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# Stability of Ag@SiO<sub>2</sub> core–shell particles in conditions of photocatalytic overall water-splitting

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## ABSTRACT

Core-shell nanoparticles containing plasmonic metals (Ag or Au) have been frequently reported to enhance performance of photo-electrochemical (PEC) devices. However, the stability of these particles in water-splitting conditions is usually not addressed. In this study we demonstrate that Ag@SiO<sub>2</sub> core-shell particles are instable in the acidic conditions in which WO<sub>3</sub>-based PEC cells typically operate, Ag in the core being prone to oxidation, even if the SiO<sub>2</sub> shell has a thickness in the order of 10 nm. This is evident from *in-situ* voltammetry studies of several anode composites. Similar to the results of the PEC experiments, the Ag@SiO<sub>2</sub> core-shell particles are instable in slurry-based, Pt/ZnO induced photocatalytic water-splitting. This was evidenced by *in situ* photodeposition of Ag nanoparticles on the Pt-loaded ZnO catalyst, observed in TEM micrographs obtained after reaction. We explain the instability of Ag@SiO<sub>2</sub> by OH-radical induced oxidation of Ag, yielding dissolved Ag<sup>+</sup>. Our results imply that a decrease in shell permeability for OH-radicals is necessary to obtain stable, Ag-based plasmonic entities in photo-electrochemical and photocatalytic water splitting.

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## 1. Introduction

Photo-electro-chemical or photocatalytic solar water splitting are promising technologies to produce hydrogen sustainably, without significant CO<sub>2</sub> emissions associated with *e.g.* methane steam reforming or coal gasification. Since the first demonstration of this concept in 1972 by Honda and Fujishima based on TiO<sub>2</sub> [1], researchers aimed to develop improved semiconductor materials which could be used as photo-electrodes or photocatalysts for such process [2]. Besides doping to induce visible light activity, and deposition of catalytic nanoparticles to improve conversion efficiency, a third approach to enhance performance of semiconductors in photon induced processes is by functionalization of the surface with plasmonic nanoparticles [3–5]. Visible light photons then induce plasmonic resonance, thereby significantly stimulating/enhancing photocatalytic activity of the semiconductor [6]. Generally, metal nanoparticles are positioned in direct contact with the semiconductor to induce such plasmonic effects. A drawback of such configuration is that adverse recombination of electrons and holes at the metal/semiconductor interface might occur, or alterna-

tively metal corrosion/oxidation induced by the electrolyte, eventually extinguishing the plasmonic enhancement.

To resolve these issues, and in particular metal corrosion, utilization of core-shell particles, preventing direct contact of the metal with the electrolyte and semiconductors used in photocatalysis and PEC cell configurations, has been demonstrated promising. Several reviews and excellent papers have appeared recently, addressing the synthesis and use of core-shell particles in heterogeneous catalysis [7–9], including core/yolk-shell nanocatalysts [10], or in energy applications [11,12]. Regarding photon induced processes, Thomann *et al.* convincingly showed plasmonic enhancement of Fe<sub>2</sub>O<sub>3</sub> with Au@SiO<sub>2</sub> core-shell particles in water splitting applications [13], and Abdi *et al.* explored plasmonic enhancement by Ag@SiO<sub>2</sub> core-shell particles in contact with a BiVO<sub>4</sub>-based photoanode [5]. Although Thomann *et al.* imply stability issues might be present, since the integrity of the shell might be affected by deformation as a result of thermal processing, the stability against oxidation of Ag in water splitting conditions, when present in core shell particles, has not been extensively addressed.

Herein, we explore the stability of Ag@SiO<sub>2</sub> core-shell particles in two relevant water splitting applications: (1) in a photo-electrochemical cell in contact with WO<sub>3</sub> as active component for water oxidation, and (2) in a physical mixture with Pt-loaded ZnO catalysts contained in a photocatalytic slurry reactor. We will

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44 demonstrate by electrochemical and electron microscopy analysis  
45 that significant oxidation of the silver core occurs in both config-  
46 urations, despite the presence of the silica shell. The origin of this  
47 phenomenon is discussed.

