag-Pt/ TiO_2 _T1 (0.5 and 0.1 mol%, respectively) revealed a relatively narrower absorption band, which indicates formation of smaller nanoparticles

of noble metals. This was proved by XRD data of 3- and 9-nm platinum NPs, and 14 and 69-nm NPs of silver oxide, for Ag-Pt/TiO₂_T2 and Ag-Pt/TiO₂_T1, respectively.

Similar behavior was also noticed for samples prepared from commercial titania samples, i.e., formation of smaller and larger metallic NPs caused increase and decrease in specific surface area, respectively. The existence of various sizes of metallic NPs for Ag/Pt-TiO₂_T3 samples of the broadest LSPR peak was confirmed by the presence of 38-nm Pt (1,1,1), 74-nm Pt (2,0,0), and small silver NPs of 12 nm. The presence of very large Pt (2,0,0) particles of 145 nm could be responsible for additional LSPR peak at long wavelength of 570 nm for Ag-Pt/TiO₂_T4.

3.4. Atomic composition and microscopy analyses

Figure 3 a–b shows the TEM images of Pt/TiO₂_1 and Pt/TiO₂_2 photocatalysts with different size of Pt NPs deposited on titania. Sample Pt/TiO₂_1 contained fine monodisperse Pt particles with diameter of about 2–6 nm, whereas Pt/TiO₂_2 had polydisperse size distribution of large (20–40 nm) and small (5–10 nm) Pt NPs deposited on titania surface. The fringe spacing, which is the interplanar separation between the growth direction planes of the nanocrystal, could be estimated as 0.235 nm, which corresponds to the fringe spacing characteristic of Pt.

The particle size and composition of the bimetallic NPs located at the TiO₂ surface was studied by STEM imaging supplemented with EDS mapping as shown in Figure 3 c–d.

The sample obtained by thermal reduction of metal ions on TiO₂ surface possessed small platinum nanoparticles in the range of 1 to 3 nm and two kinds of silver NPs, i.e., small with diameter of about 5–10 nm and large aggregates in the range from 20 to 45 nm (biggest observed) as shown in Figure 3c. For the sample obtained by chemical reduction of silver and platinum ions using sodium borohydride, the presence of larger platinum (c.a.

10 nm) and nano-sized (c.a. 1–5 nm) silver NPs was detected (see Figure 3d) confirming XRD data.

Atomic composition and chemical characters of elements incorporated in the surface layer of Ag-Pt modified titania were investigated by XPS and SEM/EDS. The presence of platinum and silver was confirmed in all analyzed samples by SEM/EDS, as presented in Table 2. However, silver was not detected in some of the samples by XPS analysis, which indicates that either low amount of silver was deposited on titania (below detection limit) or silver was covered with platinum. The first assumption could be refuted since silver was detected by SEM/EDS of higher detection limits. Thus, it is thought that large silver particles are covered by fine platinum NPs resulting in additional light absorption at longer wavelength, as shown in Fig. 1 for Ag-Pt/TiO₂_T3. For Ag-Pt/TiO₂_T1-T4 samples two kinds of bimetallic structures could be considered, i.e., i) silver NP covered by fine platinum NPs (as has been proposed above) or ii) core(Ag)-shell(Pt) structure. It is expected that for Ag-Pt/TiO₂_T3 sample the core-shell should be formed since it possesses: i) fine NPs of silver (12 nm) and large NPs of platinum (38 and 74 nm), ii) and two plasmonic peaks where longer one is bathochromically shifted than monometallic modified sample (Pt/TiO₂_2). Similar behavior was reported for core(Au)-shell(Ag) modified titania [12].

It should be noticed that higher amounts of platinum detected by XPS (1.8-3.1%) than used for modification (0.5%) was expected since surface modification of titania resulted in preparation of samples enriched with metals on the surface [9,10,18]. It must be pointed that though metals were detected in all samples by SEM/EDS, their amounts were usually much lower (e.g., 0.06, 0.09, 0.34, 0.23, 0.58% of platinum and 0, 0, 0.38, 0.34 and 0.38% of silver for Pt/TiO₂_2, Pt/TiO₂_4, Ag-Pt/TiO₂_T2, Ag-Pt/TiO₂_T3 and Ag-Pt/TiO₂_T4, respectively), than used for deposition (as shown in Table 2) for thermal

reduction method, which indicates that only part of metallic precursor was deposited on titania.

