

Bismuth-based materials as a novel substrate for surface enhanced Raman spectroscopy



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By

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Summary and future scope of the work

6.1 Summary

This thesis concerns experimental results of the study on bismuth based SERS materials and its application for the detection of synthetic colorants and some important bio-molecules. Three different types of bismuth based substrates were prepared via chemical methods: bismuth heterostructure (β - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$), bismuth oxybromide ($\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$), CTAB-AgBr- $\text{Bi}_3\text{O}_4\text{Br}/\text{BiOBr}$ ($\text{Ag}_{0.15}$ BOB). The crystal structure, phase and the vibrational modes of the prepared samples were confirmed through X-ray diffraction (XRD), Raman spectroscopy, and Fourier-transform infrared spectroscopy (FT-IR). The morphology and surface chemical state or elemental composition of the synthesized materials were studied using scanning electron microscope (SEM) and X-ray photoelectron microscope (XPS). The as-synthesized materials were used for SERS application. The potential SERS activity of the synthesized substrates were demonstrated by the detecting various analytes like rhodamine B (RhB), methylorange (MO), p-nitrophenol (4-NP), and rhodamin 6G (R6G). Moreover, these synthesized novel SERS substrates were further assessed on other alaytes as well. Vitamine C (Vit C), Melamine (MEL), and p-aminothiophenol (PATP) were effectively identified on bismuth heterostructure. Synthetic food colorants allura red (AR), amaranth (AM), tartrazine (TZ), and sunset yellow (SY) were detected on $\text{Ag}_{0.15}$ BOB substrate and Bismuth oxybromide. $\text{Ag}_{0.15}$ BOB were used in the in situ detection sudan I (SuI) in chilli powder. Bio-molecules such Isatin and its derivative and acetylcholine neurotransmitter were successfully detected on α - Bi_2O_3 prepared from bismuth heterostructure.

Summary and future scope of the work

The finding of this thesis works are summarized as follows

1. Bismuth based substrate for surface enhanced Raman spectroscopy

Bismuth heterostructure as SERS substrate is being reported for the first time. The lowest detection limit for MO was determined to be 20 μM with huge enhancement in Raman signal with high stability and reproducibility. Genuine SERS spectra of p-aminothiophenol (PATP) on bismuth heterostructure instead of dimerization into 4,4'-dimercaptobenzene (DMAB) was observed.

2. Bismuth oxybromide based substrate for surface enhanced Raman spectroscopy

Bismuth oxybromide ($\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$) was explored for the detection of organic pollutants RhB, MO, and 4-NP, and this is the first such study to the best of our knowledge. RhB display enhanced Raman signal in ethanolic medium on bismuth oxybromide compared to aqueous medium due to the higher adsorption, the solvent effect was not observed with MO and 4-NP significantly. The lowest detection limit was found to be 20 μM for RhB

3. Bismuth oxybromide based novel SERS substrate for label-free, non-invasive quantitative detection of detrimental synthetic food colorants

The prepared novel substrate showed excellent SERS activity with the lowest detection limit 10 μM for R6G compared to the aforementioned bismuth substrates. In addition, the efficiency of bismuth oxybromide based substrate for the detection of adulterated SuI in chilli powder was demonstrated indicating this novel bismuth oxybromide material can be used as an alternative choice for the detection of adulterated species.

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4. Quantitative estimation of Isatin and its derivative and acetylcholine neurotransmitter on bismuth based SERS substrate

Using α - Bi_2O_3 nanoparticles with enhanced SERS activity for the detection of Isatin and derivatives 1-Misa, 1-Phisa, 5-Fisa, and 5-Iisa and neurotransmitter Ach is the first of its kind of study to the best of our knowledge, hitherto. Due to pH effect on Isatin and its derivate molecules complete transformation of Isatin into anthranilic acid were observed using Raman spectroscopy, hydrolysis of Ach was also performed at the lowest concentration of 1mM.

5. Our research on differently prepared bismuth based materials opens up the potential to future development in SERS technology.

6.2 Future scope of the work

1. In Future bismuth heterostructure, bismuth oxybromide or bismuth oxide and Bismuth sulfide can be explored to prepare different composites of transition metals/ coinage metals (Cu, Ag, Au) or p-block elements to improve the SERS activity.
2. The role of charge transfers in the enhancement of SERS mechanism between bismuth based substrate and the considered analytes can be prove computationally.
3. Quantitative analysis of Isatin and its derivative can be explored with coinage metals with different laser source to determine the spectral change and the interaction with metals (Cu, Ag, Au) experimentally as well as theoretically.

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4. Through the comprehensive analysis of the configuration and modification in geometric and energy parameters we can able to distinct characteristics of Isatin's tautomers.
5. The interaction of Acetylcholine with Isatin and how Isatin mediates the concentration of acetylcholine using Raman and SERS with metals (Cu, Ag, Au) can be investigated experimentally as well as computationally.

Table 6.1 Summary of all studied analytes on bismuth based substrate (Note: numerical entries represent the lowest detection limit; $\sqrt{}$ means the substrate was active for the analyte but the LoD was not checked and \times means the substrate was not active for the analyte.)

Analytes	β -Bi ₂ O ₃ /Bi ₂ O ₂ CO ₃	α -Bi ₂ O ₃	Bi ₂₄ O ₃₁ Br ₁₀	Ag _{0.15} BOB
MO	20 μ M	100 μ M	100 μ M	100 μ M
RhB	100 μ M	100 μ M	20 μ M	50 μ M
Vit C	25 mM	50 mM	50 mM	\times
MEL	25 mM	50 mM	\times	\times
4-NP	500 μ M	50 mM	100 μ M	\times
PATP	1mM	50 mM	10 mM	\times
R6G	50 μ M	400 μ M	100 μ M	10 μ M
AR	400 μ M	$\sqrt{}$	400 μ M	50 μ M
AM	400 μ M	$\sqrt{}$	400 μ M	50 μ M
TR	100 μ M	$\sqrt{}$	100 μ M	40 μ M
SY	100 μ M	500 μ M	100 μ M	40 μ M
SuI	500 μ M	1mM	80 μ M	100 μ M
Ach	10 mM	1mM	50 mM	10 mM
Isatin	10 mM	800 μ M	10 mM	25 mM