EFFECT OF NOBLE METALS ON THE PROPERTIES OF NANOCOMPOSITES BASED ON SILICON STRUCTURES AND TITANIUM DIOXIDE, SYNTHESIZED FOR SOLAR COLLECTORS

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Abstract: This article analyzes the developments on the subject and draws conclusions for the study 1722/M-2017. Most metals are highly chemically reactive, especially at nanoscale, without having properties that can be easily used with TiO_2 composites. As such, most of the metals below will be considered metal oxides of precious metals. In addition, the most common oxide TiO_2 will be discussed, as other oxides are probably unstable and thus do not form stable composites.

Keywords: nanocomposites , silicon structures, titanium dioxide

I. INTRODUCTION

A detailed consideration of all precious metals is given in study 1722 / M-2017 at the UZNIT of Technical University-Gabrovo and [1]. Only palladium, platinum, silver and gold are considered here.

II. EXPOSITION

The development of Pd/TiO_2-based palladium composites on visible light radiation was studied by Mohapatra. TiO_2 nanoparticles were synthesized by Ti foil anodization followed by $PdCl_2$ functionalization and subsequent H_2/Ar calcining to crystallize TiO_2 and converting the Pd salt to pure Pd. The synthesized composite with optimized 1.25 wt % Pd showed significant photocatalytic improvement compared to naked TiO_2 nanotubes. A nitrogen-dosed Pd/TiO_2-active to the visible light composite is also prepared. Prepared TiO_2 nanotube matrices through a three-stage anodization of Ti foil, followed by calcination and hydrothermal reduction of Pd-nanoparticles on the crystal TiO_2 nanotubes in the presence of polyvinylpyrrolidone (PVP) and Na I allow for controlling the PVP-concentration and the hydrothermal reaction time. Figures 1a and 1b show a Scanning electron microscope (SEM)-image of a preconditioned nanotube matrix, and Figures1c and 1d show the mass after hydrothermal deposition of Pd. Figure 1 shows a Tunnel electron microscope (TEM)-image of the nanotube with clearly placed Pd-nanoparticles. No such silicon matrix composites are known.

Photocatalytic production of Pt/TiO_2 composites consistently shows increasing growth with the advancement of nanoscale synthesis and controllable/tunable properties of nanomaterials. These composites allow optimi-
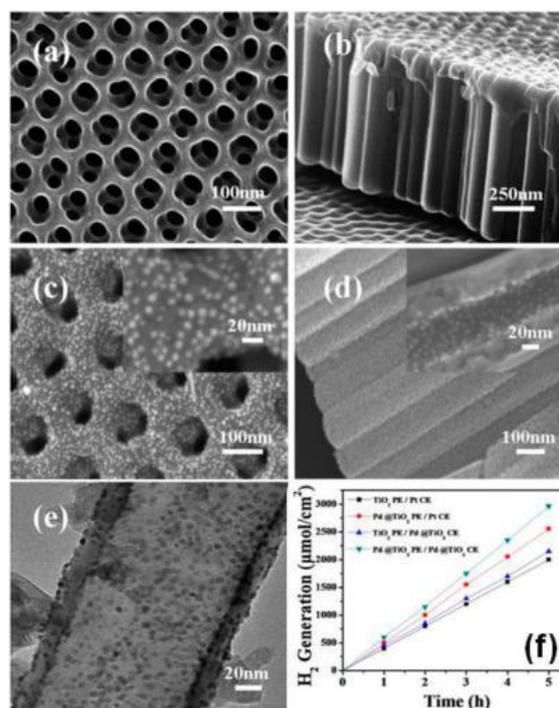

Figure 1. (a) and (b) SEM-images in cross-section of nanotubes TiO_2 (TNTAs) obtained from electrochemical anodization. SEM-images of Pd composites deposited on TNTAs: (c) a top view of small and large magnifications; (d) a cross-sectional view (a large magnification of a broken tube is shown in the insert). (d) TEM-image of TiO_2 nanotubes with deposited Pd composites showing that they are uniformly dispersed on nanotubes. f) A graph of the amount of hydrogen generated by TiO_2 nanotubes and Pd/TNTA nanocomposites such as photon and Pt foil and Pd/TNTA nanocomposites as cathodes. Pd%= =2.15% wt. PE and CE respectively indicate photo anode and cathode electrodes

zation of parameters such as morphology, crystalline phase, crystallinity, porosity and surface area, each of which can alter the photoactivity of the composition. Improving photocatalytic activity with the introduction of Pt is typically attributed to the formation of a Schottky barrier at the metal-TiO_2 interface. This happens because the work function of Pt (~ 5,36-5,63 eV) is greater than that of TiO_2 (~

4,6-4,7 eV), so that electrons are transferred at Pt and holes Localized in TiO_2 media to improve photocatalytic efficiency. In order to improve the Pt/TiO_2 composites, steps have been taken to optimize the interaction between Pt and TiO_2 from Kandiel, effectively effecting the surface area and crystal structure of TiO_2 in the resulting Pt/TiO_2 composite and demonstrating that although the large Area is useful, increasing crystallinity is preferential. Increasing photocatalytic activity is due to the reduction of site defects that act as charge recombination centers when crystallinity increases.

