Tailoring optical and magnetic properties of molybdenum disulphide nanosheets by incorporating plasmonic gold nanoparticles

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Abstract: In present paper, a systematic growth of plasmonic gold nanoparticles (Au NPs) on molybdenum disulphide (MoS\textsubscript{2}) nanosheets has been studied and effect of Au NPs on the optical and magnetic properties has been explored. The crystallinity of the nanocomposites is confirmed by using X-ray diffraction and transmission electron microscopic techniques. The optical properties are investigated using absorption and Raman spectroscopic techniques. The electron paramagnetic resonance technique is used to explore the magnetic response of the nanocomposites. The study provides a fundamental understanding of the two dimensional nanomaterials based composites for their applications in the magnetic and optical devices.

I. INTRODUCTION

In recent years, transition metal dichalcogenides (TMDs) have gained significant interest due to their vast applications in the field of energy transfer, catalysis, optical and electronic devices\cite{1,2}. Among these TMDs materials, molybdenum disulphide (MoS\textsubscript{2}) and tungsten disulphide (WS\textsubscript{2}) have been explored for various semiconducting devices. The bulk TMDs comprise many layer of nanosheets. The weak van der Waals interaction in the interlayer of TMDs causes binding of these layers to form bulk materials. The optical and electrical properties of MoS\textsubscript{2} strongly depend on number of layers. The TMDs possess numbers of layer dependent band gap. In bulk form, they have indirect band gap while in case of monolayer, direct band gap is observed\cite{3}. The transition from indirect to direct band gap results in to high photoluminescence from TMDs nanosheets\cite{4}. Having a band gap in the visible region causes more usefulness of the TMDs nanosheets in optoelectronic devices as compared to graphene, where zero band gap is observed\cite{5}. In the monolayer of TMDs there are three layers of atoms; a layer of transition metal (Mo/ W) sandwiched between two layers of chalcogenides (S/Se)\cite{6}. Thus it forms MX\textsubscript{2} structure. In bulk form, MoS\textsubscript{2} has 1.2 eV band gap while the monolayer has 1.9 eV band gap. Similarly, WS\textsubscript{2} has 1.3 eV band gap.

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gap in bulk and 2.1 eV in the single layer form.\(^{12,13}\) Owing to this characteristic, finite band gap MoS\(_2\) monolayer could complement the weakness of gapless graphene, making it a promising 2D material for next generation applications in switching and optoelectronic devices. Thus, MoS\(_2\) finds its applications in diverse fields like sensors, energy storage in lithium-ion batteries, optoelectronic devices, flexible electronic devices, photoluminescence, valleytronics and field-effect transistors.\(^{14,15}\) MoS\(_2\) has also been explored as catalyst for hydrodesulphurization and hydrogen evolution in recent years.\(^{16,17}\) Atomically thin MoS\(_2\) sheets have relatively large in-plane mobility and mechanical stability.

The physical and chemical properties of MoS\(_2\) nanosheets can be manifested many folds by incorporating noble metal nanoparticles. Hence, nanocomposites can be used in vast area of applications. Among noble metal nanoparticles, gold nanoparticles have advantage due to its non-toxic nature and excellent stability. Further, Au is known to have a strong affinity for sulphur, which has been exploited to enhance charge transportation along interplanar directions and act as spacers to inhibit restacking of the TMDs. Recently, various research groups have synthesized and used Au-MoS\(_2\) nanocomposites in photocatalysis, surface enhanced Raman scattering, photovoltaic applications. Few research groups have worked in the field of synthesis of Au NPs decorated on MoS\(_2\) sheets and its various applications as hydrogen catalysis, Fermi level engineering, photoluminescence quenching, etc.\(^{15,17}\)

There are various studies on the optical and electrical properties of metal based MoS\(_2\) nanosheets.\(^{23,24}\) Besides these studies, there are very few reports on the magnetic properties of metal based two dimensional nanosheets, especially the electron paramagnetic resonance (EPR) studies. In present paper, we report chemical exfoliation of MoS\(_2\) nanosheets for spontaneous decoration of Au NPs on MoS\(_2\) sheets. A direct redox reaction has been done with a gold precursor hexachloroauric acid (HAuCl\(_4\)) and sodium dodecyl benzene sulfonate as stabilizing agent. The Au NPs have been successfully deposited on chemically exfoliated sheets. The optical and magnetic properties of the nanocomposites have been explored using optical spectroscopic techniques and EPR spectroscopy.

II. EXPERIMENTAL METHODS

A. Materials

Molybdenum disulphide (MoS\(_2\)) powder, N-Methyl 2-pyrrolidone (NMP), Isopropyl alcohol (IPA), Hydrogen tetrachloroaurate trihydrate (HAuCl\(_4\).3H\(_2\)O), Sodium dodecyl benzene sulfonate (SDBS) were obtained from Sigma Aldrich. All the chemicals were used without further purification.

