

Core/Shell Ag/SnO₂ Nanowires for Visible Light Photocatalysis

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Abstract: This study presents core/shell Ag/SnO₂ nanowires (Ag/SnO₂NWs) as a new photocatalyst for the rapid degradation of organic compounds by the light from the visible range. AgNWs after coating with a SnO₂ shell change optical properties and, due to red shift of the absorbance maxima of the longitudinal and transverse surface plasmon resonance (SPR), modes can be excited by the light from the visible light region. Rhodamine B and malachite green were respectively selected as a model organic dye and toxic one that are present in the environment to study the photodegradation process with a novel one-dimensional metal/semiconductor Ag/SnO₂NWs photocatalyst. The degradation was investigated by studying time-dependent UV/Vis absorption of the dye solution, which showed a fast degradation process due to the presence of Ag/SnO₂NWs photocatalyst. The rhodamine B and malachite green degraded after 90 and 40 min, respectively, under irradiation at the wavelength of 450 nm. The efficient photocatalytic process is attributed to two phenomenon surface plasmon resonance effects of AgNWs, which allowed light absorption from the visible range, and charge separations on the Ag core and SnO₂ shell interface of the nanowires which prevents recombination of photogenerated electron-hole pairs. The presented properties of Ag/SnO₂NWs can be used for designing efficient and fast photodegradation systems to remove organic pollutants under solar light without applying any external sources of irradiation.

Keywords: AgNWs; SnO₂; silver nanowires; core-shell nanostructures; photocatalytic activity; visible-light photocatalysis



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1. Introduction

In recent years, due to high environmental pollution and fast industrial development, considerable interest has been paid to designing efficient, rapid, and widely applicable photocatalytic systems that are based on semiconductor nanostructures. The unique physical and chemical properties of semiconductors such as TiO₂, ZnO, ZnS, and CdSe make them extensively studied materials as photocatalysts [1]. One of the most promising semiconducting metal oxides is SnO₂ because of its high chemical, thermal, and mechanical stability as well as its high performance of organic pollutant degradation. However, a key issue in applying semiconducting nanostructures for practical purposes is the impossibility of visible light utilization. The efficient application of SnO₂ is limited by a large band gap of 3.6–4.1 eV and a very quick recombination of photogenerated electrons and holes [2,3]. To overcome these limitations, various metal nanostructures have been applied to form a heterojunction with semiconductors to induce efficient carrier separation under visible light irradiation. Ag-SnO₂ nanocomposite that is synthesized using an electrochemically active biofilm was proposed as a visible light-driven photocatalyst for the degradation of methyl orange, methylene blue, 4-nitrophenol, and 2-chlorophenol [4]. TiO₂/Ag/SnO₂ ternary

heterostructures that were obtained by a one-step reduction approach demonstrated a visible-light photocatalytic effect with high stability and reusability due to the Ag nanoparticle surface plasmon resonance (SPR) influence [5]. An Ag/SnO₂ composite was also fabricated by the one-pot hydrothermal method and revealed high efficiency towards the photodegradation of phenol under visible light irradiation [6]. At the same photocatalytic conditions, Ag/Ag₂O/SnO₂ nanoparticles removed malachite green [7]. Ag-doped SnO₂ nanoparticles that were modified with curcumin were found to be an efficient photocatalyst for the degradation of rhodamine B under visible light [8]. The composition of Ag and SnO₂ nanoparticles was applied for the photocatalytic removal of nitrogen oxide under solar light [9]. In addition, Ag-SnO₂ nanocomposites were presented not only as a photocatalytic agent but also their antibacterial and antioxidant properties were investigated [10].

Ag nanostructures of various dimensionalities were used to form Ag/SnO₂ composites for photocatalytic applications, but Ag nanowires (AgNWs), despite their many advantages, have not been applied previously for these purposes. AgNWs reveal high transmittance, excellent plasmonic properties, high electrical performance, mechanical flexibility, nanometric size, and one dimensional (1D) geometry [11]. Moreover, the facile separation process of the AgNWs by filtration or sedimentation allows simple processing and improves their applicability in comparison to other silver nanostructures. In the core/shell Ag/SnO₂NWs heterojunction, the advantageous properties of both the nanomaterials can be combined.

This study presents a new photocatalytic system that is based on AgNWs that are coated with an SnO₂ shell. The efficiency of the novel core/shell Ag/SnO₂NWs photocatalyst was studied based on the absorbance intensity decrease during the decomposition process of rhodamine B, used as a model dye and under light irradiation at the wavelength from the visible range. Rhodamine B decomposes within 50 and 90 min under 395 nm and 450 nm illumination, respectively. Additionally, malachite green decomposes completely within 40 min with the presence of a new Ag/SnO₂NWs catalyst whereas typical TiO₂ photocatalyst only slightly affects the dye under 450 nm irradiation due to the low absorption in the visible region. The proposed Ag/SnO₂NWs system combines 1D morphology and the excellent physico-chemical properties of silver nanowires such as photoabsorption from the visible light region as well as the photocatalytic ability of tin oxide. Moreover, the metal/metal oxide arrangement significantly enhances the semiconductor photocatalytic properties due to fast carrier separation and preventing the recombination of photogenerated electron-hole pairs.