Due to their low price compared to other precious metals, intensive localized surface plasma resonance (LSPR) and easy shape control, silver nanomaterials are used in TiO_2 composites to a considerable extent. Silver is widely used with TiO_2 to produce composites to decompose photocatalytic organic molecules, DSS-composites, photoactive bactericides, photochromic materials and other applications. Although silver can not recombine H + atoms for hydrogen production, on the basis of its slightly larger function, ~ 4.7 and 4.6 eV for Ag and TiO_2, respectively still has the ability to attract photogenerated electrons of TiO_2 and thus improve the separation of the charge. Many reports show improved UV-photocatalytic degradation of organic pollutants from Ag/TiO_2 composites compared to pure TiO_2. Although the precise nature of LSPR on improved photocatalytic activity has not been fully investigated, it is clear that it improves the photocatalytic activity of TiO_2 and the generation of photoelectrochemical currents. In the Awazu study, it can be seen that direct contact between Ag and TiO_2 is not necessary for photocatalytic amplification, which suggests that the reason is the increase of the Ag LSPR electromagnetic field.

In this study, silver nanoparticles are embedded in SiO_2 layers of varying thickness, followed by a TiO_2 layer, which is of particular interest to the topic. It is shown that when the SiO2 layer is thinner, photocatalytic degradation increases even without contact with TiO_2. The system consists of Ag nanoparticles, coated with different TiO_2 thickening particles. As shown in Figure 2b, TiO_2's finest coatings give the greatest

improvement in IPCEs, due to the larger electromagnetic field attributed to silver nanoparticles. This in turn leads to greater cellular efficacy as shown in Figure 2c.
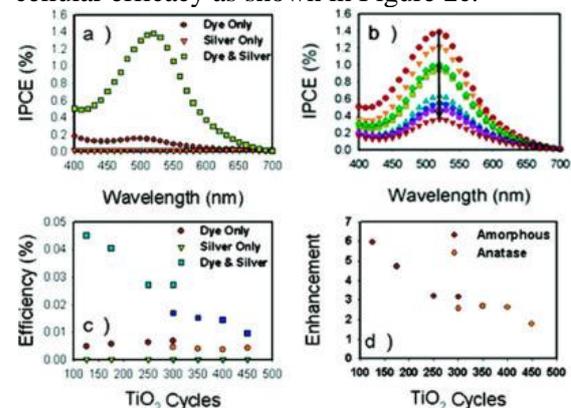

Figure 2. IPCE and general trends in cells. (a) IPCE for cells with 125 cycles of amorphous TiO_2. (b) IPCE for silver-plated cells. The indicator shows an increase in TiO_2 thickness. The first four spectra and the two spectra correspond to amorphous and anode TiO_2. (c) Cell efficiency. Dark blue, orange and green symbols match the anatomy samples. Light blue, red, and yellow symbols correspond to amorphous samples. (d) Calculated plasma increase factor as a function of TiO_2 thickness

In order to better investigate the effects of the metal-TiO_2 interaction in the Ag/TiO_2 composite, core Ag/TiO_2 structures were synthesized. The original core composites were manufactured by Liz-Marzan and others, but the Ag/TiO_2 composite nuclear coatings specifically made for interaction studies were first synthesized and tested by Hirakawa and Kamat. Reversible charge and dilution of the Ag core of photocurrent electrons from the TiO_2 shell is observed, and when the composite is irradiated, the electrons are moved to the Ag core because the holes generated in TiO_2 are extracted from ethanol. Details can be seen in study 1722 / M-2017.

Compared to platinum and silver, gold has advantages over each of them. Like silver, gold has an adjustable LSPR, that can be used to improve photocatalytic activity, but also has a stronger chemical stability similar to platinum. In addition, gold has a high duty function (~ 5.1-5.3 eV). Based on this, the Au/TiO_2 composites are used for many of the same applications as Pt and Ag, with some improvements depending on the case. Typically, Au/TiO_2 composites have a better Ag/TiO_2 photoactivity because the higher gold function compared to silver allows better separation of the TiO_2 charge. In addition to applications for degradation of organic

molecules and hydrogen production, the Au/TiO_2 composites are heavily used for CO oxidation, which is of importance to the environment due to its release from combustion of fuels in internal combustion engines. It is known that Au/TiO_2 composites effectively convert CO to CO_2, even at temperatures below 0° C. Various factors may influence the activity of CO/CO_2 oxidants, in particular the particle size of Ag, but also the TiO_2 crystallinity and the method of composing the composite. The deactivation of the composite, due to Au particle sintering, is particularly important because in practical applications such as catalytic converters the composite would be subjected to high temperatures ($> 750^o$ C). In order to prevent this deactivation, Lee's study uses an Au/TiO_2 catalyst of methyl-orange that can effectively prevent the sintering of Au nanoparticles by placing a physical TiO_2 barrier.

