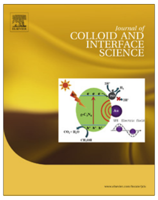
Journal of Colloid and Interface Science 477 (2016) 209–219

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis



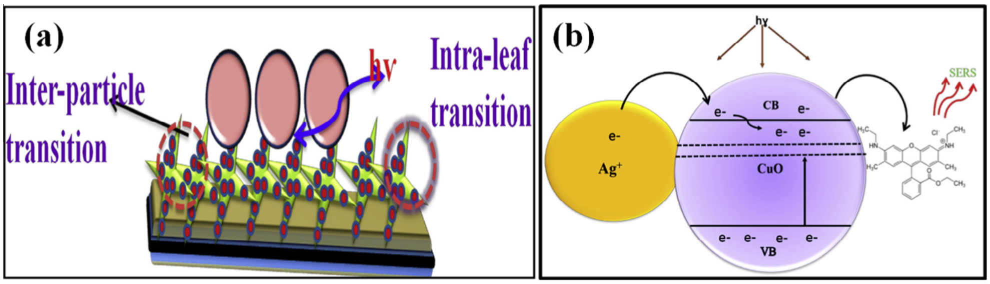
Regular Article

Analysis on superhydrophobic silver decorated copper Oxide nanostructured thin films for SERS studies

Naidu Dhanpal Jayram [a,b], D. Aishwarya [a], S. Sonia [a,c], D. Mangalaraj [a,*], P. Suresh Kumar [d], G. Mohan Rao [e]

[a] Department of Nanoscience and Technology, Bharathier University, Coimbatore 641 046, India
[b] Department of Science and Humanities, KIT-Kalaignar Karunanidhi Institute of Technology, Kannampalayam, Coimbatore, Tamil Nadu 641402, India
[c] Department of Physics, Holy Cross College (Autonomous), Nagercoil 629004, India
[d] Environmental & Water Technology, Centre of Innovation, Ngee Ann Polytechnic, Singapore 599489, Singapore
[e] Plama Processing Lab, Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore 560012, India

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 April 2016
Revised 22 May 2016
Accepted 24 May 2016
Available online 25 May 2016

Keywords:
Ag@CuO
Nanoflowers
SILAR
Superhydrophobic
Rhodamine 6G

ABSTRACT

The present work demonstrates the superhydrophobic and Surface Enhanced Raman Spectroscopy (SERS) active substrate performance of silver coated copper oxide (Ag@CuO) nanostructured thin films prepared by the SILAR process. Super hydrophobic substrates that combine super hydrophobic condensation effect and high enhancement ability of Ag@CuO nanoflowers are investigated for SERS studies. The possible growth mechanism for the formation of nanoflower arrays from nanospindles has been discussed. Morphology and crystallinity of the Ag@CuO thin films are confirmed using FESEM and XRD. The results obtained in the present study indicate that the as-deposited hydrophobic nanospindles structure converts to super hydrophobic nanoflower arrays on annealing at 200 °C. The Ag@CuO super hydrophobic nanoflowers thin film based SERS substrates show highly enhanced Raman spectra with an EF value of 2.0×10^7 for (Rhodamine 6G) R6G, allowing a detection limit from a 10^{-10} mol L^{-1} solution. The present study may provide a new perception in fabricating efficient super hydrophobic substrates for SERS, suggesting that the fabricated substrates are promising candidates for trace analysis of R6G dye and are expected to be widely used as highly sensitive SERS active substrates for various toxic dyes in the future.

1. Introduction

Superhydrophobic surfaces are fascinating in view of their widespread and potential applications in various industrial fields and in self-cleaning processes such as in drug delivery, anticorrosion, and lab-on-chip systems. Their performance can be controlled by well-mannered nanostructures and chemical composition of solid surfaces [1]. In addition to the above applications they have also been used for Surface Enhanced Raman studies (SERS) [2,3]. One of the most dynamic research fields in SERS is related to the search for new substrates with improved enhancement efficiency,

---

* Corresponding author.
E-mail addresses: dhanpal.dj@gmail.com, dmraj800@yahoo.com (D. Mangalaraj).

http://dx.doi.org/10.1016/j.jcis.2016.05.051
0021-9797/

reproducibility and stability [4]. During the past few decades, there has been a significant development of SERS active substrates. Noble metals and transition metals, such as Ag, Au, Cu, Pd, Co, and Ni, have been widely employed to obtain a higher value of the enhancement [5]. Metal oxides have also been investigated as SERS substrates as they are used in many applications. However, it is found that the direct SERS activity of metal oxide semiconductors is much lower than that of noble metals. Hence it is essential to further improve the SERS activity of these semiconductors for practical applications. Semiconductor/noble metal nanocomposites exhibit a strong Raman enhancement associated with tuning of the Localized Surface Plasmon Resonance (LSPR) of the metallic nanoparticles, inducing a charge transfer (CT) effect at the semiconductor/metal interface [6]. Various metal oxides, namely TiO_2, CuO and SiO_2 were modified by coating with Ag, resulting in improved SERS effect [7–9]. Thus there is a great opportunity in the near future for the development and engineering of metal oxide nanostructure-based SERS substrates [10,11].

