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1	Plasmonic 'rainbow' photocatalyst with broadband solar
2	light response for environmental applications
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4	Sammy W. Verbruggen ^{1,2} *, Maarten Keulemans ^{1,2} , Bart Goris ³ , Natan Blommaerts ¹ ,
5	Sara Bals ³ , Johan A. Martens ² , Silvia Lenaerts ¹
6	
7	¹ Sustainable Energy, Air & Water Technology, DuEL, Department of Bioscience Engineering, University
8	of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium, ² Center for Surface Chemistry and
9	Catalysis, Department of Microbial and Molecular Systems, KU Leuven, Kasteelpark Arenberg 23, 3001
10	Heverlee, Belgium, ³ EMAT, Department of Physics, University of Antwerp, Groenenborgerlaan 171,
11	2020 Antwerp, Belgium
12	
13	* Corresponding author: Sammy.verbruggen@uantwerpen.be ,
14	Sustainable Energy, Air & Water Technology, Department of Bioscience Engineering, University of
15	Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium
16	tel: +32 3 265 32 60, fax: +32 3 265 32 25
17	

1 Abstract

We propose the concept of a 'rainbow' photocatalyst that consists of TiO₂ modified with gold-silver alloy nanoparticles of various sizes and compositions, resulting in a broad plasmon absorption band that covers the entire UV-VIS range of the solar spectrum. It is demonstrated that this plasmonic 'rainbow' photocatalyst is 16% more effective than TiO₂ P25 under both simulated and real solar light for pollutant degradation at the solid-gas interface. With this we provide a promising strategy to maximize the spectral response for solar to chemical energy conversion.

8

9 Keywords: photocatalysis; plasmon (SPR); broadband; solar; stearic acid

10

11 1. Introduction

12 Plasmon resonance can be described as an energetic collective oscillation of conduction band electrons 13 on a metal particle. Energetic coupling of this plasmon resonance with a semiconductor is a proven 14 strategy for increasing the spectral response of photoactive materials in the visible light region of the 15 spectrum [1,2]. It has been shown that plasmonic enhancement is maximized when there is a good 16 overlap between the plasmon absorption band and the intensity spectrum of the light source [3,4]. In 17 most cases this requires careful tuning of the plasmonic nanostructures to the utilized light source, 18 which often has a narrow emission spectrum (e.g. lasers, LEDs and monochromatic filtered light). 19 Conversely, for actual solar-driven applications it is more useful to design plasmonic nanostructures 20 that respond to a much broader wavelength range. In that regard the concept of 'broadband plasmons' 21 is beginning to find its way in the field of dye sensitized solar cells (DSSCs), [5–7] where mainly large 22 nanoparticles are used for plasmonic light scattering in order to more effectively utilize incident 23 photons in the solar cell and increase the number of dye excitations. On the other hand the broadband 24 plasmon concept remains unexplored in the field of photocatalytic environmental remediation, where the use of sensitizing dyes is complicated due to severe stability issues [8] and plasmonic enhancement
thus takes place through direct interaction with the semiconductor in the absence of sensitizing dyes.
In our work the plasmonic nanoparticles are significantly smaller than those envisaged for broadband
plasmonic response in DSSCs (i.e. well below 80 nm).

5 It is known that the plasmon wavelength can be tuned by altering the size or shape of metal 6 nanostructures [9,10]. An alternative versatile way of wavelength tuning is offered by alloying. In the 7 particular case of colloidal gold-silver alloys, plasmon resonance in colloidal solutions can be obtained 8 between ca. 390 nm for pure silver nanoparticles up to 530 nm for pure gold [11]. In this work, we 9 have prepared gold-silver alloys with compositions ranging from 20% to 100% gold, with increments 10 of 10% using a modified Turkevich method. Alloy nanoparticle suspensions with higher silver content 11 do not remain stable for longer periods. So far, only very few reports exist on the photocatalytic activity 12 of gold-silver alloy on TiO₂ nanocomposites, all in liquid phase, such as the production of hydrogen 13 peroxide under UV [12] and the degradation of phenol and rhodamine B under visible light (using high 14 power Xe sources) [13,14]. Applications of plasmonic photocatalysis in gaseous environment are 15 altogether scarce [15–18]. Furthermore the concept of broadband plasmons has never been explored 16 in that context. Therefore in this work the photocatalytic activity is evaluated by means of stearic acid 17 degradation at the solid-gas interface, a widely recognized model reaction for organic fouling on solid 18 substrates [19,20].

