

## Free Reducing Agent, One Pot, and Two Steps Synthesis of Ag@SiO<sub>2</sub> Core-shells using Microwave Irradiation

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In this work a new method for the fabrication of Ag@SiO<sub>2</sub> nanoparticles have been proposed that is completely different from Stober method. Ag nanoparticles were synthesized using microwave irradiation. polyvinylpyrrolidone was used as stabilizer and capping agent, 3-Aminopropyltriethoxysilane as functionalizer of silver particles in fully ethanol solution. The Ag nanoparticles were used subsequently without any subtraction and treatment in the preparation of Ag@SiO<sub>2</sub> core-shell nanoparticles. UV-Vis spectroscopy shows a characteristic plasmon peak at 400 nm and 430 nm for Ag nanoparticles and Ag@SiO<sub>2</sub> core-shells. Transmission electron microscope images show that Ag nanoparticles have the average size of 10 nm. It is also depicted that SiO<sub>2</sub> shell structure was formed uniformly with the average size of 10 nm. The application of 3-Aminopropyltriethoxysilane in the preparation of core-shells yields single Ag core structure.

**Keywords:** Ag@SiO<sub>2</sub>, Microwave, APTS, Polyvinylpyrrolidone, Plasmon.

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81.05.Dz

### 1. INTRODUCTION

The engineering of materials in nanometer scale has become an emerging interdisciplinary field based on physics, chemistry, biology, and materials science [1-5]. Ag nanoparticles have attracted great attention owing to their visible-light plasmon resonance for many years [6-15]. They have found versatile applications in different areas of science and technology such as biology [16, 17], sensor design [18], optics [19], and energy conversion [20-23]. There are many reports on the synthesis of Ag nanostructures with different methods; but there are few about microwave irradiation method [24-26]. There are many reports concerning the synthesis of Ag@SiO<sub>2</sub> core-shell material [18, 20, 27, 28]; but, their method of preparation involves many steps, long preparation time, and complex chemical routes. Synthesis of Ag@SiO<sub>2</sub> nanoparticles using microwave irradiation has been reported elsewhere [28, 29]. Recently we have reported a direct method for the preparation of silver-silica core-shells using oleylamine [30]. Despite its success and the ease of preparation, the size control of Ag nanoparticles were difficult and the average size of nanoparticles were found to be more than 50 nm. Zhipeng et al has recently reported a free ammonia preparation of Ag@SiO<sub>2</sub> core-shells [31], But they have employed NaOH as reducing agent. Thus in a further attempt in this work, a non-aqueous and completely free reducing agent, direct, fast and facile method is presented for the synthesis of fine Ag nanoparticles and Ag@SiO<sub>2</sub> core-shells in ethanol solution and with the aid of polyvinylpyrrolidone (PVP) and 3-Aminopropyltriethoxysilane (APTES) as capping and functionalizer agents, respectively.

### 2. EXPERIMENTAL METHOD

#### 2.1 Synthesis of Ag Nanoparticles

The microwave synthesis of Ag nanoparticles was performed using Shikoku Keisoku SMW 064, with a 2.45 GHz working frequency, attached with a refluxing system. This system had maximum power of 1000W and a built-in magnetic stirring system. The temperature was controlled using feedback system with a thermocouple. Ag(NO<sub>3</sub>) (Merck) was used as a starting material. polyvinylpyrrolidone (PVP-40) (Sigma-Aldrich) was applied as a stabilizer and capping agent and also to reduce Ag ions and ethanol (96 %) was used as solvent. To synthesis Ag nanoparticles, 0.05gr Ag(NO<sub>3</sub>) was dissolved in 40ml of ethanol and stirred for 5 min. Then, 1gr PVP was added to the initial solution and stirred for another 10 min. The prepared transparent solution was exposed to microwave irradiation at 360 W for one minute.

#### 2.2 Preparation of Ag@SiO<sub>2</sub> Core-shells

The prepared PVP-capped Ag nanoparticles in the ethanol were directly used as starting solution in the preparation of core-shell structure. In order to investigate the effect of APTS in functionalization of Ag nanoparticles, two different solutions - with and without injection of 100  $\mu$ liter APTS into the starting solution - were prepared and both stirred for 1 hr. Thereafter a subsequent aliquot (1.2 mL, 5 mmol) of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TEOS) was injected directly to both solutions and stirred for 5 minutes. Then, the solutions were transferred to a refluxing flask and placed in the microwave oven. They were irradiated at the power of 360 W for 10 minutes until an orange solution was obtained in

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both cases. The irradiated solutions were left to be cooled naturally. Thereafter a mixture of acetone, and toluene (1:1 in volume ratio) was added to the irradiated solutions to obtain an orange precipitation. Then, the core-shell nanoparticles were centrifuged and the obtained powders were washed with ethanol, and re-dispersed again in ethanol for further analysis.