2. Results and Discussion

Ag/SnO₂NWs that were applied to the study were prepared in two processes, the first one was polyol synthesis to obtain AgNWs and then hydrolysis of sodium stannate in the presence of the nanowires to form a SnO₂ shell on the nanowire surface (Figure 1a). The core/shell Ag/SnO₂ nanowires were composed of 14 nm (± 2 nm) thick SnO₂ shell consisting of 7 nm (± 2 nm) rutile-type crystals surrounding the metallic core.

Our previous report describes, in detail, both synthesis stages, stability studies, morphological, and structural analysis of the core/shell Ag/SnO₂NWs system [12]. Despite the fact that AgNWs are characterized by fast atmospheric corrosion, nine weeks are enough to decompose completely; the Ag/SnO₂NWs are stable for over four months at ambient conditions. The core/shell Ag/SnO₂NWs show significant stability in the highly complexing environment of KCN solution. They are resistant to harsh CN[−] ions at the concentration range of 0.01 to 0.0001 wt.%. The high stability allows further applying them as a catalyst into various environments for the different pollutant decompositions [12]. The core/shell arrangement allows the formation of the metal-semiconductor junction to prevent the recombination of the photogenerated electron-hole pairs and to enhance photocatalytic efficiency by photoabsorption from the visible region [13]. Moreover, the SnO₂ shell acts as a protective coating on silver nanostructures against the influence of different environmental conditions [12], which provides high stability of the system. The absorbance spectra of AgNWs shows two major bands that are centered around 349 nm

and 376 nm, respectively, that are responsible for the longitudinal and transverse modes in the SPR of the nanowires (Figure 2a). After SnO₂ shell synthesis the above-described peaks were red-shifted to 360 nm and 420 nm for the longitudinal and transverse SPR modes of AgNWs, respectively (Figures 2a and S1). It was shown previously that the SPR of silver nanowires is sensitive to the applied different coating as a result of the surrounding media dielectric constant changes [14]. In this study, the redshift allowed tuning of the absorbance properties and shifting the maxima of main absorbance bands to the visible light region. The absorbance spectra, typical for SnO₂, showed a peak at about 193 nm [15]. To study, in detail, the optical properties of the system, the hydrolysis process of sodium stannate in the aqueous solution without the silver nanowires presence was carried out. In this reaction, the pure SnO₂ nanoparticles (SnO₂NPs) were prepared that were similar in morphology and structure to the SnO₂ shell (Figure 1b). The nanoparticles revealed a mean diameter of about 25 nm (STEM analysis) and their properties were described in our previous report [16]. The absorbance spectra of SnO₂NPs shows the band with the maximum at 195 nm (Figure S2) that was suitable for photocatalysis induced by UV light. The value of the band gap for semiconducting nanostructures that was obtained by our method was calculated based on the Tauc plot (Figure S2) to be about 4.17 eV. This value is in good agreement with the reports for tin oxide nanoparticles [2].

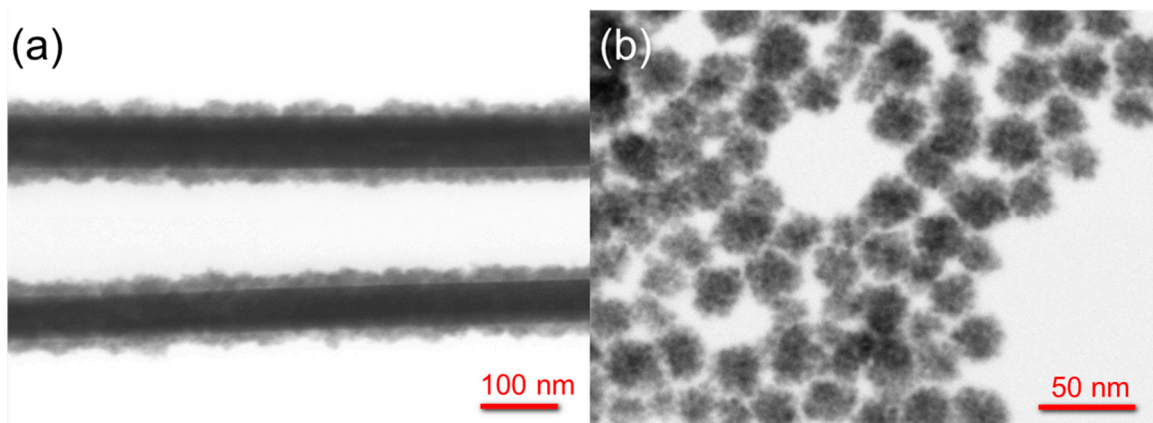


Figure 1. STEM images of (a) core/shell Ag/SnO₂NWs and (b) SnO₂NPs.

