TiO_2 nanotubes decorated with Ag spheres for electrochemical sensing applications

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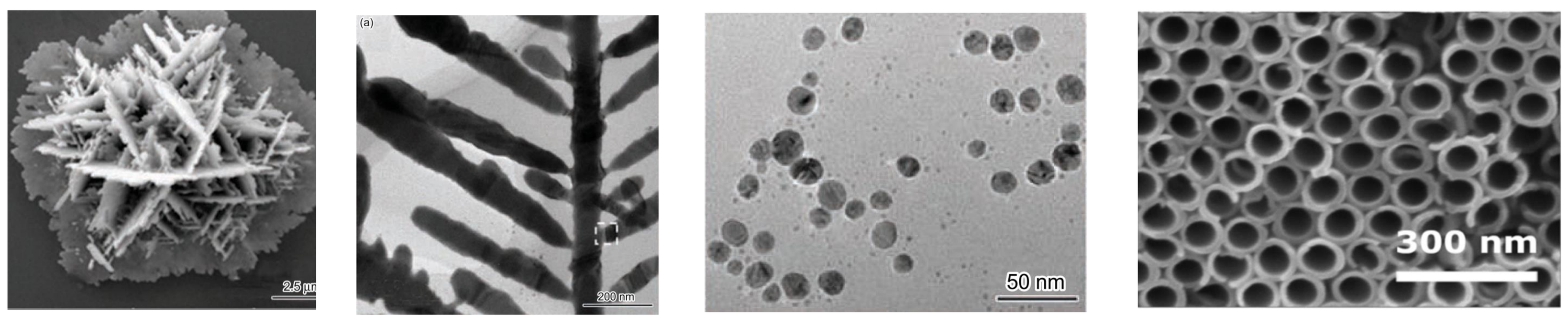
ABSTRACT

The detection of organic and inorganic compounds using electrochemical sensors has garnered attention due to their low-cost fabrication and excellent sensitivity. To enhance the sensitivity of the sensor using metal oxides as active materials, defect states such as oxygen vacancies have been studied. These defects operate as donor levels near the conduction band of the metal oxide. In this study, we present the synthesis of TiO_2 nanotubes decorated with Ag spheres, along with an investigation into their chemical, structural, and optical properties for electrochemical sensing applications. TiO_2 nanotubes were synthesized through a three-step anodization process, while Ag spheres were deposited using electrochemical deposition. The electrolyte solution for the growth of TiO_2 nanotubes consisted of ammonium fluoride and ethylene glycol, while silver nitrate and citric acid were employed as the electrolyte solution for Ag sphere deposition. FE-SEM analysis revealed the successful deposition of Ag spheres with a spherical morphology over TiO_2 nanotubes, with the morphology being significantly influenced by the concentration of organic acid in the electrolyte solution. Stoichiometry analysis was performed on both the TiO_2 nanotube film and on the film decorated with Ag spheres. Additionally, the band gap energy was calculated from the diffuse reflectance spectroscopy (DRS) spectrum. According to photoluminescence analysis, a larger area associated with oxygen vacancies in TiO_2 nanotubes decorated with Ag spheres was identified. The presence of localized energy levels w TiO_2 thin the band gap resulting from oxygen vacancies and Ag spheres led to a reduction in the band gap energy of the semiconductor. This phenomenon is particularly relevant for creating more active sites suitable for the adsorption of compounds in electrochemical sensing applications.

Topic: Ag spheres, TiO_2 nanotubes, electrodeposition, electrochemical sensing.

INTRODUCTION

The Ag nanostructures have gained the scientific community's attention due to their higher thermal conductivity, catalytic behavior, plasmon effect, and high conductivity and their applications on SERS substrates, catalysis, solar cells, and sensors. The main silver morphologies fabricated are nanoparticles, nanosheets, dendrites, nanocubes, and nanowires, which are fabricated by a variety of methods, including hydrothermal method, electrodeposition, chemical reduction, and microwave heating [1, 2]. On the other hand, due to its higher band gap energy and enhanced photocatalytic activity. TiO_2 nanotubes with numerous oxygen vacancies and a higher surface area have been extensively studied for various applications, including pollutant degradation, gas sensing, electrochemical sensing, chemical sensing, and biosensing [3].