## 48 2. Experimental

### 49 2.1. Synthesis and characterization of Ag@SiO<sub>2</sub> nanoparticles

50 Ag@SiO<sub>2</sub> core-shell nanoparticles were synthesized using a sol-  
51 gel method. A typical preparation procedure is as follows [14]. A  
52 500 ml beaker was filled with 180 ml of aqueous solution includ-  
53 ing 0.145 g of CTAB under vigorous magnetic stirring. 10 ml of an  
54 aqueous solution of 0.1 M silver nitrate was added to this solu-  
55 tion. 20 ml of 0.1 M ascorbic acid in aqueous solution was subse-  
56 quently drop-wise added in a period of approximately 5 min. Af-  
57 terwards, the mixture was stirred for 10 min, and 0.1 M sodium  
58 hydroxide was added to accelerate the chemical reaction, and to  
59 adjust the pH of the mixed solution to about 6.6. Subsequently,  
60 50 ml of ethanol and 1 ml of TEOS were added to the silver col-  
61 loid suspension, to create the silica shell. The solution was stirred  
62 for three more hours at room temperature. The thus synthesized  
63 Ag@SiO<sub>2</sub> core-shell particles were separated from the solution by  
64 a centrifuge, and dried in an oven at 80 °C in air, yielding a yellow-  
65 ish powder.

### 66 2.2. Preparation of WO<sub>3</sub> films on FTO glass

67 The preparation of the WO<sub>3</sub> photo-anode was performed as fol-  
68 lows. First a WO<sub>3</sub> precursor solution was prepared, by dissolving  
69 1.14 g of dark-blue WCl<sub>6</sub> (Sigma Aldrich) in 20 ml of ethanol in an  
70 inert atmosphere. It took several days to dissolve the WCl<sub>6</sub> salt  
71 accompanied by the disappearance of the original blue color, fi-  
72 nally resulting in a transparent colorless liquid. The possible reac-  
73 tion path for the dissolution of WCl<sub>6</sub> in ethanol is described else-  
74 where [15]. For the preparation of the WO<sub>3</sub> film, the WO<sub>3</sub> pre-  
75 cursor solution was spin-coated on fluorine-doped tin oxide glass  
76 (FTO; a thickness of ~600 nm, 16 Ω/cm<sup>2</sup>) at 600 rpm for 30 s. After  
77 coating, the glass was heated on a hot plate at 100 °C for 1 min,  
78 and cooled. This process was repeated three consecutive times.  
79 Finally the samples were heated in a calcination oven at 500 °C  
80 (10 °C/min) for 2 h in static air. A SEM image of the resulting film  
81 is displayed in the supporting information (Fig. S1), demonstrating  
82 the WO<sub>3</sub> film is porous and has a thickness of ~300 nm.

### 83 2.3. Preparation of Ag@SiO<sub>2</sub> core-shell particles solution and coating

84 Several photo-anode configurations were prepared. For the  
85 preparation of an 'on top' configuration, an ethanol suspension  
86 containing Ag@SiO<sub>2</sub> core-shell particles (2 mg/4 ml) was treated  
87 for 30 min in an ultrasonic bath. Then 100 μl of such prepared  
88 suspension was spin coated on the pre-prepared WO<sub>3</sub> film at  
89 1000 rpm for 40 s. After spin coating, the glass was heated on a hot  
90 plate to 100 °C for 1 min. This process was repeated consecutively  
91 to create a homogeneous layer of Ag@SiO<sub>2</sub> core-shell particles.  
92 For the preparation of an 'enclosed' configuration, a distilled wa-  
93 ter suspension containing Ag@SiO<sub>2</sub> core-shell particles (2 mg/4 ml)  
94 was treated for 30 min in an ultrasonic bath. Then 100 μl of the  
95 prepared suspension was spin coated on FTO glass at 2000 rpm  
96 for 40 s. After coating, the glass was heated on a hot plate at  
97 100 °C for 1 min. This process was repeated consecutively to cre-  
98 ate a homogeneous layer of Ag@SiO<sub>2</sub> core-shell particles. Subse-  
99 quently WO<sub>3</sub> was deposited according to the previously described  
100 procedure (Section 2.2).