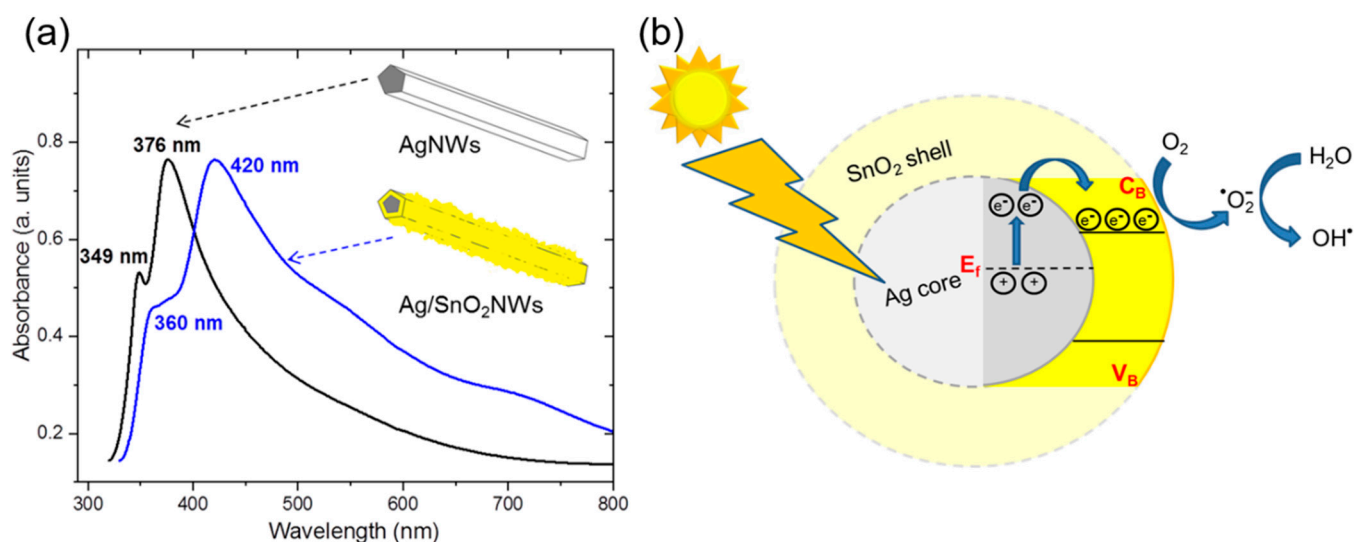


Figure 2. (a) The absorbance spectra of AgNWs and the core/shell Ag/SnO₂NWs. (b) Schematic illustration of the photocatalytic mechanism of Ag/SnO₂NWs under visible light irradiation.

The core/shell Ag/SnO₂NWs were used for the degradation of rhodamine B as a model organic dye that is characterized by an absorbance band with a maximum of 553 nm. Rhodamine B is widely applied for the photocatalytic model reaction study because it is broadly representative of organic compounds in its class and, since it strongly absorbs light, this allows facile monitoring of its degradation by UV/Vis spectroscopy [17]. The intensity of the band was studied under the irradiation of precisely defined sources, 395 nm and 450 nm LED lamps, corresponding electromagnetic radiation from the wavelength range of visible light. This approach can optimize the future photodegradation system for removing pollutants using solar irradiation instead of applying sophisticated and expensive UV-light sources (Figure S2). After coating AgNWs with an SnO₂ shell, the nanowires revealed effective photoabsorption at the visible light region due to the absorption band at 420 nm and partially by longitudinal mode at 360 nm (Figure 2a). The core/shell Ag/SnO₂NWs were dispersed homogeneously in an aqueous solution of rhodamine B. The shell formation prevented the nanowires from the aggregation process because SnO₂ is an efficient inorganic stabilizer of silver colloidal suspensions [16]. This phenomenon allows AgNWs introduction to the hydrophilic environment without aggregation and acting as a part of efficient photocatalyst as well as can also facilitate the redispersion process of Ag/SnO₂NWs after sedimentation. Figure S3a shows the separation process by sedimentation of the nanowires after 48 h. The nanowires were collected as sediment on the bottom of the vessel. This simple separation process of nanomaterials from the solution can be applied as a method of removing solvent with the decomposed pollutants after the photocatalysis process. A gentle mixing of the solution after sedimentation resulted in obtaining a homogenous mixture due to the SnO₂ coating on AgNWs, preventing the aggregation process (Figure S3b).