19 2. Experimental

20 **2.1 Synthesis of plasmonic 'rainbow' photocatalyst**

Colloidal Au_xAg_(1-x) nanoparticles were prepared using a modified Turkevich procedure as follows:
Appropriate amounts of 0.01 M HAuCl₄·3H₂O (Sigma–Aldrich, >99.9%) and 0.01 M AgNO₃ (Sigma–
Aldrich, >99%) precursor solutions were diluted to a total resulting metal concentration of 0.1 mM to
avoid precipitation of AgCl. The solution was stirred vigorously and brought to boil after which 1 mL of
a freshly prepared 1 wt% sodium citrate (Sigma–Aldrich, 99%) solution was quickly added and left

boiling for exactly 30 min. This procedure was repeated in order to obtain nine colloidal solutions with
the gold fraction x varying from 0.2 to 1 with increments of 0.1. For the 'rainbow' sample, equal
amounts of each of the nine colloidal gold-silver solutions were mixed together under vigorous stirring.

The plasmonic photocatalysts ($Au_{0.3}Ag_{0.7}-P25$ and 'rainbow'-P25) were prepared by photoimpregnating [21] commercially available P25 (Evonik, surface area ± 55 m² g⁻¹, 80% anatase, 20% rutile) with the corresponding colloidal nanoparticle solution ($Au_{0.3}Ag_{0.7}$ nanoparticle solution or 'rainbow' mixture) under vigorous stirring and UVA illumination (Philips Cleo UVA, 25 W, 365 nm) for 60 min, so the resulting metal loading was 1.5 wt%. The resulting suspension was centrifuged, washed and dried overnight at 383 K.

10 2.2 Characterization

11 HAADF-STEM images and EDX maps were acquired using an Osiris electron microscope operated at 12 200 kV and equipped with a super-X detection system. The total acquisition time for the EDX maps was 13 3 minutes. UV-VIS spectra of the colloidal alloy suspensions were recorded with a Shimadzu UV-VIS 14 2501PC double beam spectrophotometer. UV-VIS absorbance spectra of the plasmonic catalyst 15 powders were collected on the same apparatus, equipped with a 60 mm BaSO₄ coated integrating 16 sphere and a photomultiplier R-446 detector. Dynamic Light Scattering is used for determining the 17 colloidal particle sizes on a BIC 90 Plus apparatus (Brookhaven) with a 15 mW 659 nm laser. Igor Pro 18 (v.6.02) was used to analyze the collected correlation functions. Absolute irradiance measurements of 19 the different light sources are performed with a calibrated Avantes Avaspec 3648 spectrometer.

20 2.3 Photocatalytic testing

The photocatalytic activity was evaluated by means of the degradation of stearic acid. The coating and measurement protocols are comparable to our earlier work [3,22]. The photocatalysts were suspended in ethanol (1 wt%) and stirred ultrasonically. 50 μ L of the suspension was drop casted on a pre-cleaned silicon wafer (1.5 cm x 3 cm), so the resulting coverage was 88 μ g cm⁻². Reference samples that only contain metal nanoparticles without TiO₂ are prepared by drop casting a volume of the corresponding

1 colloidal alloy solution containing the equivalent amount of metal nanoparticles on a bare silicon wafer 2 and evaporating the solvent. The resulting metal coverage is thus 1.33 μ g cm⁻². After drop casting the 3 samples were dried in an oven at 363 K. The investigated samples consist of (i) pristine P25, (ii) P25 4 modified with 1.5 wt% Au_{0.3}Ag_{0.7} alloy nanoparticles, (iii) the 'rainbow' photocatalyst (containing 1.5 5 wt% mixed metal alloy nanoparticles), (iv) a blanc silicon wafer, (v) silicon wafer containing the same 6 amount of Au_{0.3}Ag_{0.7} alloy nanoparticles as sample (ii), but without TiO₂ and (vi) silicon wafer containing 7 the same amount and composition of mixed alloy nanoparticles as the 'rainbow' sample, but without 8 TiO_2 . The last three samples are used for performing reference experiments to rule out the effect of 9 photolysis (blanc wafer) and stearic acid degradation due to plasmonic heating or direct plasmonic 10 catalysis (silicon wafer containing only noble metal particles but no TiO₂) [23,24]. In all experiments 11 these reference samples showed no activity (see below and in Figure 6) and are therefore not 12 considered in the further discussion. The sample containing 1.5 wt% Au_{0.3}Ag_{0.7} alloy nanoparticles on 13 P25 was added for comparison purposes as it has its plasmon absorption band maximum exactly at 14 490 nm, corresponding to λ_{max} of the visible LED light source.