3.5. Photocatalytic activity of pure TiO_2 and (Ag-Pt)-modified TiO_2

The kinetics of phenol photodegradation in aqueous solution under UV/Vis and Vis irradiation ($\lambda > 420$ nm) in the presence of Pt/ TiO_2 , Ag/ TiO_2 and Ag-Pt/ TiO_2 nanoparticles is shown in Fig. 4 and in Table 1. All modified samples showed similar photocatalytic activity under full irradiation spectrum (UV/Vis) of ca. $4.8\text{--}4.9 \cdot 10^{-2} \text{ min}^{-1}$. Those activities were slightly higher than that of pure titania, which proves reported data on participation of metallic NPs in electron scavenging, which inhibits the recombination between charge carriers [18].

Under visible light irradiation modification with Pt leads to better enhancement in the photocatalytic properties compared to modification with Ag. Fine platinum nanoparticles with diameter of about 1-3 nm revealed the highest activity under visible light irradiation. The apparent rate constants of the first-order kinetic of phenol photodegradation increased from $0.3 \cdot 10^{-2} \text{ min}^{-1}$ to $1.24 \cdot 10^{-2} \text{ min}^{-1}$ and $1.84 \cdot 10^{-2} \text{ min}^{-1}$ for pure TiO_2 , Pt/ TiO_2 _1 and Pt/ TiO_2 _3 obtained from TIP hydrolysis, respectively.

Considering the effect of platinum particles size on the photocatalytic activity the constant rate of phenol degradation decreased to $1.06 \cdot 10^{-2} \text{ min}^{-1}$ and $1.45 \cdot 10^{-2} \text{ min}^{-1}$ for the samples Pt/ TiO_2 _2 and Pt/ TiO_2 _4 obtained by deposition of platinum on commercial TiO_2 P25 and ST-01, respectively. DRS data and grey colour of these samples suggested aggregation and presence of polydisperse Pt particles with size larger than 10 nm.

Compared to pure TiO_2 , Ag-Pt/ TiO_2 samples loaded with 0.5 mol% of Pt and 2.5 mol% of Ag exhibited a significant increase in Vis-driven phenol degradation rate. The maximum in the photocatalytic activity under Vis light irradiation was observed for Ag-Pt/ TiO_2 _T2 sample containing small silver (6 nm) and small platinum (3 nm) nanoparticles

and Ag-Pt/TiO₂_R1 with small silver (5 nm) and platinum (9 nm) nanoparticles deposited on TIP titania surface (see Figure 4). For Ag-Pt/TiO₂_T3 and Ag-Pt/TiO₂_T4 samples obtained by deposition of noble metals on P25 and ST-01, respectively, the efficiency of phenol degradation was about 30% lower compared to Ag-Pt/TiO₂_T2 sample prepared from TIP as TiO₂ precursor. The sizes of metallic nanoparticles deposited on TiO₂ P25 (silver NPs size 12 nm, platinum ca. 38 nm) and TiO₂ ST-01 (silver NPs size 2 nm, platinum NPs size ca. 42 nm) were larger than that on TIP TiO₂.

Although Ag-Pt/TiO₂_T2 sample exhibited a narrower DRS absorption band and the sizes of metal particles were much smaller than those of Ag-Pt/TiO₂_T1 sample, its photocatalytic activity was almost twice higher (opposite to Au modified titania for which the larger particle size was, the larger was photocatalytic activity [5, 10]). Present results indicate the main impact of fine platinum particles on photoactivity under visible light irradiation. While, the size of silver NPs is not so crucial because of the much lower photocatalytic activity of silver deposited on TiO₂ surface. The reason of size-dependent photocatalytic activity under Vis light irradiation is presently under study.