Figure 3. (a) TEM-image of the prepared $Au/TiO2$ structure. (b) TEM-image of the Au/TiO_2 calcite structure. c) TEM-image of the prepared Au/P25 sample. d) TEM-image of the Au /P25 sample after calcification. e) Time dependence of carbon oxide coating on gold and partial pressure of carbon dioxide during oxidation of CO at room temperature of CO with gold/titanium base catalysts. The two left panels correspond to the Au/TiO_2

catalyst and the right panel to the reference Au/TiO_2-P25 sample. First and third panels are obtained by first introducing CO at a pressure of 200Torr into the cell; In the second and fourth panel the sequence is reversible. CO coating of Au in gas phase CO_2 is calculated from the integrated intensities of DRIFT signals in the regions 2090-2145 and 2300-2400 cm^{-1} respectively.

In this study is suggested an Au/TiO_2 composite consisting of a nanoparticle of gold (~ 15nm) in porous TiO_2 and is also available. The composite is made by applying the nanoparticles Au first with a SiO_2 layer and then coating the TiO_2 layer composite. The SiO_2 can then be removed from the composite by dissolution with NaOH as shown in Figure 3a. The composite can then be calcined and crystallized TiO_2 without alteration of the Au nanoparticles, as shown in Figure 3b. This result is compared with the Au/TiO_2-P25 composite calcification, where it is clear that Au nanoparticles are synthesized significantly (Figure 3d). All this and the applicationis the subject of further research.

III.   CONCLUSIONS

1.No precious metal (Pd) composites of silicon matrix and metal oxides-TiO_2 are known.

2.In this study, silver nanoparticles are proposed to be embedded in SiO_2-layers of varying thickness, followed by a TiO_2 layer. It is shown that when the SiO_2 layer is thinner, photocatalytic degradation increases even without contact with TiO_2.

3.An Au/TiO_2 composite, consisting of a nanoparticle of gold (~ 15nm) in porous TiO_2 is synthesized. The composite is made by applying the nanoparticles Au first with a SiO_2 layer and then coating the TiO_2 layer composite. The SiO_2 can then be removed from the composite by dissolution with NaOH. The composite can then be calcined and crystallized TiO_2 without alteration in the Au nanoparticles. All this is the subject of further research on solar collectors.

References

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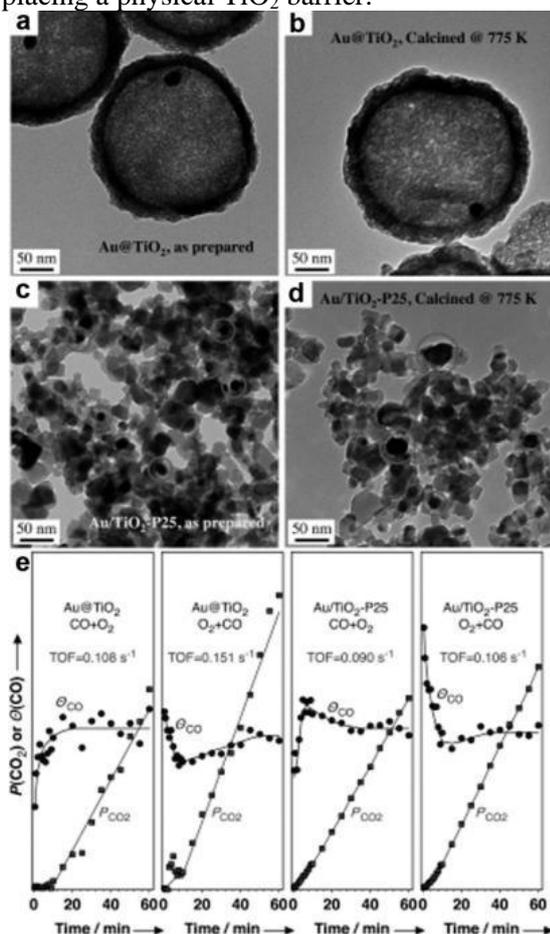Prof. Dr-Ing. Stefan Kartunov, TU Hadji Dimitar Str. 4, Department MU, Mechanical Engineering, Tel.++35966827365, Lab. Micro- and Nanotechnologies