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Molybdenum Disulfide as Surface Enhanced Raman Scattering Substrates for Sensing Polycyclic Aromatic Hydrocarbons

Transition metal dichalcogenides (TMDs) are at the forefront of the current research investigations of 2D layered materials beyond graphene [1]. Various methodologies for exfoliating TMDs have already been developed, mainly based on wet chemistry approaches allowing mass production of material suitable for basic research and proof-of-concept studies. Recently, the potential use of TMDs as SERS platforms promoting stable physicochemical tethering of aromatic molecules onto their surface have been announced, however, the Raman enhancement for organic species still modest [2]. In order to improve the SERS effect, TMDs need to be functionalized, for example by decoration with metal nanoparticles [3]. Different synthetic strategies have been employed for the fabrication of TMD-based SERS substrates ranging from simple wet chemistry procedures to sophisticated ones, involving micropatterning. Alternatively, oxygen and argon plasma treated MoS_2 sheets have been also examined, in which the creation of local dipoles resulted in enhanced SERS phenomena on MoS_2 surface [4]. Based on the aforementioned points, the preparation of robust sensing platforms using TMDs still remains a daunting challenge.

Herein, we report a simple one-pot functionalization of few-layered MoS_2 sheets, using nitrogen plasma treatment and simultaneous decoration with silver nanoparticles (Ag_{NPs}). The successful surface modification was evaluated through Raman and X-ray photoelectron spectroscopy (XPS), while transmission electron microscopy (TEM) imaging verified the decoration with Ag_{NPs}. N-MoS_2/Ag_{NPs} nanohybrids were employed as SERS substrates to detect Rhodamine B (RhB) at very low-concentration. Charge-transfer phenomena between RhB and N-MoS_2/AgNPs, along with the polarized character of the hybrid system, causing dipole-dipole coupling interactions, were associated to the Raman signal enhancement. Finally, considering the coordination of aromatic moieties via π-S interactions with TMDs, we used N-MoS_2/AgNPs hybrids, prepared with different functionalization parameters, as substrate for the sensitive recognition at low levels of polycyclic aromatic hydrocarbons. These widespread organic pollutants in the atmosphere are known to be highly carcinogen and mutagen species [5], therefore the engineering of highly-sensitive sensors capable of in-situ detection is a key technology for helping innovative environmental security policies. To this end we have investigated the performance of the N-MoS_2/Ag_{NPs} nanohybrids towards the detection of three hazardous aromatic hydrocarbons: pyrene, anthracene and 2,3-dihydroxy naphthalene were investigated, observing a sensitive detection at very low levels.

Rhodamine B (RhB), a Raman probe molecule, was selected as model analyte. For comparison, RhB was drop-casted onto bare Si as well as onto exfoliated MoS_2 (i.e. non-modified) and N-MoS_2/Ag_{NPs} for Raman signal detection. The Raman spectrum of the dye adsorbed on the Si substrate showed only a strong fluorescent background, while the Raman spectrum of RhB deposited onto as-exfoliated MoS_2 showed low intensity bands.

In sharp contrast, when SERS measurements were performed on N-MoS$_2$/Ag$_{NPs}$ high intensity bands were observed (Fig. 1). The recorded Raman spectrum of RhB, shows distinct modes at 625 cm^{-1} (C–C–C ring in plane bending), 760 cm^{-1} (C–H out of plane bending), 943 cm^{-1} (C–H stretching), 1195 cm^{-1} (C–H in plane bending), 1278 cm^{-1} (C–O–C stretching), 1360 cm^{-1}, 1505 cm^{-1}, 1563 cm^{-1}, 1648 cm^{-1} (aromatic C–C stretching) and 1594 cm^{-1} (C=C stretching), in full agreement with previous reports [6]. Focusing on the 1648 cm^{-1} band, the SERS signal was enhanced by 8 times for the 10 s nitrogen plasma silver decorated substrates compared to the substrates functionalized only 5 s. This result emphasizes the influence of the amount of nitrogen-grafting and silver-nanoparticles size on MoS$_2$ in the Raman enhancement for detecting RhB. We choose the substrate with higher enhancement factor for SERS sensing of small quantities of pyrene, anthracene and 2,3-dihydroxy naphthalene.
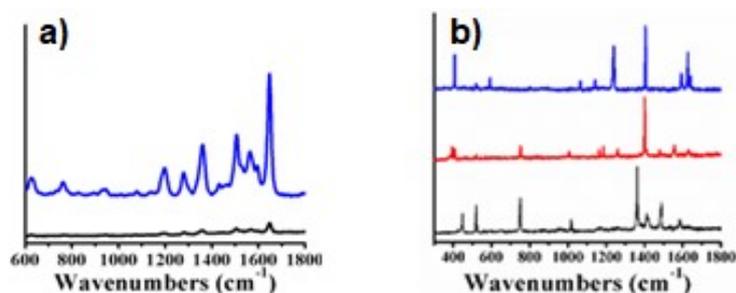
Figure 1: SERS spectra (514 nm) of (a) aqueous RhB (10^{-5} M) on exfoliated MoS$_2$ (black), and N-MoS$_2$/Ag$_{NPs}$ (blue) substrates. b) pyrene (blue), anthracene (red) and 2,3-dihydroxy napthalene (black) at 10^{-5} M deposited onto N10-MoS$_2$/Ag$_{NPs}$ substrate.

The Raman spectra of the studied polyaromatics are governed by strong fluorescence background, making impossible the detection of characteristic Raman signals. However, in the recorded SERS spectrum of pyrene using N-MoS$_2$/Ag$_{NPs}$ as substrate, seven distinctive modes at 407, 592, 1241, 1406, 1592, 1627, and 1643 cm^{-1} can be identified, while for anthracene and 2,3-dihydroxy naphthalene bands at 752, 1006, 1183, 1402 and 1557 cm^{-1} and at 448, 750, 1363, 1412, 1488 and 1585 cm^{-1}, were respectively observed. These bands can be divided into three main regions: (a) bands below 550 cm^{-1}, which are attributed to C–C out-of-plane bending vibrations, (b) bands at 600–1000 cm^{-1} which are associated with C–H out-of-plane bending and at 1000–1300 cm^{-1}, which are related to C–H in-plane bending and rocking, and (c) bands at 1300–1650 cm^{-1}, which are due to aromatic C–C stretching [7]. These results testify the use of MoS$_2$ functionalized with nitrogen and silver particles as an effective SERS platform for the sensitive detection of polycyclic aromatic hydrocarbons. It is important to mention that the SERS detection of polycyclic aromatic hydrocarbons by other substrates requires special modification methodologies of metal nanoparticles to ensure effective interaction between the substrate and the analyte, as the aromatic rings exhibit low affinity for metals [8,9]. However herein, π-S interactions with MoS$_2$ were exploited, therefore the SERS application of functionalized TMDs as analytical, environmental and biomedical sensors can be envisioned.

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