3.6. Antimicrobial properties

Silver nanoparticles and silver ions have strong antimicrobial activity. The impact of silver on microorganism is related to generation of Ag complexes with biomolecules containing sulfur, oxygen and nitrogen such as thiols, carboxylates, amides, imidazols, indoles, and hydroxyls [19]. The images of the zone of growth inhibition for *S. cerevisiae* and *E. coli* are shown in Fig. 5. The Ag/TiO₂, Ag-Pt/TiO₂ and pure TiO₂ nanoparticles are well visible as white spots labeled as: (1) sample Ag-Pt/TiO₂_T4; (2) sample Ag-Pt/TiO₂_T3; (3) sample Ag-Pt/TiO₂_T2; (4) Pt/TiO₂_3; (5) sample Ag/TiO₂_1; (6) sample Pt/TiO₂_1; (7) sample Ag/TiO₂_3; (8) sample Ag/TiO₂_2 and (9) pure TiO₂. Growth inhibition zones appearing around the spots were lined for easier detection (see Fig. 5).

Based on the zone of inhibition analysis, shown in Table 3, it was observed that the Ag/TiO₂ particles (discs numbers: 4, 7, 8) inhibited the growth of bacteria and yeast. The diameter of inhibition zone depended on amount and size of silver particles in the sample. The best antimicrobial activity was observed for Ag/TiO₂_1 sample. The diameters of zones of inhibition for Ag/TiO₂_1 were 9 mm for *C. albicans*, 19 mm for *E. coli* and 18 mm for *S. aureus*. Photocatalyst which exhibited the best efficiency of phenol degradation (Ag-Pt/TiO₂_T2) containing small silver NPs (6 nm) and fine platinum NPs (3 nm) revealed only antifungal properties. The diameter of zone of inhibition measured for *C. albicans* (disc no. 3) was 11 mm. Ag-Pt/TiO₂_T4 and Ag-Pt/TiO₂_R1-R3 samples containing fine (~2-3 nm) silver nanoparticles revealed higher antimicrobial activity than Ag-Pt/TiO₂_T2 with larger silver NPs of 6-nm size. The Ag/TiO₂ and Ag-Pt/TiO₂ samples showed higher antibacterial activity against Gram-negative bacteria *E. coli* than Gram-positive *St. aureus*. The decreased susceptibility of Gram-negative bacteria can be explained by the fact that the cell wall of Gram-positive bacteria is thicker than that of Gram-negative bacteria and exhibits only a thin peptidoglycan layer (2~3 nm) between the cytoplasmic membrane and the outer membrane. In contrast, Gram-positive bacteria does not have the outer membrane, but possesses 30-nm thick peptidoglycan layer, which is negatively charged, and therefore more silver species may get trapped to peptidoglycan in Gram-positive bacteria [20].

To determine the lowest concentration of photocatalyst at which complete inhibition of microorganism growth would be visible noticed, the minimum inhibitory concentration (MIC) was determined. The obtained MIC data for mono and bimetallic samples against bacteria and fungi are shown in Table 4.

For pure TiO₂ and Pt/TiO₂_3 sample containing 0.5 mol% of Pt, the inhibition in microorganisms' growth was not observed even for photocatalyst concentration higher

than $250 \mu\text{g}\cdot\text{cm}^{-3}$. The lowest MIC value (the highest bioactivity) was observed for *C. albicans* ATCC 10231 in the presence of Ag/TiO₂_1 sample containing 0.5 mol% of silver. The increase in silver content to 4.5 and 6.5 mol% resulted in slight increase in the MIC value, possibly due to aggregation of silver and its different distribution on TiO₂ surface.