The intensity absorbance of rhodamine B was measured every 10 min after illumination by the selected light source. The samples were centrifuged for photocatalyst separation and further study of the optical properties of the supernatant with the dye. Figure 3a shows absorbance spectra of the supernatant with rhodamine B at the selected time points after 395 nm LED light irradiation. The absorbance intensity significantly decreased after 10 min of illumination and the dye was completely degraded in less than 1 h. It indicates the high efficiency of Ag/SnO₂NWs as a photocatalyst under the irradiation from the visible light region. To study the process in detail and the influence of different factors on the photodegradation process, rhodamine B degradation was studied under various conditions (Figure 3b). It is essential to study all the conditions and system components to avoid the possibility of spectral interferences by transformation intermediates which may absorb radiation at the wavelength of the dye's absorption maximum [18]. The ability of the degraded substance to inject electrons into the conduction band of a semiconductor should be primarily tested. Rhodamine B with the Ag/SnO₂NWs photocatalyst presence but not light-irradiated (dark experiment) did not show any degradation process (Figure S4). The dye sample without the Ag/SnO₂NWs but illuminated by 395 nm LED lamp revealed a slight decrease in the absorbance intensity (Figure S5) and proved that the photodegradation effect appears only in the presence of Ag/SnO₂NWs. Moreover, the contribution of SnO₂ in the photodegradation process in this range of illumination was verified. For these purposes, SnO₂ was synthesized using stannate precursor as in the case of the shell but without AgNWs presence. The process resulted in SnO₂ nanoparticles (SnO₂NPs) formation, described in our previous report [16]. To compare the influence of SnO₂ on the photocatalytic activity the Ag/SnO₂NWs, SnO₂NPs were added to the dye solution at the concentration of the whole core/shell complex (2 mg/mL) and at the concentration of the tin oxide in the shell (0.66 mg/mL) (Figure 3b). The weight percentage of the SnO₂ shell in Ag/SnO₂NWs complex was determined on the EDS studies and was about 33 wt.% (Figure S6). SnO₂ is known as an efficient photocatalyst under UV irradiation [19–21]. In our system, after irradiation by light from the visible region, both concentrations of SnO₂NPs showed a slight degradation rate of rhodamine B as a result of the negligible influence of this radiation on tin oxide nanostructures (Figures 3b and S7).

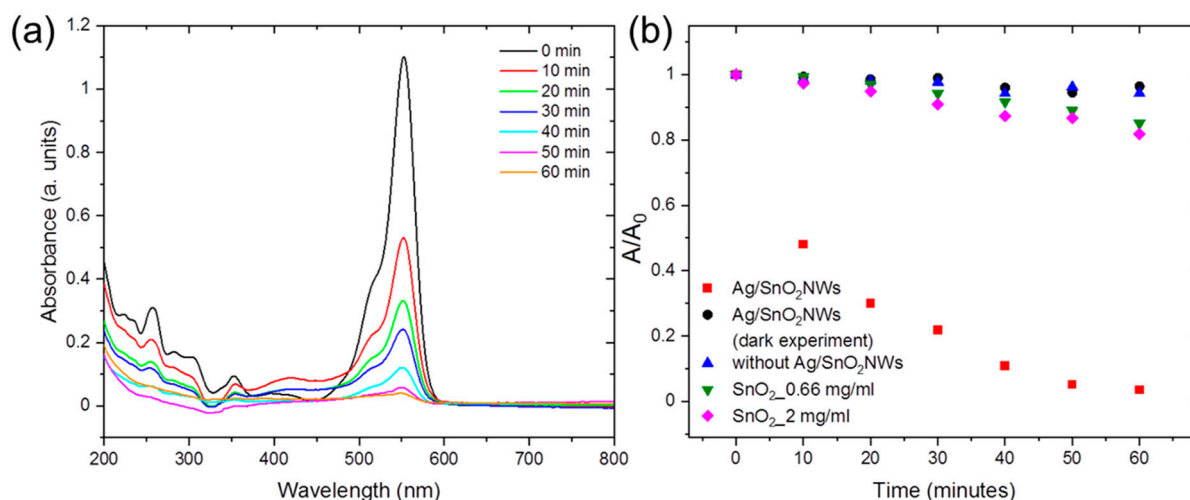


Figure 3. (a) The absorbance spectra of rhodamine B with Ag/SnO₂NWs photocatalyst presence under 395 nm light irradiation. (b) The degradation of rhodamine B with 2 mg/mL of Ag/SnO₂NWs catalyst (■), without photocatalyst (▲), with 0.66 mg/mL (▼), and 2 mg/mL (◆) of SnO₂NPs under 395 nm light irradiation and Ag/SnO₂NWs without irradiation (dark experiment, ●).

The rapid photodegradation of the dye under 395 nm illumination for about 60 min using Ag/SnO₂NWS is due to the formation of a metal/semiconductor heterostructure which prevents the fast recombination of photogenerated electron-hole pairs. The irradiation at the wavelength of 395 nm can excite only SPR of AgNWs in the core/shell composite and cause electron transfer from AgNWs to the conduction band (CB) of SnO₂ (Figure 2b). The carrier migration is a result of combining two materials with different work functions; Ag is characterized by a work function of 4.26 eV and SnO₂ with a work function of about 4.84 eV [22,23]. The photoinduced electrons can get sufficient energy to surmount the Schottky barrier on the Ag/SnO₂ interface despite the uniform energy levels of both components. The electrons are transferred to the semiconductor material to equilibrate the metal-metal oxide alignment and form a new Fermi energy level (Figure 2b). The transferred free electrons are trapped by dissolved oxygen molecules in the water and form a high oxidative species, such as superoxide radical anions (O₂^{•−}) and hydroxyl radicals (HO•) [4]. In the core/shell heterostructure arrangement, the recombination of the photoinduced hole-electron pairs is inhibited mainly by forming a complex of free electrons from the CB with oxygen molecules. The trapped electrons can facilitate the formation of O₂^{•−} and HO• reactive radicals and significantly enhance the rate of their formation, increase photocatalytic activity, and reduce organic substance degradation time. The absorbance intensity of rhodamine B decreased by half after 10 min of irradiation. Moreover, the strong confinement and anisotropic effect in the 1D core/shell metal/semiconductor structures can facilitate carrier separation and increase photocatalytic efficiency.