### 2.4. Characterization of the PEC cell in water splitting

101

The photoelectrochemical anodic properties of the WO<sub>3</sub>/  
Ag@SiO<sub>2</sub> core-shell particle composites were determined in an  
aqueous electrolyte solution containing 0.1 M of sodium sulfate (pH  
~3.5). The potential of the working electrode was controlled by  
a potentiostat (VERSASTAT 4, Princeton applied research). In the  
three-electrode measurements, a Pt wire and an Ag/AgCl electrode  
(3 M NaCl, BASi) were used as the counter and reference electrode,  
respectively. The photoactive area was defined by an o-ring posi-  
tioned in front of the WO<sub>3</sub> anode, being 2.54 cm<sup>2</sup> [16]. Photocur-  
rents were measured under illumination of an AM 1.5 solar simu-  
lator (100 mW cm<sup>-2</sup>), with a 300 Xe lamp and air mass 1.5 global  
filter. The intensity of the simulated sunlight was calibrated using  
a standard reference Si solar cell.

### 2.5. Photo-deposition of Pt nanoparticles on ZnO

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1 g of ZnO (Sigma Aldrich) suspended in Milli-Q water (40 ml)  
was mixed with 7 ml of 0.0019 M H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O solution in a  
quartz glass beaker for 30 min in dark conditions. The beaker was  
capped by a quartz glass plate to prevent evaporation, and covered  
by aluminum foil. 3 ml of methanol was added to the thus pre-  
pared solution as sacrificial agent, followed directly by illumination  
using UV light (18 W TL-D Blacklight Blue, Philips) for 1h. The to-  
tal light intensity was 3.21 mW cm<sup>-2</sup> with the wavelength ranging  
from 360 to 380 nm. The thus synthesized Pt-loaded ZnO was cen-  
trifuged and washed 3 times by Milli-Q water and then dried in an  
oven at 80 °C under atmospheric conditions.

### 2.6. Characterization of photocatalyst activity by gas chromatography

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H<sub>2</sub> evolution was measured for the Pt-loaded ZnO photocat-  
alyst in a continuously stirred tank reactor (CSTR) connected to  
a gas chromatograph (CompactGC Interscience), equipped with a  
pulsed discharge detector. 25 mg of photocatalyst was dispersed  
in 25 ml of 0.01 M K<sub>2</sub>SO<sub>4</sub> (pH ~7.7) within an optical glass cu-  
vette of 50 ml, used as CSTR. After removing air from the reac-  
tor by continuous purging with purified He, the suspension was  
illuminated by a solar simulator at 100 mW cm<sup>-2</sup> (Abet Tech-  
nologies, Inc., 150 W ozone free arc lamp). The amount of H<sub>2</sub>  
evolution was continuously measured using Helium as purge gas  
(10 ml/min). To determine the effect of Ag@SiO<sub>2</sub> core-shell par-  
ticle on the water splitting efficiency, Ag@SiO<sub>2</sub> core-shell particles  
were added after 4 h of illumination of the Pt-loaded ZnO sample  
in suspension. Before introduction of the Ag@SiO<sub>2</sub> core-shell par-  
ticles, the reactor was purged to remove H<sub>2</sub> from the reactor in dark  
conditions.

### 2.7. Analysis of photo-electrode

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The various photo-anodes and photocatalyst samples were an-  
alyzed using field emission scanning electron microscope (FE-  
SEM, Zeiss LEO 1550), Transmission electron microscopy (HR-  
TEM, FEI Instruments), X-ray photoelectron spectroscopy (XPS,  
Quantera SXM from Physical Electronics), X-ray diffraction (XRD,  
Bruker D2 phaser), and inductively coupled plasma atomic emis-  
sion spectroscopy (ICP-AES, Varian Liberty II, Sequential ICP-AES).  
UV/vis spectroscopy was performed in transmission mode, using a  
Thermo Scientific Evolution 600 spectrometer and Millipore water  
as reference. Pt and Ag particle sizes, oxidation states, crystallinity  
of the semiconductors and Pt loading, were thus obtained, respec-  
tively.

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