3.7. Discussion

Bimetallic modified TiO₂ with silver and platinum NPs exhibited improved photocatalytic activity under visible-light irradiation in comparison to monometallic photocatalysts (Ag/TiO₂ and Pt/TiO₂). Synergistic effect of silver and platinum nanoparticles on photocatalytic activity of TiO₂ in visible light was confirmed. The best photocatalytic activity was observed for Ag-Pt/TiO₂_T2 and Ag-Pt/TiO₂_R1 samples containing small NPs of silver and platinum deposited on TIP titania surface. Obtained results showed that enhanced photocatalytic activity under visible light for bimetallic Ag-Pt/TiO₂ photocatalysts was affected by Ag and Pt nanoparticles size as well as surface properties of TiO₂ matrix. Smaller platinum nanoparticles observed on the surface of TiO₂ obtained from TIP hydrolysis (anatase, particles size=10 nm, $S_{\text{BET}}=81 \text{ m}^2\text{g}^{-1}$) and small anatase nanoparticles (ST-01, particles size=8 nm, $S_{\text{BET}}=250 \text{ m}^2\text{g}^{-1}$) revealed higher photocatalytic activity than larger platinum nanoparticles obtained by deposition on TiO₂ P25 support (mixture of anatase, rutile and amorphous titania, particles size ca. 30 nm, $S_{\text{BET}}=55 \text{ m}^2\text{g}^{-1}$). Recently, we have reported the effect of TiO₂ matrix on the size of noble metal nanoparticles and photocatalytic activity [10]. For Au/TiO₂ nanocomposites the obtained results suggested that deposition of large gold nanoparticles (60-110 nm) on the surface of TiO₂ resulted in enhancement of visible light photoactivity. Higher photoactivity was observed for large gold NPs deposited on the surface of small rutile or anatase TiO₂ nanoparticles [10]. On the other hand, it is well known that fine nanoparticles of noble metal often improves the reaction efficiency working as a co-catalyst through: (i)

enhancement of the electron-hole separation and thus preventing recombination of charge carriers, and (ii) extension of the light absorption into the visible range and enhancing surface electron excitation by plasmon resonance excited by visible light. Haruta et al. observed that small gold nanoparticles less than 5 nm in size were very active as “dark” catalysts [21]. Recently it was also found that fine platinum nanoparticles in the size range from 1 to 4 nm revealed the highest activity under visible light irradiation for reaction of organic pollutants degradation from aqueous stream [11]. Kohtani et al. reported that fine platinum particles loaded on photocatalyst greatly improved the efficiency of hydrogen evolution from water or alcohol under irradiation [22]. Shiraishi et al. found that Pt-Cu bimetallic nanoparticles deposited on anatase with particle size from 3 nm to 5 nm exhibited the highest photocatalytic activity [23]. Larger particles (>5 nm diameter) contained a decreased number of surface Pt atoms and therefore revealed decreased activity.

Based on literature, it is also known that platinum possesses higher affinity for the TiO₂ surface compared to silver. Therefore, the size of titania determines much more the size of platinum than silver [24, 25]. Our results have shown that smaller (1-3 nm) platinum NPs than silver (5-12 nm) were formed on TiO₂ surface by thermal treatment method. Platinum ions interact stronger with TiO₂ matrix than silver which protects them from agglomeration during thermal process. On the other hand, smaller silver nanoparticles (~5 nm) and larger platinum NPs (~10 nm) were obtained using sodium borohydride as a reducing agent during preparation procedure (samples Ag-Pt/TiO₂_R1-R3).

4. Conclusions

For the first time, inhibition of microorganism growth and photocatalytic activity under visible light irradiation for phenol degradation on Ag-Pt/TiO₂ photocatalysts is reported in this article. Photoactivity of Pt/TiO₂ and Ag-Pt/TiO₂ powders depends mainly

on platinum nanoparticles size. The smaller size of platinum is, the higher is efficiency of phenol degradation. The DRS, XRD, TEM and BET measurements corroborate that the most active photocatalyst under visible light (Ag-Pt/TiO₂_T2) contains fine Pt NPs (~3 nm) and small silver nanoparticles (~6 nm) deposited on self-synthesized TiO₂ surface. The antibacterial activities of silver nanoparticles (Ag-NPs), studied with respect to yeast *C. albicans*, Gram-positive *St. aureus* and Gram-negative *E. coli*, depends on content and size of silver NPs. Silver nanoparticles with size below 5 nm are recommended for the inhibition of pathogenic microorganisms growth.

Acknowledgments

This research was financially supported by Norway Grants in the Polish-Norwegian Research Programme (Small Grant Scheme) operated by the National Centre for Research and Development, grant no. POL-NOR/207659/23/2013 ~~Polish Ministry of Science and Higher Education (grant Juventus Plus No. IP2011063971)~~, Bill & Melinda Gates Foundation (Grand Challenges Explorations Grant, GCE R8, OPP1060234) and Catalysis Research Center through Target Oriented Research Assembly for “Research Cluster for Photofunctional Plasmonic Particles”.