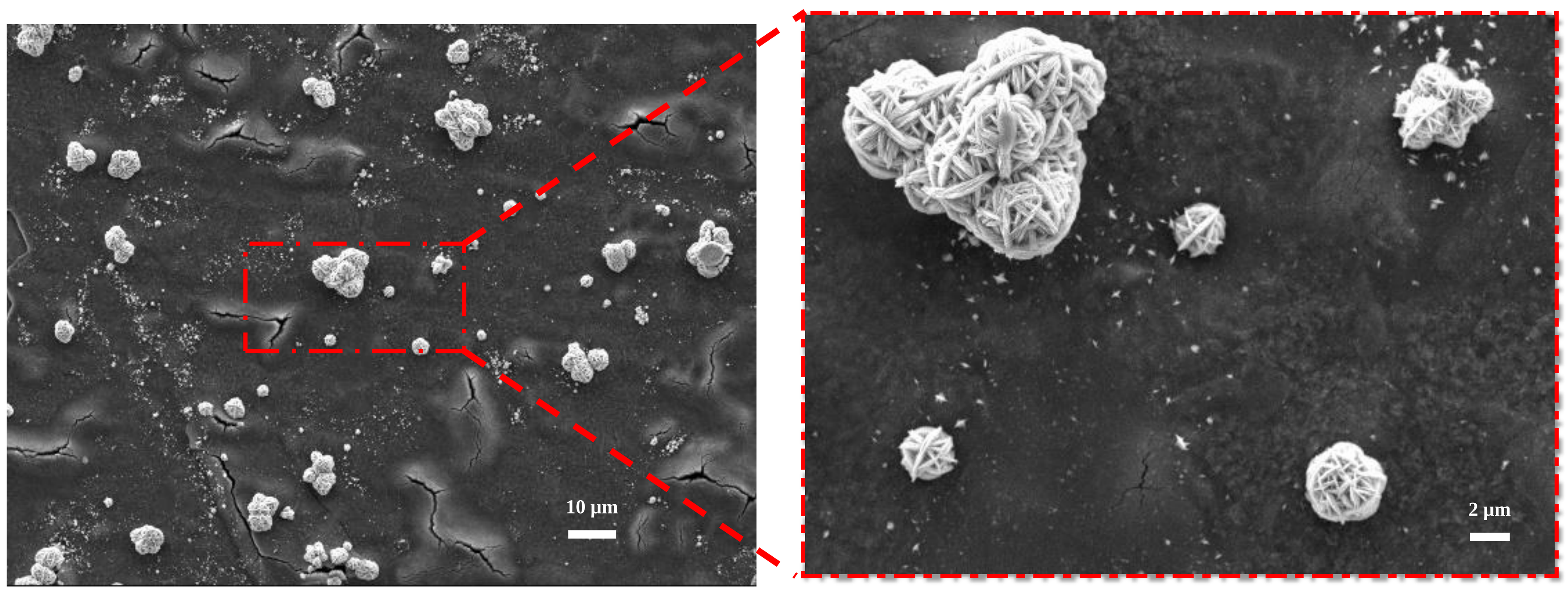


EXPERIMENTAL PROCEDURE

TiO_2 nanotubes were prepared with electrolyte solution: 0.255 wt% NH_4F with 1 wt% of deionized water in ethylene glycol. A voltage of 30 V and Inter-Electrode Spacing of 1 cm were used for the anodization process. TiO_2 nanotubes were grown through a three-step anodization process of 1, 4 and 20 h. A Two-step detachment process was used after the first anodization step, in order to obtain a template Ti-nb.
Ag spheres were grown by electrodeposition using TiO_2 nanotubes as an support. Ag spheres were prepared with a solution composed of $AgNO_3$ and a reducing agent.
The surface morphology was observed by SEM (JEOL) and the DRS spectra of samples was obtained by a Cary 5000 UV-Vis spectrophotometer (Varian Agilent) whereas the Photoluminescence (PL) spectra of materials were recorded using a NanoLog FR3 spectrophotometer (Horiba Jobin Yvon).