To the best of our knowledge, it is the first report presenting the photocatalytic properties of the 1D core/shell Ag/SnO₂NWs nano-system. It can broaden the range of AgNWs applications since SnO₂ revealed a high environmental stability [12]. The silver nanostructures tend to aggregate and dissolve in the aquatic environment, so the protective shells are also applied to increase stability, processability, and range of applications. The ability of the new catalyst to decompose organic compounds under solar irradiation combined with a high resistance even to harsh conditions can allow the designing of photodegradation systems for various environments and without any external irradiation sources. The advantage of the presented Ag/SnO₂NWs photocatalyst is its high stability under different conditions in comparison to other silver/wide band semiconductor composites. An example of that hybrid is Ag/ZnO heterostructure, which, although revealed high photocatalytic activity [24], both its components show a low stability. Silver nanostructures are affected by atmospheric corrosion due to the effective interaction of Ag⁺ ions with

sulphides and the formation of a silver sulphide layer [25]. ZnO is easily degraded at the nanoscale in hydrophilic environments [26]. Another, more stable semiconductor of TiO₂ that was combined with various Ag nanostructures revealed photocatalytic activity that was characterized by a degradation time of 60 min [27] and more than 90 min [28], but under UV-light. Ag nanowires that were modified with an α -Fe₂O₃ show similar efficiency and time of the process; methylene blue was degraded for 30 min under visible light illumination, according to the authors, due to the synergetic effect of LSPR and the effective separation of photogenerated carriers between both materials [29]. A ternary TiO₂/Ag/SnO₂ system was applied for the photodegradation of methylene blue for more than 140 min for 40 mg of the photocatalyst of 3.12×10^{-5} methylene blue (100 mL) under visible light irradiation [5]. Ag/Ag₂O/SnO₂ nanocomposites removed malachite green (20 mg/L) after 120 min by using 30 mg of the photocatalyst [7]. The photocatalysis process under visible light with the addition of Ag-SnO₂ nanocomposites that were synthesized using electrochemically active biofilm was measured in hours, but was significantly efficient than for pure SnO₂ [4]. The sphere-like plasmonic Ag/SnO₂ photocatalyst revealed a phenol decomposition time of 50 min that was similar to our results but with different dimensionalities allowing the application of them to other purposes [6].

To study the photodegradation process with Ag/SnO₂NWs catalyst that was induced by the light from the visible region, an additional light source from this area at the wavelength of 450 nm was chosen. The removal efficiency of rhodamine B was similar for 395 nm and 450 nm light sources and was calculated to be about 87% and 88% for irradiation at 395 nm and 450 nm (Figure S8). However, the degradation time was not comparable; the process took about 50 and 90 min for irradiation at 395 nm and 450 nm, respectively. The efficiency of the degradation was also high, but the time that was needed to decompose the dye increased to about 90 min (Figure 4a). Both the SPR bands that were irradiated at 450 nm were not so effectively excited as for the 395 nm source. The AgNWs absorbed only the irradiation above 450 nm and their absorbance spectrum was only partially excited (Figure 2a). The process was still efficient and significantly higher than for pure SnO₂ irradiated under 450 nm (Figure 4b).