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Figure 1. DR-UV/Vis absorption spectra of Ag, Pt and Ag-Pt nanoparticles deposited on TiO₂ surface

Figure 2. XRD patterns of bare and modified TIP titania with platinum and silver; a-anatase, b-brookite, Ag* - silver, Pt – platinum NPs.

Figure 3. TEM microscopy images for Pt/TiO₂_1 (a), TEM and FFT analysis for sample Pt-TiO₂_2 (b), STEM image and STEM-EDS mapping images of Ag-Pt/TiO₂_T2 nanoparticles (c), STEM microscopy analysis for sample Ag-Pt/TiO₂_R1

Figure 4. The effect of silver and platinum particles size and the type of TiO₂ matrix used during preparation of Ag-Pt/TiO₂ on photocatalytic activity under UV and visible light ($\lambda > 420$ nm).

Figure 5. Zone of inhibition for pure TiO₂, Ag-TiO₂ and Ag-Pt/TiO₂ nanoparticles, (1) sample Ag-Pt/TiO₂_T4; (2) sample Ag-Pt/TiO₂_T3; (3) sample Ag-Pt/TiO₂_T2; (4) Pt/TiO₂_3; (5) sample Ag/TiO₂_1; (6) sample Pt/TiO₂_1; (7) sample Ag/TiO₂_3; (8) sample Ag/TiO₂_2 and (9) pure TiO₂

Ag nanoparticles - high antimicrobial activity

Pt nanoparticles - photocatalytic enhancement, produce the highest Schottky barrier

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1. Preparation conditions, characteristics and photoactivity of Ag/TiO₂, Pt/TiO₂ and Ag-Pt/TiO₂ photocatalysts

Table 2. XPS and SEM/EDS results of the content of noble metals in modified titania samples

Table 3. Zone of inhibition for Ag-Pt/TiO₂ nanoparticles, diameter of zone (mm)

Table 4. Minimum inhibitory concentration for Ag/TiO₂, Pt/TiO₂ and Ag-Pt/TiO₂ nanoparticles

Table 1

Sample no.	TiO ₂	Amount of platinum precursor [mol%]	Amount of silver precursor [mol%]	BET surface area [m ² /g]	Crystallite size [nm]						Phenol degradation constant rate [min ⁻¹].10 ⁻²		Sample color
					TiO ₂		Pt		Ag		under UV/Vis	under Vis λ> 420nm	
					a	r	111	200	Ag*	Ag ₂ O			
TiO ₂	TIP	0	0	81	10	-	-	-	-	-	4.58 ± 0.28	0.30 ± 0.02	white
TiO ₂ _P25	P25	0	0	55	28	33	-	-	-	-	4.81 ± 0.27	0.46 ± 0.01	white
TiO ₂ _ST01	ST01	0	0	250	8	-	-	-	-	-	4.76 ± 0.27	0.39 ± 0.01	white
Ag/TiO ₂ _1	TIP	0	2.5	84	12	-	-	-	2	12	4.96 ± 0.25	0.28 ± 0.01	beige
Ag/TiO ₂ _2	TIP	0	4.5	87	13	-	-	-	3	13	4.72 ± 0.28	0.52 ± 0.02	grey
Ag/TiO ₂ _3	TIP	0	6.5	72	14	-	-	-	14	5.1	4.94 ± 0.25	0.81 ± 0.04	grey
Pt/TiO ₂ _1	TIP	0.1	0	101	8	-	2	-	-	-	4.89 ± 0.26	1.24 ± 0.10	yellow
Pt/TiO ₂ _2	P25	0.1	0	54	21	31	-	-	-	-	4.95 ± 0.25	1.06 ± 0.08	grey
Pt/TiO ₂ _3	TIP	0.5	0	108	8	-	-	5	-	-	4.97 ± 0.25	1.84 ± 0.15	yellow
Pt/TiO ₂ _4	ST01	0.1	0	188	10	-	1	3	-	-	4.98 ± 0.26	1.45 ± 0.10	yellow
Ag-Pt/TiO ₂ _T1	TIP	0.1	2.5	68	8	-	2	9	4	69	4.95 ± 0.25	2.04 ± 0.13	yellow
Ag-Pt/TiO ₂ _T2	TIP	0.5	2.5	93	9	-	2	3	6	14	4.94 ± 0.25	3.69 ± 0.20	yellow
Ag-Pt/TiO ₂ _T3	P25	0.5	2.5	51	21	31	38	74	12	-	4.89 ± 0.26	1.40 ± 0.11	beige
Ag-Pt/TiO ₂ _T4	ST01	0.5	2.5	154	15	-	42	145	2	18	4.90 ± 0.26	1.20 ± 0.10	dark yellow
Ag-Pt/TiO ₂ _R1	TIP	0.5	2.5	95	9-10	-	9	-	5	-	4.98 ± 0.25	3.56 ± 0.19	yellow
Ag-Pt/TiO ₂ _R2	P25	0.5	2.5	45	25	24	14	-	4	1	4.99 ± 0.26	1.74 ± 0.08	yellow
Ag-Pt/TiO ₂ _R3	ST01	0.5	2.5	109	11	-	11	-	3	3	4.98 ± 0.25	2.33 ± 0.10	yellow