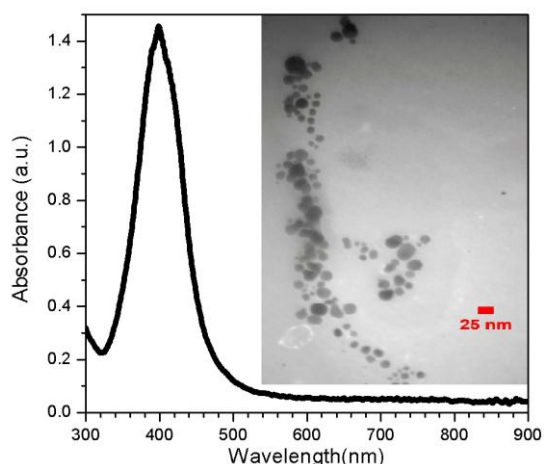
### 2.3 Characterizing Ag and Ag@SiO<sub>2</sub> Nanoparticles

Characteristic plasmon resonance of Ag and Ag@SiO<sub>2</sub> nanoparticle was confirmed by UV-Vis spectroscopy using AvaSpec-ULS3648TEC in the wavelength range of 200-1100 nm. Fourier transformed infra-red (FTIR) data were collected using an AVATAR-370-FTIR THERMONICOLET spectrometer using two separate procedures. The sample was unpacked into a tablet shape and put onto a polished silicon wafer before analysis. To obtain transmission electron microscope (TEM) images, a LEO912 AB electron microscope operating at the bias voltage of 200 kV was employed.

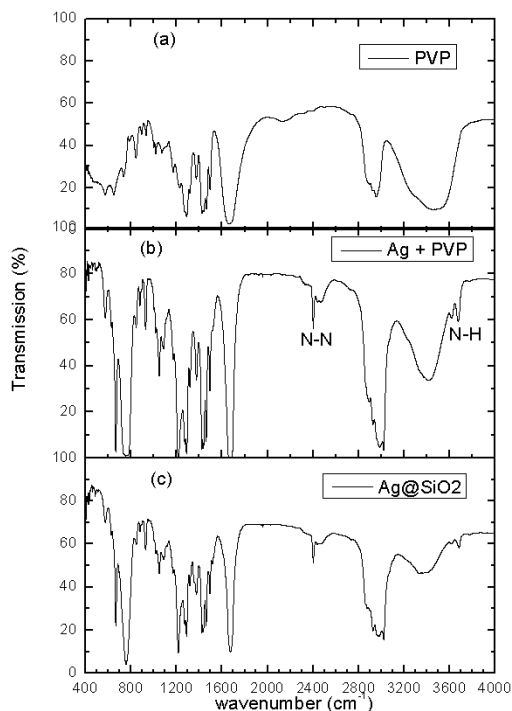
## 3. RESULTS AND DISCUSSION

### 3.1 TEM and FTIR Characterization of Ag Nanoparticles

The Ag nanoparticles in ethanol, with the preparation parameters of 360 W and 10 min show a sharp and narrow absorbance characteristic peak at 400 nm (Fig. 1). It demonstrates that the particles are very small and have a narrow size distribution. TEM image (Fig.1-inset) shows the formation of Ag nanoparticles with average size of 15 nm. FTIR analysis (Fig. 2) demonstrates various types of bonds on the surface of Ag nanoparticles. Several peaks at 673, 734, 846, 1024, 1287, 1459, 1665, 2959, and 3496 cm<sup>-1</sup> are attributed to PVP molecular structure, indicating that Ag nanoparticles were successfully capped with PVP. The appearance of peaks at 2400 cm<sup>-1</sup> and 3650 cm<sup>-1</sup> are due to three bonds N-N molecules and N-H bonds, respectively. Moreover peak at 1104 cm<sup>-1</sup> can be assigned to Si-O-Si bond and peak at 945 cm<sup>-1</sup> can be attributed to Si-OH [32].



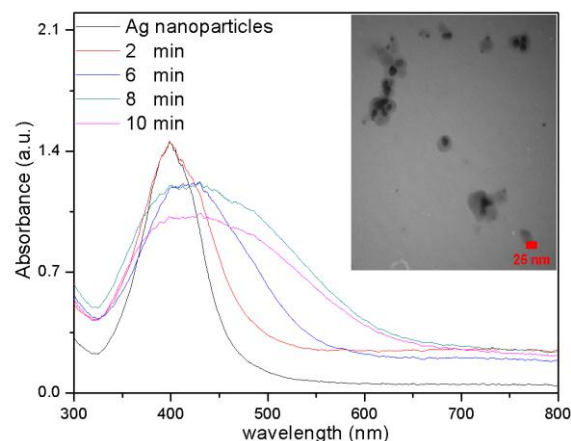
**Fig. 1** – Absorbance spectra and correspondence TEM image of Ag nanoparticles synthesized with PVP