15 Three different light sources were used for studying the photocatalytic performance of the 16 samples in a lab-environment: UVA (λ_{max} = 385 nm, provided by LEDs), narrow band visible light (λ_{max} 17 = 490 nm, provided by LEDs) and combined simulated solar light (300 W Xe source (Oriel Instruments) 18 equipped with AM1.5 solar simulator). The corresponding incident irradiance spectra and integrated 19 intensity outputs at sample distance (5 cm) are given in Figure 1. An additional experiment was 20 performed to test the photocatalytic activity of all samples under realistic outdoor conditions.

The degradation of stearic acid was monitored by FTIR on a NicoletTM 380 (Thermo Fisher Scientific) with ZnSe windows at a resolution of 1 cm⁻¹ by integration of the wavelength range 2800-3000 cm⁻¹ [25]. The samples were placed at an angle of 9° to minimize internal reflection effects.

- 24 **3. Results and discussion**
- 25 **3.1 Plasmonic 'rainbow' photocatalyst**

The resulting colloidal solutions appear bright yellow to ruby red (Figure 2a) and display plasmon resonance over a broad wavelength range (Figure 2b). The plasmon wavelength varies linearly with the gold fraction of the alloy (Figure 3, red curve), which is consistent with literature [26,27]. In addition, we noticed for the first time that the particle size gradually increases with decreasing gold content and can be fitted well by a second order polynomial (Figure 3, blue curve).

6 For the 'rainbow' sample, equal amounts of each of the nine colloidal alloy suspensions were 7 mixed and stirred vigorously. The resulting UV-VIS spectrum stretches out over a very broad 8 wavelength range. Furthermore, this 'rainbow' sample spectrum is a perfect linear combination of the 9 individual UV-VIS spectra of the constituting alloys (Figure 2c). This is a good indication for the stability 10 of the individual alloy nanoparticles, even when they are intermixed. The 'rainbow' photocatalyst is 11 prepared by depositing the intermixed alloy nanoparticles on the surface of TiO₂ P25 (Evonik) by a 12 photo-impregnation method so that the resulting metal loading is 1.5 wt%. This method enables a 13 homogeneous distribution and retention of the particle size [21]. On the microscopic level the 14 'rainbow' sample consists of homogeneously distributed gold-silver alloy nanoparticles of various sizes 15 and compositions on the surface of TiO₂ P25 aggregates. This is confirmed by HAADF-STEM imaging 16 and EDX spectroscopy as presented in Figure 4. Since the intensity in HAADF-STEM scales with the 17 thickness of the sample and with the atomic number Z of the elements that are present, the metallic 18 nanoparticles (indicated by white arrows in Figure 4) appear with higher intensity in comparison to the 19 TiO_2 support. From the EDX mapping, the co-presence of gold and silver over the entire metal 20 nanoparticle clearly indicates alloy formation.

The resulting absorption spectrum of the 'rainbow' photocatalyst is depicted in Figure 5 (white curve). The combined plasmon absorption band of all composing alloy nanoparticles stretches out over nearly the entire UV-VIS range, in contrast to pristine TiO₂ P25 that has a cut-off in the blue range of the spectrum (gray curve). The maximum of the plasmon absorption band lies in the green range of the spectrum, corresponding to those solar wavelengths with highest intensity output. A strong tail of

- the plasmon band towards longer wavelengths results in some absorption of red light. This way the
 entire broad visible light region of the spectrum is spanned by one single catalyst.
- 3