Table 2

Sample no.	TiO ₂ source	Amount of platinum [mol%]			Amount of silver [mol%]		
		used for deposition	deposited		used for deposition	deposited	
			EDS	XPS		EDS	XPS
Pt/TiO ₂ _2	P25	0.1	0.06	n.a.	0	0	n.a.
Pt/TiO ₂ _4	ST01	0.1	0.09	1.9	0	0	0
Ag-Pt/TiO ₂ _T1	TIP	0.1	0.2	n.a.	2.5	2.24	n.a.
Ag-Pt/TiO ₂ _T2	TIP	0.5	0.34	1.8	2.5	0.38	0.3
Ag-Pt/TiO ₂ _T3	P25	0.5	0.23	3.0	2.5	0.34	0
Ag-Pt/TiO ₂ _T4	ST01	0.5	0.58	3.1	2.5	0.38	0

n.a.- not analyzed

Table 3

	Zone of inhibition (mm)		
	<i>Candida albicans</i> ATCC 10231 (YNBG)	<i>Escherichia coli</i> ATCC 10536 (TSB)	<i>Staphylococcus aureus</i> ATCC 6538 (TSB)
DMSO	0	0	0
TiO ₂	0	0	0
Ag/TiO ₂ _1	9	19	18
Ag/TiO ₂ _2	9	16	13
Ag/TiO ₂ _3	9	21	19
Pt/TiO ₂ _3	0	0	0
Ag-Pt/TiO ₂ _T2	11	0	0
Ag-Pt/TiO ₂ _T3	9	9	9
Ag-Pt/TiO ₂ _T4	9	15	0
Ag-Pt/TiO ₂ _R1	9	15	12
Ag-Pt/TiO ₂ _R2	9	14	11
Ag-Pt/TiO ₂ _R3	9	14	11

Table 4

	Minimum inhibitory concentration ($\mu\text{g}\cdot\text{cm}^{-3}$)		
	<i>Candida albicans</i> ATCC 10231 (YNBG)	<i>Escherichia coli</i> ATCC 10536 (TSB)	<i>Staphylococcus aureus</i> ATCC 6538 (TSB)
TiO ₂	> 256	> 256	> 256
Ag-TiO ₂ _1	8	125	64
Ag-TiO ₂ _2	32	> 256	> 256
Ag-TiO ₂ _3	8	256	64
Pt-TiO ₂ _3	> 256	> 256	> 256
Ag/Pt-TiO ₂ _T2	32	> 256	> 256
Ag/Pt-TiO ₂ _T3	64	> 256	256
Ag/Pt-TiO ₂ _T4	32	> 256	256
Ag/Pt-TiO ₂ _R1	8	> 256	256
Ag/Pt-TiO ₂ _R2	64	> 256	> 256
Ag/Pt-TiO ₂ _R3	16	> 256	> 256