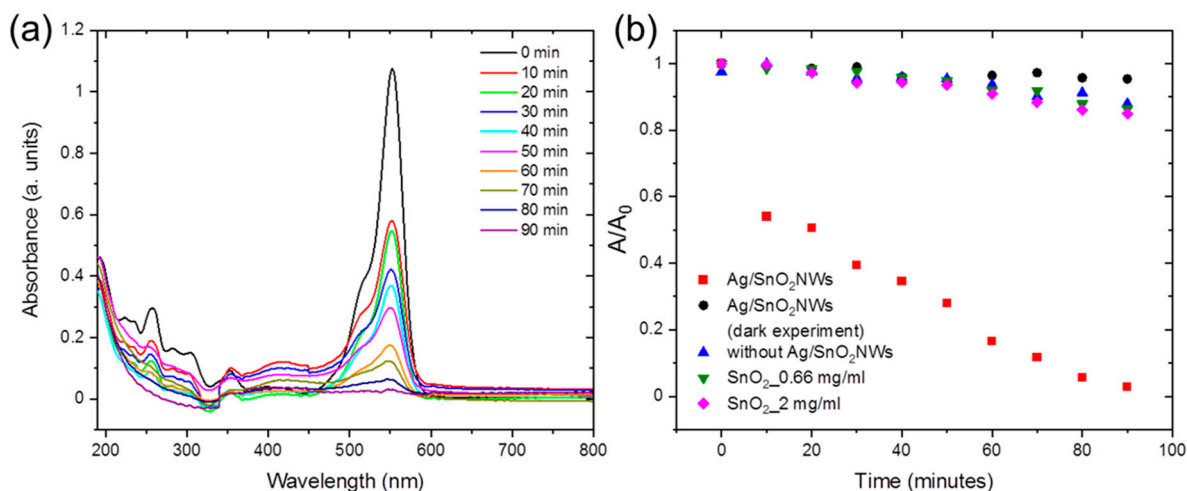


Figure 4. (a) The absorbance spectra of rhodamine B with Ag/SnO₂NWs photocatalyst presence under 450 nm light irradiation. (b) The degradation of rhodamine B with 2 mg/mL of Ag/SnO₂NWs catalyst (■), with no photocatalyst (▲), with 0.66 mg/mL (▼), and 2 mg/mL (◆) of SnO₂NPs under 450 nm light irradiation and Ag/SnO₂NWs without irradiation (dark experiment, ●).

Similar to the 395 nm excitation source (Figure 3b), the absorbance intensity of the dye under illumination at the wavelength of 450 nm without the photocatalyst did not change significantly, indicating the minimal influence of the irradiation on the optical properties of rhodamine B (Figures 4b and S9). The experiment with Ag/SnO₂NWs photocatalyst, without applying irradiation (dark experiment, Figure S4), showed only a

minimal decrease in the absorbance intensity and demonstrated the stability of the dye and the essential influence of light illumination in the decomposition process. The irradiation at the wavelength of 450 nm on SnO₂NPs at both concentrations, 2 mg/mL as Ag/SnO₂NWs and 0.66 mg/mL corresponding to SnO₂ amount in the core/shell complex, showed a slight degradation rate of rhodamine B (Figure S10). It indicated that the selected irradiation source did not significantly affect the organic substances when using pure semiconductor as a photocatalyst, only the Ag/SnO₂ heterojunction can be considered as a source for the utilization of organic pollutants under visible light.

Ag/SnO₂NWs were also applied for the degradation of malachite green, which is present in the environment and its remediation is highly required. Malachite green is a dye that is commonly used in the textile and food industry. It should be removed after industrial processes due to the fact that it is highly toxic, especially for aquatic flora and fauna [30–32]. Figure 5a shows the rapid degradation of malachite green by Ag/SnO₂NWs under the light from the visible range (450 nm); malachite green was completely decomposed after 40 min. The absorbance intensity of the dye with Ag/SnO₂NWs photocatalyst presence but without any irradiation did not change significantly (Figures 5b and S11). The dark experiment proved the photodegradation mechanism for fast malachite green decomposition. Malachite green irradiation at the wavelength of 450 nm without photocatalyst revealed only a slight decrease in the absorbance intensity (Figures 5b and S12). The irradiation of SnO₂NPs at both concentrations, 2 mg/mL as Ag/SnO₂NWs and 0.66 mg/mL corresponding to SnO₂ amount in the core/shell complex also showed only a slight degradation rate of malachite green (Figures 5b and S13). Moreover, to compare Ag/SnO₂NWs photocatalyst efficiency at the visible range to a well-known commercial photocatalyst, malachite green was treated with TiO₂ under 450 nm irradiation. TiO₂ as a semiconductor that is characterized by absorption in the UV range, decomposed the dye only to a minimal extent (Figures 5b, S14 and S15) [33]. The core/shell Ag/SnO₂NWs system shows a high degradation rate of organic pollutants under visible light irradiation and can be used in practical photocatalysis reactions for efficient remediation.