**Fig. 2** – FTIR spectra of (a) pure PVP, (b) PVP-capped Ag nanoparticles and (c) Ag-PVP-SiO<sub>2</sub> core-shells

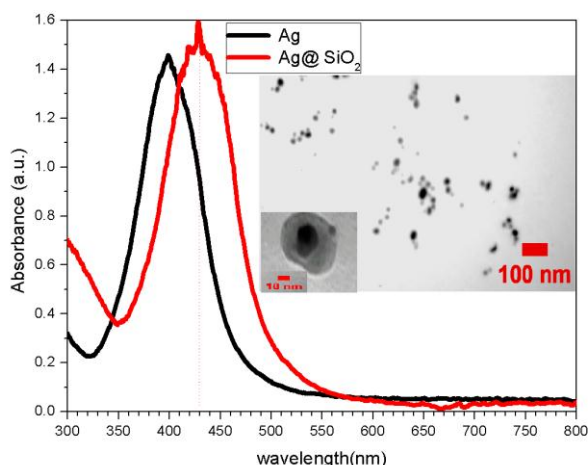
### 3.2 Characterization of Ag@SiO<sub>2</sub> Nanoparticles

Fig. 3 shows the effect of irradiation time on the absorbance of Ag@SiO<sub>2</sub> nanoparticles in the absence of APTES. It shows that the plasmon peak shifts non-uniformly to higher wavelengths such that there is a shoulder on the right side of the spectrum and it is broad. It could be due to agglomeration of Ag nanoparticles [30]. The particles coated with PVP-40 have an inhomogeneous coating thickness and some particles with multiple silver cores are observed. If a polymer is used that is very large compared to Ag radius such as PVP-40, Ag particles appear to be only partially coated with silica [33]. TEM image (Fig. 3-inset) depicts that



**Fig. 3** – Absorbance spectra of Ag-capped PVP@SiO<sub>2</sub> with various microwave irradiation times in the absence of APTES. Inset: TEM image of core-shells formed after 10 minutes of irradiation

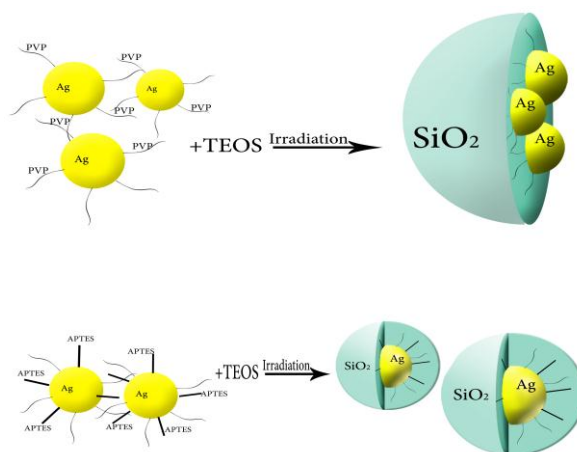
the nanoparticles contain multi-core structure and the shell has not uniformly grown as well. The sample functionalized with APTES shows completely different absorbance spectra (Fig. 4) It shows that the plasmon resonance of Ag nanoparticles shifts from 400 nm to 428 nm due to the microwave irradiation for 10 minutes. TEM image (Fig. 4-inset) shows clearly the formation of SiO<sub>2</sub> shell around Ag nanoparticles. This could be explained by following discussion: In the absence of ammonia PVP is not capable of reducing Si-O-H bonds on the surface of Ag particles uniformly [33], and it has been shown that the electrostatic charges distributed on the surface of Ag particles causes that PVP-40 binds to the surface non-uniformly and results in the formation of non uniformly PVP-coated Ag particles (Fig. 5). APTES functionalizes the Ag surfaces from the NH<sub>2</sub> side as it has been also reported previously for Au seeding growth [32]. APTES links to the Ag surface form NH<sub>2</sub> group and has Si-OH free link to connect with TEOS from the other side (Fig. 5). In this mechanism ethanol is reducing agent Thus there is no need to use H<sub>2</sub>O and ammonia as reduction agent anymore.



**Fig. 4** – Absorbance spectra of Ag@SiO<sub>2</sub> with various microwave irradiation times using APTES. Inset: TEM image of core-shells formed after 10 minutes of irradiation

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**Fig. 5** – Schematic presentation of Ag@SiO<sub>2</sub> core-shell formation with/without functionalizing Ag nanoparticles with APTES

## 4. CONCLUSIONS

PVP-capped Ag nanoparticles were successfully synthesized using microwave irradiation in fully ethanol solution. Ag nanoparticles were prepared firstly with the average size of 10-15 nm with the plasmon peak at 400 nm. Ag@SiO<sub>2</sub> core-shell material with a plasmon peak at 430 nm was directly prepared with continuous microwave irradiation for 10 min. The application of APTES as functionalizer of Ag particles for the formation of silica shell in the absence of ammonia and water demonstrates the formation of single core Ag@SiO<sub>2</sub> core-shells.

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