SYNTHESIS OF SINGLE LAYER MOS2 ARRAY FOR SURFACE RAMAN ENHANCEMENT SPECTROSCOPY

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ABSTRACT

We present direct synthesis of high quality single-layer MoS\textsubscript{2} array on substrates with pre-deposited sulfur seeds for the first time with strong Raman signals of diluted Rhodamine 6G (R6G) due to Surface-Enhanced Raman Scattering (SERS). This work has following unprecedented accomplishments: (1) the usages of sulfur terminated substrate for the synthesis of CVD MoS\textsubscript{2} array; (2) SERS using the monolayer MoS\textsubscript{2} array with partially bowtie structures. (3) First time demonstration of SERS and photoluminescence (PL) on MoS\textsubscript{2} covered with Al\textsubscript{2}O\textsubscript{3}, which address the possibility of the physical enhancement mechanism. As such, the newly developed processes can enable large scale growth of MoS\textsubscript{2} for applications in bio-chemical sensing, and bring great inspiration in the 2D chalcogenide SERS mechanism.

KEYWORDS

2D materials; Molybdenum disulfide; surface enhance Raman scattering (SERS); photoluminescence; R6G;

INTRODUCTION

The field of transition metal dichalcogenide (TMDC) have witnessed tremendous research progresses in the past several years [1, 2]. Great effort has been put into the development of synthesis techniques for very large scale, uniform, layer-controlled TMDC growth, including chemical vapor deposition, annealing from solution, and ALD (Atomic Layer Deposition) [3]. However, even the most studied MoS\textsubscript{2} structures can only be synthesized in the wafer scale by the highly sophisticated and expensive metal organic chemical vapor deposition (MOCVD) [4]. A more effective and condition tolerant method is eminently desired. Inspired by adding seed promoter in the CVD template to get higher yield of MoS\textsubscript{2} nucleation, we demonstrate that the synthesis of large area MoS\textsubscript{2} can be achieved in a normal CVD process by coating the substrate with a thin layer of sulfur. Such technique provides promising solution for large scale synthesis that is less dependent on the surface morphology for epitaxial growth and other parameters such as pressure and temperature. Optimizing this technique will also bring inspiration in versatile method for CVD synthesis of large scale TMDC with controlled layer growth.

On the other hand, SERS on 2D materials has attracted great amount of interested recently [5]. For example, SERS based on 3D metal nanoparticles can use local surface resonance of free electron to amplify the tiny signals of highly diluted molecules with noble metals such as Ag, Au, and Pt to provide strong enhancement factors in the visible light range due to their coherent resonance frequency [6]. The TMDC materials, with near metallic conductivity and carrier density, provide new possibilities for metal-free SERS with potentially low manufacturing cost [7]. The study of TMDC-SERS will also help investigating the optical interactions in 2D materials, charge transfers from molecule to 2D materials … etc. The SERS mechanism based on the 2D materials including graphene and TMDC has never been thoroughly studied [8]. Even though there are arguments that graphene and MoS\textsubscript{2} can work as SERS substrate due to a photon-induced charge transfer process or dipole-dipole interaction (chemical enhancement), there is no solid evidence to eliminate the possibility of physical enhancements [9]. Although the conventional metal surface plasmon resonance (SPR) model cannot be applied to semiconductor materials such as TMDC, there are potential mechanisms for field enhancements such as the local 2D Bowtie structures and Forster resonance energy transfer (FRET) [10]. This work first examines the chemical SERS mechanism in the 2D TMDC due to the charge transfers between the LUMO orbital of molecules and the valence band by adding an isolation layer to cut off the electron transfer path. We observed that the as-grown MoS\textsubscript{2} has SERS which can detect the diluted Rhodamine 6G (R6G) at a level of 10^{-5} M concentration (Figure 1). Experimental results on the SRES for R6G on the as-grown MoS\textsubscript{2} substrate and Al\textsubscript{2}O\textsubscript{3}-isolated MoS\textsubscript{2} substrate show 10\textsuperscript{2} and 10\textsuperscript{3} enhancement factors, respectively. The 10\textsuperscript{2} enhancement factor implies a surprising non-chemical charge transfer effect and both the FDTD and FRET model are discussed to qualitatively explain this phenomenon.

RESULTS

As shown in Figure 2, our synthesis results are based on the silicon substrate with a 285nm-thick silicone oxide layer with S and MoO\textsubscript{3} as the precursors with the proper stoichiometric ratio using Ar as the carrier gas flowing at 300scm. It is observed that the MoS\textsubscript{2} flakes grown on the sulfur coat wafer show large domains (3~5 µm), under a processing temperature of 650°C. Furthermore, the distance of the in-plane vibration E\textsubscript{2g} peak and inter-plane stretching band peak A\textsubscript{1g} is ~19.5 cm\textsuperscript{-1} in the Raman spectroscopy which implies the formation of single layer MoS\textsubscript{2}. As such, substrates with these MoS\textsubscript{2} nano flakes are used for SERS and PL experiments in this work.
Meanwhile, sulfur will easily evaporate away during the CVD process to leave clean MoS$_2$. As shown in the SEM in Figure 2, we observe that the triangle flakes of monolayer MoS$_2$ can form many random pairs of Bowtie structures and some with nano scale distance between their tips. The Bowtie structures have been used as antennas to enhance local electromagnetic fields for SERS applications in various previous publications in the literature.