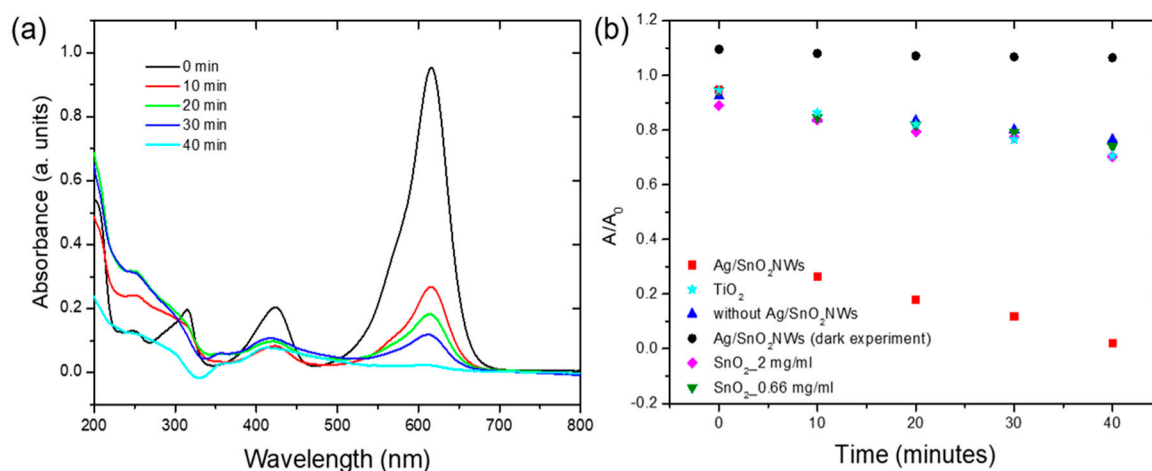


Figure 5. (a) The absorbance spectra of malachite green with Ag/SnO₂NWs photocatalyst presence under 450 nm light irradiation. (b) The degradation of malachite green with 2 mg/mL of Ag/SnO₂NWs catalyst (■), with no photocatalyst (▲), with 0.66 mg/mL of SnO₂NPs (▼), 2 mg/mL of SnO₂NPs (◆), and with 2 mg/mL TiO₂ catalyst (★) under 450 nm light irradiation and Ag/SnO₂NWs without irradiation (dark experiment, ●).

3. Experimental Section

3.1. Preparation of Core/Shell Ag/SnO₂NWs

In the first stage, AgNWs were synthesized by a polyol process and then covered by an SnO₂ shell as a result of the hydrolysis process of sodium stannate; both stages were described in detail in our previous studies [12,34]. In brief, 0.408 g of AgNO₃ solution

(purity 99.9999%, Sigma-Aldrich, St Louis, MO, USA) in ethylene glycol (EG, POCH) was added (feed rate of 16 mL/h) to the mixture of 40 mL of EG, 2 g of polyvinyl pyrrolidone (PVP, molecular weight of 55 kDa, Sigma Aldrich) and 0.028 g of sodium chloride (NaCl, Chempur, Karlsruhe, Germany) was constantly heated to 170 °C, refluxed, and stirred at 570 rpm. Then, the solution was maintained at the same conditions for 1 h and cooled to room temperature. The mixture of AgNWs was diluted by acetone followed by dispersion in 60 mL of ethanol (anhydrous, POCH).

An SnO₂ shell on AgNWs was obtained in a one-step process by adding 5.051 g of an aqueous solution of sodium stannate trihydrate (0.25 wt.%, Na₂SnO₃·3H₂O, Sigma-Aldrich, 95%) to the AgNWs mixture that was heated to 100 °C, refluxed, and stirred at 300 rpm. The solution was kept at the above-described conditions for 15 min and then cooled in a cold water-bath. The mixture of AgNWs was previously dispersed in water by adding 2.5 g of AgNWs that was obtained in polyol process (ethanol solution), to 92.7 g deionized water and 1 wt.% aqueous solution of sodium citrate (Na₃C₆H₅O₇·2H₂O, purity 99.0%, Sigma Aldrich).

The core/shell Ag/SnO₂NWs were filtered (Merck Millipore (Burlington, MA, USA) type RTTR, Isopore membrane Filter, the pore size of 1.2 µm) to remove any by-products of the reactions and obtain high purity samples. To obtain pure SnO₂ that was relevant to the shell part of the complex for the control experiments, 5.70 g sodium stannate trihydrate (0.25 wt.% aqueous solution) was added to 40 g of boiling water and this sample was heated to 100 °C and stirred at 600 rpm for 15 min. As a result, the SnO₂ nanoparticles (SnO₂NPs) were synthesized. Their morphology and structure were described in our previous work [16].

3.2. Photocatalytic Activity Study

Photocatalytic activities of the core/shell Ag/SnO₂NWs were determined by the decomposition of rhodamine B (≥95%, Sigma Aldrich) as a model system. The aqueous solution of Ag/SnO₂NWs (2 mg/mL) and rhodamine B (5 mg/L, 10.4 µM) was irradiated by 395 nm and 450 nm LED lamps (100 W). The removal efficiency of rhodamine B by Ag/SnO₂NWs photocatalyst for both irradiation sources was calculated based on the initial (C₀) and final concentration (C) of the dye according to Equation (1).

$$H (\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

As control samples, SnO₂NPs were also illuminated by 395 nm and 450 nm as well as 365 nm LED lamps at concentrations of 2 mg/mL (the same as Ag/SnO₂NWs system) and 0.66 mg/mL (as shell SnO₂ percentage wt.% in the whole complex). The weight percentage of the shell and core of the Ag/SnO₂NWs composite was determined based on EDS (Energy Dispersive X-ray Spectroscopy) studies using an FEI Nova NanoSEM 450 microscope that was equipped with EDAX Roentgen spectrometer (EDS) and an Octane Pro Silicon Drift Detector (SDD). The samples were previously collected on silicon wafers for EDS measurements.