RESULTS

Fig. 1. SEM images of (a) TiO_2 nanotubes decorated with (b) silver spheres



RESULTS

Fig. 2. PL spectra of TiO_2 nanotubes (TiO_2 -NT) and Ag spheres.

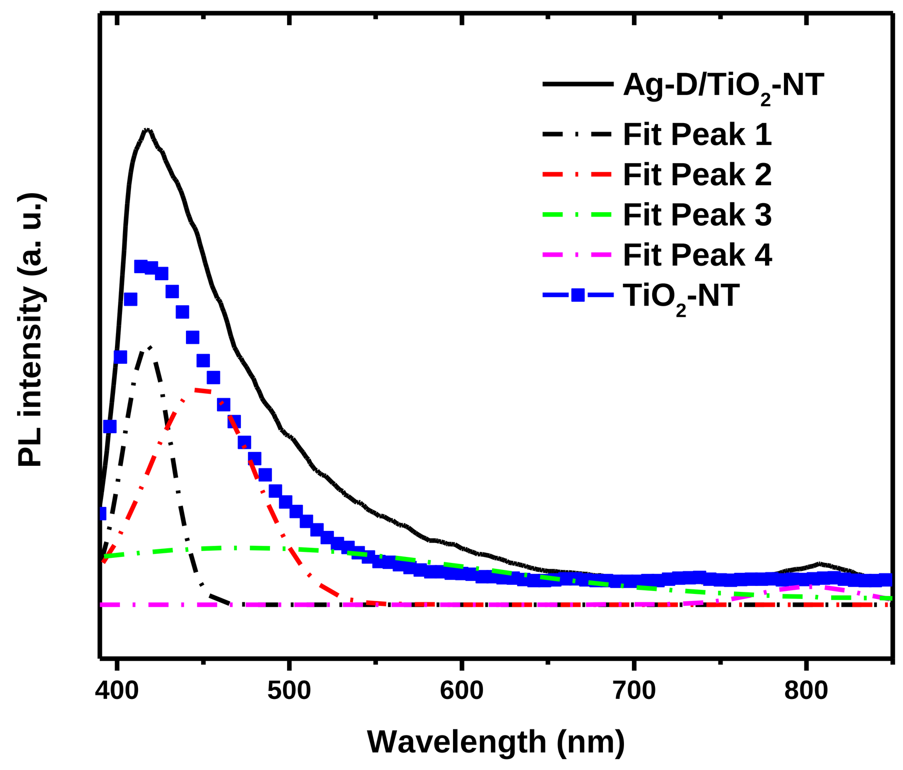
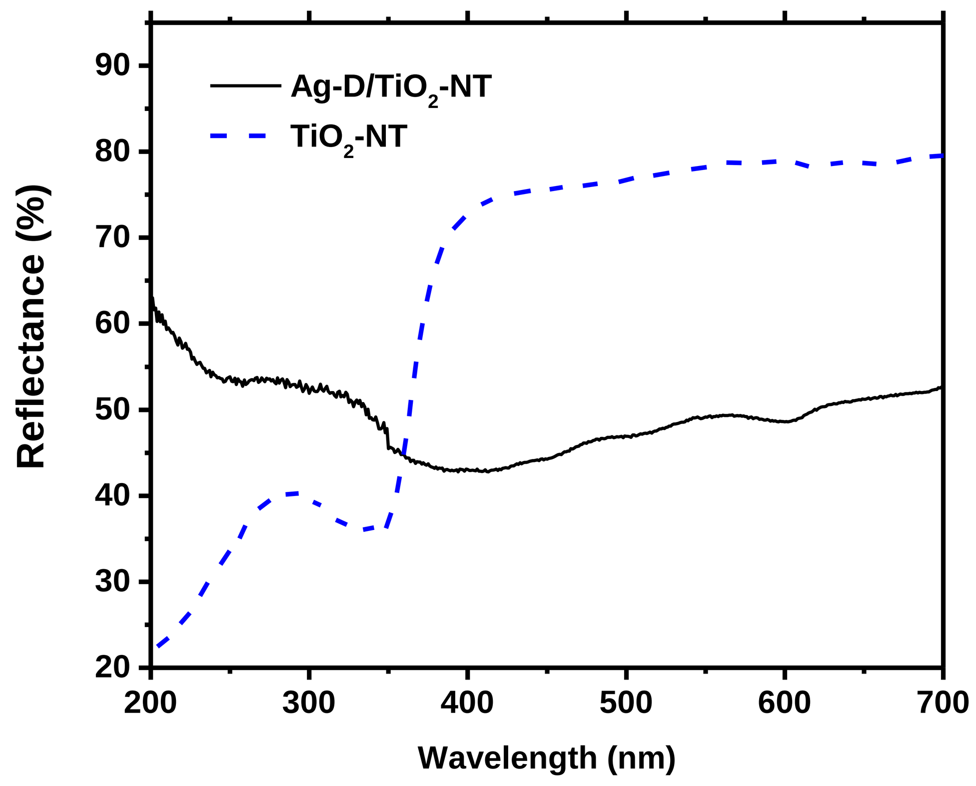
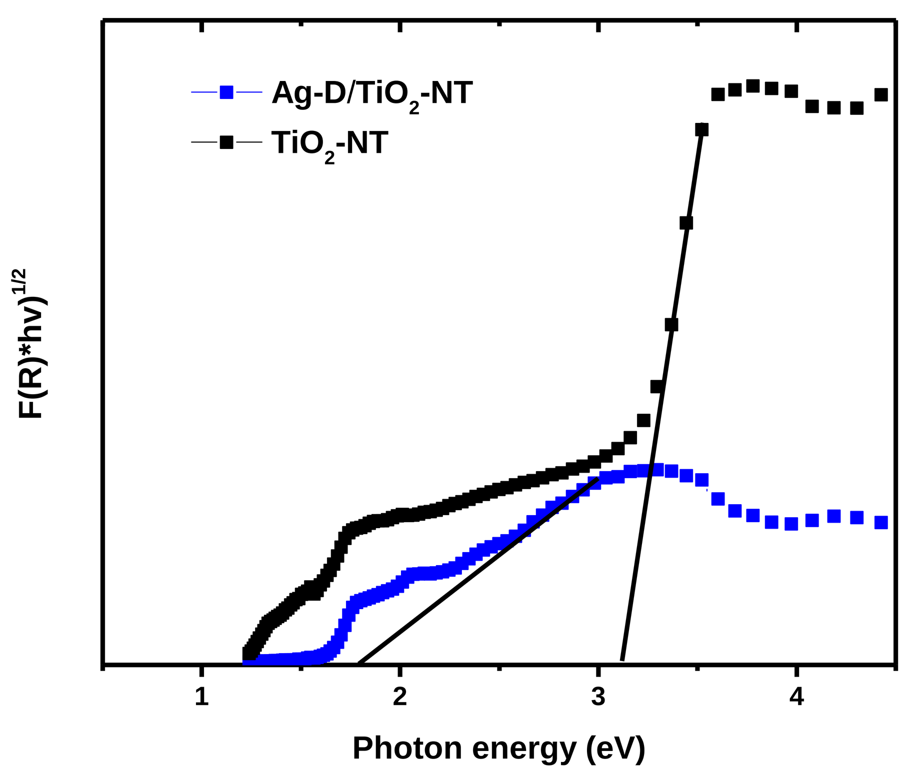


Fig. 3. (a) DRS spectra of TiO_2–NT decorated with Ag spheres and (b) their band gap energy



(a)



(b)

CONCLUSIONS

In this work, silver spheres were deposited homogeneously on TiO_2 nanotubes by electrodeposition using a two-electrodes configuration. The amount of $AgNO_3$ and reducing agent affected the morphology of the deposited silver, with a higher amount of reducing agent, a spherical morphology of silver is observed. A considerable amount of oxygen vacancies was detected for Ag-D/TiO_2 -NT compared with nanotubes film. Therefore, due to the morphology of deposited silver and the number of oxygen vacancies in the semiconductor, the active sites generated by silver spheres could increase sensor response since silver spheres function as donor levels near the conduction band.

References

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