B. Chemical exfoliation of MoS\(_2\) nanosheets

MoS\(_2\) nanosheets have been synthesized via liquid phase exfoliation method. For the synthesis of MoS\(_2\) nanosheets, 0.05g of bulk MoS\(_2\) powder was dispersed in 20 mL of NMP, IPA and distilled water (volume ratio 3:1:1) mixed solvent. The solution was ultrasonicated continuously for 24 hours at room temperature. After 24 hours of sonication the colour of solution changes from dark greyish black to greenish. The resultant green dispersion obtained was retained for 30 min for settling down the un-exfoliated MoS\(_2\). Clear supernatant was collected and 10 mg of SDBS was added. The solution was then allowed to settle down for next 30 min.

C. Synthesis of Au-MoS\(_2\) nanocomposites

For the synthesis of Au-MoS\(_2\) nanocomposites, stock solution of 10 mM Au salt (HAuCl\(_4\).3H\(_2\)O) was prepared. Four sets each of 2 mL dispersion of exfoliated MoS\(_2\) nanosheets were taken
for the further synthesis of Au-MoS$_2$ nanocomposites. In these four sets different quantities of Au salt solution (2µL, 4µL, 6µL and 8µL) were added and the mixtures were kept for aging for 48 hours and named SET-I, SET-II, SET-III and SET-IV, respectively.

D. Characterization techniques

The physical properties of MoS$_2$ and Au-MoS$_2$ nanocomposites were characterized by using spectroscopic and microscopic techniques. The morphology of the nanomaterial was investigated using transmission electron microscopy (TEM). The TEM analysis of MoS$_2$ and Au-MoS$_2$ nanocomposites was done using JEOL 2100F transmission electron microscope operated at 200 kV. The crystallinity of MoS$_2$ and Au-MoS$_2$ nanocomposites was explored using X-ray diffractometer from PANalytical with Cu Kα (0.15 nm) as X-ray source. The Raman spectra of MoS$_2$ and Au-MoS$_2$ nanocomposites were recorded by a confocal Raman microscope with an excitation source as 532 nm laser. The absorption spectra of MoS$_2$ and Au-MoS$_2$ were recorded using UV-Vis absorption spectrophotometer (Labtronics, LT-2700, India). The EPR spectra were obtained at room temperature using EPR spectrometer (Bruker, EMX MicroX).

III. RESULTS AND DISCUSSION

A. TEM

The shape and size of MoS$_2$ and that of Au NPs on the MoS$_2$ nanosheets were investigated using transmission electron microscopy (TEM) set-up. The TEM images of MoS$_2$ and Au-MoS$_2$ nanosheets are shown in Fig. 1. In the Fig 1(a), a sheet like structure is observed, which corresponds to exfoliated MoS$_2$. In MoS$_2$, the lattice spacing is of the order of 0.27 nm, which corresponds to (100) plane. In case of Au-MoS$_2$, the Au NPs are found to be of spherical shape and size of these particles is around 20 nm (Fig 1(b)). The lattice plane spacing in the Au NPs corresponding to FCC lattice of Au is observed and spacing is of the order of 0.22 nm, which corresponds to (111) plane of gold lattice.

B. XRD

The XRD technique was used for investigating the crystal structure and lattice planes of the Au NPs and MoS$_2$ nanosheets. The XRD patterns of pristine Au and MoS$_2$ along with the Au-MoS$_2$ nanocomposites are shown in Fig. 2. In these XRD patterns, the diffraction peaks at 29.19°, 32.88°, 33.68°, 36.09°, 39.75°, 44.34°, 49.99°, 56.19°, 58.50°,
60.61° and 62.95° are observed which are attributed to lattice planes (004), (100), (101), (102), (103), (006), (105), (106), (110), (008) and (107) of MoS\textsubscript{2} respectively (JCPDS No. 37-1492). After Au NPs decoration, the Au-MoS\textsubscript{2} shows additional diffraction peaks at 37.34°, 44.17° and 64.40° corresponding to the (111) (200) and (220) planes, respectively of Au phase (JCPDS No. 04-0784) which indicates that FCC Au NPs have been successfully decorated on the MoS\textsubscript{2} surface. Intensity of peaks corresponding to Au enhances as the concentration of Au increases in the nanocomposites, while the peaks of MoS\textsubscript{2} decrease correspondingly in SET-I SET-II SET-III and SET-IV which is clearly observed in Fig. 2. Lowering in diffraction intensity is due to decrease in the exposure area of MoS\textsubscript{2} nanosheets in presence of Au NPs. The presence of Au NPs hinders the exposure area of the MoS\textsubscript{2}.