Moreover, malachite green oxalate salt (7 mg/L, 15.1 µM, Sigma Aldrich) was degraded with the presence of Ag/SnO₂NWs (2 mg/mL) under irradiation of a 450 nm LED lamp (100 W). To compare the photocatalytic ability of Ag/SnO₂NWs to commercial photocatalyst, 2 mg/mL of TiO₂ (titanium (IV) oxide, anatase, nanopowder, <25 nm particle size, 99.7%, Sigma Aldrich) was added to malachite green oxalate salt solution (7 mg/L, 15.1 µM) and irradiated by 450 nm LED lamp (100 W). The degradation reactions of rhodamine B and malachite green were monitored by measuring the UV/Vis absorption spectra (UV5600 spectrophotometer, Biosens) of the sample solution taken out at regular intervals, every 10 min for 395 nm and 450 nm LED lamps or every 30 min for 365 nm LED lamp illumination. The sample solution was constantly stirred (400 rpm) and cooled during illumination. The LED lamps were fixed over the vessel that was filled with a sample solution. The absorbance spectra of each sample supernatant were recorded in the

wavelength range of 200 to 800 nm after the centrifugation process (8000 rpm, 2 min) of a 2 mL sample after selected illumination time.

4. Conclusions

The study demonstrates Ag nanowires that are covered with SnO₂ shell as a new, efficient photocatalyst under the irradiation from the visible light range. The fast degradation process is the effect of the combination of advantages of both the components forming the core/shell Ag/SnO₂NWs hybrid as well as phenomena appearing on the material interfaces. The SPR absorbance spectrum of AgNWs after coating with SnO₂ shifts towards the visible region and facilitates excitation of the electrons in the nanowires by photons at this wavelength range. The photocatalytic activity of SnO₂ is enhanced significantly and achievable without UV irradiation. The excited electrons from the metal core are transferred to the metal oxide shell and captured by oxygen molecules and involved in the formation of reactive radicals that are essential for the degradation of organic compounds. This report utilizes rhodamine B as a model organic dye for studying the activity of novel 1D metal/semiconductor Ag/SnO₂NWs photocatalyst. The rhodamine B is degraded after 50 and 90 min under irradiation at the wavelength of 395 nm and 450 nm, respectively. Moreover, malachite green as an environmental organic pollutant is decomposed after 40 min by Ag/SnO₂NWs and only slightly degraded by the common catalyst of TiO₂ under 450 nm irradiation. High photocatalytic activity of the Ag/SnO₂NWs system is attributed to the core/shell metal/semiconductor arrangement which results in carrier separations and prevents the recombination of photogenerated electron-hole pairs. The facile processing of an Ag/SnO₂NWs hybrid by simple separation, such as filtration or sedimentation, is beneficial for photocatalytic applications.

Our findings indicate that the core/shell of Ag/SnO₂NWs represents a very promising material that is characterized by high environmental stability for the designing of future photocatalytic systems under solar irradiation for effective remediation processes of various environments.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal12010030/s1>, Figure S1: Absorbance spectra of core/shell Ag/SnO₂NWs. Figure S2: The absorbance spectra of SnO₂NPs at the concentrations of 2 and 0.66 mg/mL and (inset) Tauc plot for SnO₂ energy gap value determination. Figure S3: The images of an aqueous solution of Ag/SnO₂NWs (a) left for 48h for sedimentation and (b) then gently mixed to redisperse the core/shell nanowires. Figure S4: The absorbance spectra of rhodamine B without any irradiation after centrifugation of Ag/SnO₂NWs photocatalyst (dark experiment). Figure S5: The absorbance spectra of rhodamine B that was irradiated under 359 nm without catalyst. Figure S6: The EDS spectrum of Ag/SnO₂NWs, inset: The weight percentage of O, Ag, and Sn in the hybrid, and STEM image of the sample area for EDS analysis. Figure S7: The absorbance spectra of rhodamine B and SnO₂NPs at a concentration of (a) 0.66 mg/mL and (b) 2 mg/mL under 395 nm light irradiation. Figure S8: The degradation of rhodamine B with Ag/SnO₂NWs photocatalysts presence under 395 nm and 450 nm irradiation. Figure S9: The absorbance spectra of rhodamine B that was irradiated under 450 nm. Figure S10: The absorbance spectra of rhodamine B with the presence of SnO₂NPs at a concentration of (a) 0.66 mg/mL and (b) 2 mg/mL under 450 nm light irradiation. Figure S11: The absorbance spectra of malachite green without any irradiation with the presence of Ag/SnO₂NWs photocatalyst (dark experiment). Figure S12: The absorbance spectra of malachite green that was irradiated under 450 nm without catalyst. Figure S13: The absorbance spectra of malachite green with the presence of SnO₂NPs at a concentration of (a) 0.66 mg/mL and (b) 2 mg/mL under 450 nm light irradiation. Figure S14: The absorbance spectra of malachite green with the presence of 2 mg/mL TiO₂ photocatalyst that was irradiated under 450 nm with. Figure S15: The absorbance spectra of TiO₂ (P25).

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