Metal oxides like ZnO, TiO_2, SnO_2 and WO_3, which are n-type semiconductors, have been generally widely used in the form of nanostructured thin films. However, p-type semiconductors exhibit wider applications when compared to the n-type semiconductors. Copper oxide (CuO), an important p-type semiconductor with a narrow band gap of 1.21 eV, has attracted great interest recently due to its wide applications in sensors, magnetic storage media, solar-energy transformers, electronics devices and in catalysis [12–14]. CuO nanocrystals especially, are frequently employed as photochemically active and photoconductive compounds. Compared to Cu_2O, CuO thin films show higher stability and reproducibility which is a major criterion for device fabrication. A report by Wang and his co-workers shows Enhanced Raman scattering from 4-Mpy molecules adsorbed on CuO nanocrystals [15]. Till date, there are only a few reports available on Ag@CuO nanocomposites for surface enhanced Raman scattering (SERS). Mao et al. [16] demonstrated that the metal-semiconductor (Ag-CuO) contact can alter the charge distribution through p-aminothiophenol (PATP) molecules. When CuO was junctioned with Ag nanoparticles, charge transfer occurred from the CuO to the Ag nanoparticles, inducing a larger electromagnetic field [17]. Hence, Ag nanoparticles could excite a more stable and intense localized surface plasmonic resonance under laser irradiation. A similar result has been reported by Hsieh et al. [17] for the improvement of the SERS activity of solution-phase Ag@CuO nanocomposites as a function of Ag content, using 4 aminothiophenol (4-ATP) as the probe molecule. The enhancement on Ag@CuO nanocomposites may be attributed to the charge transfer transition between the semiconductor and metallic nanoparticles. Even though these reports have shown good response towards the Ag@CuO and Cu nanoparticle-coated CuO nanocomposites [18], there are a few problems which have not been discussed till date. One of the basic and natural problems with Copper films is its oxidizing state, which affects the stability of the CuO films. Similarly the interdependence of SERS and nanostructures has not been discussed for copper oxide films. The present work shows the role of superhydrophobic surfaces in SERS studies and deals with the preparation of stable copper oxide thin films for obtaining stronger SERS using Ag@CuO nanoflowers array through a low cost method. It also discusses the role of interdependence of Raman spectra and SEM morphology.

2. Experimental section

2.1. Synthesis of cupric oxide thin films using SILAR method

Superhydrophobic surfaces of Copper Oxide (CuO) nanostructures have been designed by SILAR process as reported for Zinc Oxide (ZnO) [19] and CuO in our previous work [20]. The procedure for this method is schematically represented in Fig. 1. The detailed experimental procedure and reaction mechanism have been discussed in the previous work [20]. The successive cycles and the increase in the deposition times led to an increase in thickness of the deposited film. The reaction cycle was repeated 20, 40 and 60 times. Silver was deposited for SERS studies using thermal evaporation from a helical coil onto the CuO nanostructure for a deposition time of 2 min. The film was annealed at 200 °C and silver were again deposited; the desired parameter was chosen from the previous publication and resulted in the formation of silver decorated nanoflower like structure [3,20]. The thickness of the deposited silver film was recorded using a quartz crystal thickness monitor.

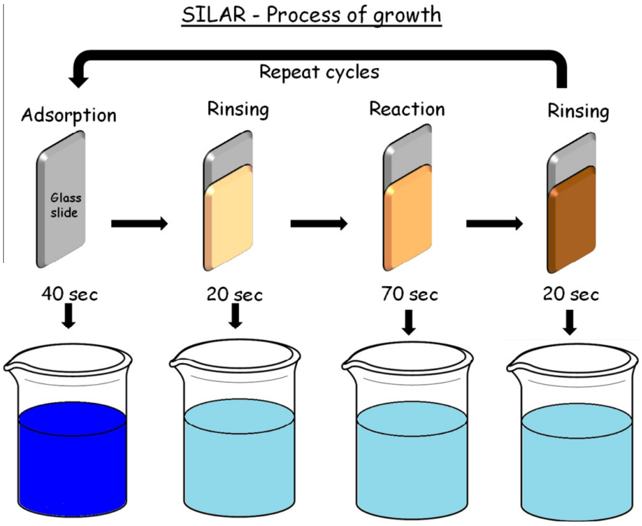


Fig. 1. Schematic illustration of growth of CuO thin films by SILAR method.

2.2. Characterization techniques

Ag@CuO nanostructured thin films were characterized using the following techniques. X-ray diffraction (XRD) patterns were obtained using a Panalytical X'Pert Pro with Cu K_α radiation (1.5406 Å), absorbance spectra were analyzed using UV–Vis spectrometer (JascoV-640) and morphological details through FE-SEM (quanta-250). SERS spectra were recorded using Raman spectrometer (LABRAM-HR) with laser excitation lines of 514 nm at room temperature. X-ray photoelectron spectra were recorded using (Kratos analytical, ESCA-3400, Shimadzu). The super hydrophobicity and the contact angle measurements of the substrate were carried out at room temperature using a contact angle meter. Contact angle measurements were recorded using the sessile drop method (about 2 μl distilled water droplet) with a video-based drop shape analyzer (FTA 135, First Ten Angstroms, Portsmouth, VA) placed on different locations of the coated and uncoated samples.

3. Results and discussion

3.1. Structural analysis

X-ray diffraction (XRD) patterns were recorded for the copper oxide thin films prepared with 20, 40 and 60 cycles of deposition. The diffraction pattern in Fig. 2(a) for the as-prepared film depicts the preferred orientation plane of the material as (−1 1 1) and (1 1 1) corresponding to the 2θ values of 35.55° and 38.82° which are attributed to monoclinic structure. These results agree with