3.2 Broadband plasmonic photocatalytic activity at the solid-gas interface

4 The measured degradation curves obtained with all different samples are plotted in Figure 6. 5 As mentioned earlier, reference experiments involving a blank wafer or wafers with only metal 6 nanoparticles and no TiO₂ displayed no photocatalytic activity. In all our other experiments the 7 photocatalytic degradation of stearic acid obeyed zero order kinetics. Since TiO_2 P25 is the universal 8 photocatalytic reference material, the formal quantum efficiencies of the Au_{0.3}Ag_{0.7}-P25 and 'rainbow' 9 photocatalysts are expressed directly with respect to P25 in Figure 7. Under pure UVA illumination, 10 both metal-modified samples are less efficient than P25. This is most likely the result of metal particles 11 blocking active sites and shielding part of the TiO₂ surface from incoming light. Under narrow-band 12 visible light (490 nm LEDs), both plasmonic samples are significantly more effective than pristine P25, 13 but altogether the efficiencies under visible light remain much smaller than under UV. Although the 14 trace activity of P25 under pure visible light is in itself surprising, it should be technically possible due 15 to the presence of intrinsic surface defect levels (e.g. at the anatase-rutile interface), that have been 16 demonstrated by means of EPR and photoluminescence studies [28,29]. Modification of P25 with 17 plasmonic nanostructures leads to a large improvement of this basal visible light activity. The 'rainbow' 18 photocatalyst is approximately 50% better than P25 and the catalyst containing specifically Au_{0.3}Ag_{0.7} 19 alloy nanoparticles induces an efficiency increase of almost 70%. This is explained by the excellent 20 match between the catalyst's peak plasmon wavelength and λ_{max} of the used light source, both at 490 21 nm and is a confirmation of some of our earlier work [3]. Interestingly, this high tunability of dedicated 22 gold-silver-alloy-on-TiO₂ catalysts is thus very useful for obtaining visible light photocatalytic activity 23 under predetermined, fixed visible light wavelengths. Under broad-band illumination (simulated 24 sunlight), however, the resulting photocatalytic efficiency of the Au_{0.3}Ag_{0.7}-P25 photocatalyst is again 25 comparable to that of unmodified P25. One can indeed expect that plasmonic coupling to one single additional visible light wavelength will not add substantially to the intrinsic photocatalytic efficiency
under UV. In contrast, the 'rainbow' photocatalyst is 16% more efficient under this broadband
illumination, which can be attributed to simultaneous multiple wavelength plasmonic coupling over
nearly the entire UV-VIS range.

5 As a proof of concept, we have also performed a 'real-life application test' under ambient 6 outdoor conditions on a Belgian spring day (Figure 8). Due to fluctuations in the incident irradiance, 7 we prefer not to refer to the results in terms of efficiencies, but use the turnover frequencies (TOFs) of all samples. The TOF on P25 was 7.76 x 10¹⁶ cm⁻² h⁻¹, the TOF on the Au_{0.3}Ag_{0.7}-P25 photocatalyst 8 9 was a bit lower, 6.69 x 10^{16} cm⁻² h⁻¹, while the TOF using the 'rainbow' photocatalyst was significantly higher: 9.05 x 10¹⁶ cm⁻² h⁻¹. Remarkably, the order of reactivity and the relative improvement in activity 10 11 for the 'rainbow' photocatalyst (16.6%) is identical to the results obtained under simulated solar light 12 under laboratory conditions. This proof of concept thus encourages the further development of this 13 type of plasmonic catalysts for real-life applications.

14 **3.3** Mechanistic considerations

15 From the current set of experiments we can definitely exclude photolysis, plasmonic heating and direct 16 catalysis on plasmonic particles as the responsible underlying mechanism for the observed 17 photoactivity [23,24]. Three major, mutually non-exclusive mechanistic explanations remain for the 18 observed plasmonic enhancement. Firstly, electrons from an excited plasmonic state can be injected 19 into the TiO_2 conduction band, which initiates the degradation pathway [30–32]. Secondly, the 20 plasmonic particles can be responsible for strong enhancement of the near-field, which in turn results 21 in more efficient electron-hole pair formation in the TiO₂ substrate in the direct vicinity of the particles 22 [33–35]. A third mechanism that can play to some degree is the extension of the useful optical path of 23 incoming light due to resonant scattering on some of the larger (> 50 nm) alloy nanoparticles [36]. The 24 combined effects of UV-driven photo-excitation of TiO2 and the excitation of plasmon modes under visible light present an additional degree of complexity in pinpointing the exact mechanism under solar
 light irradiation and is the subject of ongoing research.

Very recently we have been able to demonstrate by means of an EPR study on Au-modified TiO_2 that electron-related species are present in the TiO_2 conduction band upon illumination with (purely visible) green laser light, whereas this is not the case in pristine TiO_2 under the same conditions [37]. This provides experimental evidence for the important role of direct electron injection in the plasmonmediated reaction mechanism. This is also supported by the recent work of Nishi *et al.* based on action spectra of Au-Ag alloy on TiO_2 materials [38]. They also confirm the high degree of control that can be achieved over the optical response of this type of material by carefully tuning the alloy composition.