Rhodamine 6G is widely used to test SERS substrates with the typical stimulation florescence (FL) wavelength of ~530nm (>95% quantum yield). Thus, a 633nm laser (Renishaw inVia) is used to test Raman on R6G decorated MoS$_2$, to avoid the FL background noises. Experimental results show as-grown MoS$_2$ flakes have an enhancement factor of $10^3$ which is correlated to the common chemical enhancements induced by the HOMO-LUMO charge transfer process pumped by the valence band of the substrate, as shown in Figure 3. The charge transfer process is also demonstrated by the photoluminescence (PL) mapping of MoS$_2$ and MoS$_2$-R6G (10$^{-5}$M). Unlike the SERS test, the PL test utilizes laser with a wavelength of ~488nm. Strong PL signals at ~1.8 eV (690nm) are observed on the MoS$_2$ flakes without R6G. Strong PL signals are observed with R6G while the R6G/MoS$_2$ interactions showing the strong quenching effects, implying charge transfers between MoS$_2$ and R6G.

As shown in Figure 4, MoS$_2$ samples are covered with a 3.5nm-thick layer of Al$_2$O$_3$ with a high dielectric constant to chop off the charge transfer pathway between the MoS$_2$ and the solution. Afterwards, both the Raman and photoluminescence tests are performed.
not as big as the previous results on MoS₂ flakes without the insulation Al₂O₃ layer.

In complementary to the mapping result, PL peak of pristine MoS₂ exhibits excitation peaks at 1.8 eV and 1.95 eV; pure R6G on SiO₂ surface shows strong PL with a peak at 2.2 eV; and the MoS₂-R6G shows suppressed PL for both MoS₂ and R6G peaks. It is found that the R6G PL on Al₂O₃ is also decreased comparing to that of the R6G on SiO₂ results which could attribute to the surface roughness of the ALD Al₂O₃ layer which redistributes the molecule concentration over the surface and diffuse the reflection signals. With and without the Al₂O₃ layer, the MoS₂ flakes quench the PL of the R6G signals in different magnitudes, in which the direct contact with MoS₂ results in 10⁵ times lower PL signals, while Al₂O₃ covered MoS₂ results in 10² times lower PL signals. Furthermore, MoS₂ encapsulated with Al₂O₃ shows blue shift in the PL peak. As such, we conclude that energy transfer between MoS₂ and R6G dye occurs even with the Al₂O₃ isolation layer while the mechanism requires further investigations.

**DISCUSSION**

As shown in Figure 8, Raman spectrum with a 633 nm laser on the Al₂O₃ coated MoS₂ flake is studied, showing R6G at three standard peaks at 1180 cm⁻¹, 1350 cm⁻¹ and 1500 cm⁻¹ with an enhancement factor of 10² which is one order smaller than that on the as-grown MoS₂ substrate. The enhancement factor and PL quenching effect imply some energy transfer between the R6G and MoS₂ over the insulating Al₂O₃ layer. We investigate two possible mechanisms: local electromagnetic enhancement by the MoS₂ Bowtie structure; and the FRET effect in which the MoS₂ acts as the acceptor and R6G acts as the donor. In the FRET effect, donor transfer exciton energy to acceptor and could cause redshift in the spectrum. Such mechanism could also explain a spatial decay by Al₂O₃ spacer with a power of 6 in relationship, following the efficiency rule:

\[
E_{\text{FRET}} = \frac{1}{1 + \left( \frac{r}{R_0} \right)^6}
\]

where \( R_0 \) is the Forster radius where the energy transfer efficiency is 50% and \( r \) is the acceptor-donor distance [10].
The MoS$_2$ structures can result in a $10^3$ enhanced factor in the SERS tests while Al$_2$O$_3$-insulated MoS$_2$ structures has $10^9$ enhanced SERS results. On the other hand, the pristine or plasma-treated MoS$_2$ structures have only an enhancement factor of $10^8$ as reported previously [11]. These enhanced SERS results could be attributed to Bowtie shaped arrays for localized hotspots. Here, the Lumerical FDTD software is utilized to study the light-MoS$_2$ interactions as shown in Figure 9.

**CONCLUSION**

The band structure of 2D-materials should fit with the molecular orbital with sub-band to achieve effective SERS. This paper shows the surprising phenomenon of SERS effects from insulated MoS$_2$ flakes with preliminary investigations for possible applications of 2D materials.

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**REFERENCE**