C. Raman study

The vibrational modes of MoS\textsubscript{2} nanosheets and the effect of Au NPs on it were investigated using Raman spectrometer. The Raman spectra of MoS\textsubscript{2} and Au-MoS\textsubscript{2} nanosheets are shown in Fig 3. The Raman spectra exhibit two distinct Raman peaks; one around 385.9 cm\textsuperscript{-1} and the other around 410.9 cm\textsuperscript{-1}. These peaks are associated with E\textsubscript{1g} and A\textsubscript{1g} modes of MoS\textsubscript{2}, respectively. The E\textsubscript{1g} mode is attributed to the in-plane vibration of Mo and S atoms and this mode is sensitive to the built-in strain of 2D MoS\textsubscript{2}. The A\textsubscript{1g} mode is related to the out-of-plane vibration of S atoms which is a reflection of interlayer van der Waals interaction. For Au-MoS\textsubscript{2}, red shift in the E\textsubscript{1g} and A\textsubscript{1g} modes are observed. The shifting is attributed to the effect of lattice strain due to the curvature of MoS\textsubscript{2} shell. The frequency difference of the E\textsubscript{2g} and A\textsubscript{1g} peaks comes out to be about 25 cm\textsuperscript{-1} which
FIG. 3. Raman spectra of MoS\textsubscript{2} and Au-MoS\textsubscript{2} nanosheets, where Au-MoS\textsubscript{2}-1 is for 2 \( \mu \)L of Au-solution and Au-MoS\textsubscript{2}-4 is for 8 \( \mu \)L of Au-solution.

renders exfoliation of few-layers MoS\textsubscript{2} sheets. In presence of Au NPs the intensity of Raman peaks are also enhanced. The enhancement is due to the plasmonic effect of Au NPs. The presence of Au NPs causes enhanced electric field near the surface of Au NPs and hence the intensity of Raman signal is enhanced. This contribution is due to the effect of localized surface plasmon resonance (LSPR) of Au nanoparticle cores, typically called surface enhanced Raman scattering (SERS).

D. UV Vis absorption

The optical absorption of pristine MoS\textsubscript{2} nanosheets and Au-MoS\textsubscript{2} nanocomposites has been explored using UV-Vis absorption spectrophotometer. The absorption spectra of MoS\textsubscript{2} and Au-MoS\textsubscript{2} are shown in Fig [4]. The absorption spectrum of MoS\textsubscript{2} nanosheet shows two small humps in the visible range; one at 620 nm and other at 670 nm, which are due to B and A excitonic peaks, respectively. These peaks arise due to spin-orbit interaction causing splitting of valence band energy levels. The interlayer coupling also plays an important role in the valence band splitting. When a small aliquot of gold precursor was added into chemically exfoliated MoS\textsubscript{2}, a new absorption peak corresponding to the Au plasmon band at around 530 nm emerges, suggesting the consumption of Au\textsuperscript{3+} and formation of gold nanoparticles. As we increase the Au concentration, the surface plasmon resonance peaks of Au experiences both red shift and increase in the intensity of peaks from SET-I to SET-IV. These shifting infer to strong plasmon-exciton coupling between Au and MoS\textsubscript{2}. The surface plasmon resonance strongly depends on shape, size and separation of the nanoparticles along with the surrounding environment. The extent of Au-ion reduction by the spontaneous redox reaction can be estimated by monitoring the absorption peak of Au\textsuperscript{3+} to quantify the...
FIG. 4. Absorption spectra of MoS$_2$ and Au-MoS$_2$ nanosheets, with different concentrations of Au.

loading level of Au on the surface of MoS$_2$.

E. Electron Paramagnetic Resonance study

The EPR spectra of MoS$_2$ and Au-MoS$_2$ nanosheets are shown in Fig. 5. In the EPR signal absorption peaks around 3476 G are observed. The peaks are originated due to sulphur vacancy in the MoS$_2$ nanosheets, which matches well with the previous reports. In case of pristine MoS$_2$, the peak position is at 3476 G, while in case of Au-MoS$_2$, the peak is shifted towards higher magnetic field around 3478 G. In case of Au-MoS$_2$, apart from the shift in the peak position, the intensity of the EPR signal is also enhanced, which is due to binding of Au with the sulphur atoms. The binding of Au-S leads to an overall increase in the sulphur vacant sites.

IV. CONCLUSION

In summary, the Au-MoS$_2$ nanocomposites have been synthesized by using chemical exfoliation and reduction method. Different characterizations reveal that these Au-MoS$_2$ nanocomposites show strong response towards the optical wavelengths due to the presence of surface plasmons in the nanocomposites which enhances the charge transportation between MoS$_2$ nanosheets. The presence of plasmonic particles was found to alter the magnetic property of the nanocomposites. This study can be further extended to other plasmonic nanoparticles of different shape and size and their effect on the optical and magnetic response on the 2D nanomaterials can be explored.
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