10 Conclusion

11 We introduce the concept of a plasmonic 'rainbow' photocatalyst consisting of TiO₂ modified with 12 gold-silver alloy nanoparticles of various sizes and compositions. This plasmonic photocatalyst enables 13 simultaneous multiple wavelength absorption over nearly the entire UV-VIS range of the spectrum 14 with a maximal response at the highest intensity wavelengths of solar light. The 'rainbow' catalyst 15 shows an increased efficiency toward stearic acid degradation under both narrow-band pure visible light as well as simulated and real broadband sunlight under realistic outdoor conditions (ca. 16-17%). 16 17 This is the first demonstration of broadband plasmonic photocatalysis for environmental remediation 18 at the solid-gas interface. With this we hope to encourage the further development of plasmonic 19 photocatalysis for environmental applications.

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1 Figure Captions

Figure 1. Absolute irradiance spectra of the different light sources collected at sample distance (5 cm).
The integrated intensity (300-800 nm) for the UVA LED source (purple curve) is 1.6 mW/cm², for the
VIS-490 nm LED source (cyan curve) it is 4.7 mW/cm² and for simulated solar light (AM1.5, orange
curve) the integrated intensity is ca. 100 mW/cm².

6

Figure 2. Optical properties of gold-silver alloy nanoparticle solutions and 'rainbow' sample. a) Pictures
of the colloidal alloy nanoparticle solutions. The percentage indicated on the bottles corresponds to
the gold fraction of the gold-silver alloy. b) UV-VIS absorption spectra of the alloy samples in a). c) UVVIS absorption spectrum of the 'rainbow' sample (orange curve) and a linear combination of the UVVIS spectra of the composing alloy solutions (black dotted curve).

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Figure 3. Observed trends in particle size and plasmon wavelength for gold-silver alloy nanoparticles.
The main particle size decreases with increasing gold content of the alloy and can be fitted well by a
second order polynomial (blue ●). The plasmon wavelength varies linearly with the gold fraction of
the alloy (red ■).

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Figure 4. HAADF-STEM image and elemental maps of 'rainbow' photocatalyst sample. The HAADF-STEM image clearly reveals the presence of metal nanoparticles of different sizes (indicated by white arrows). From the elemental maps obtained with EDX mapping, the TiO₂ support is apparent and the co-presence of gold and silver inside the same nanoparticles supports the concept of alloy formation. Notice the intensity of silver is not equivalent in every particle, as expected from the presence of alloys with different concentrations.

1 Figure 5. UV-VIS powder spectra of the 'rainbow' photocatalyst (white) and pristine TiO₂ P25 (gray).

2

Figure 6. Stearic acid degradation experiment using different light sources. The different light sources used are a) UVA LED ($\lambda_{max} = 385 \text{ nm}$), b) Visible light LED ($\lambda_{max} = 490 \text{ nm}$) and c) simulated solar light (AM1.5 filter). Tested samples are pristine TiO₂ P25 (red O), Au_{0.3}Ag_{0.7}-P25 (orange O), 'rainbow'-P25 (yellow ∇), blanc wafer (green \triangle), only Au_{0.3}Ag_{0.7} nanoparticles (cyan \Box) and only 'rainbow' nanoparticles (blue \Box). Only the first three samples (those containing TiO₂) show photocatalytic activity and the data points are fitted with a linear regression curve (zero order kinetic behavior).

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Figure 7. Relative photocatalytic efficiency of $Au_{0.3}Ag_{0.7}$ -P25 (light gray) and the 'rainbow' photocatalyst (dark gray) with regard to pristine TiO₂ P25 (white) under different illumination conditions.

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Figure 8. Real-life photocatalytic experiment. a) Comparison of the turnover frequency of stearic acid molecules on P25 (white), Au_{0.3}Ag_{0.7}-P25 (gray) and the 'rainbow' photocatalyst (dark gray), measured outside under ambient conditions on the Belgian spring day June 12th 2015 between 10:34 a.m. and 10:39 a.m. b) Variation of the overall incident irradiance (300-800 nm, blue curve) and its UVcontribution (300-400 nm, red curve) during the measurement.

Figure 1.



Figure 2.



1 Figure 3.



1 Figure 4.



- 1 Figure 5.





Figure 7.



1 Figure 8.

