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Graphene-enhanced Raman imaging of TiO₂ nanoparticles

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Abstract

The interaction of anatase titanium dioxide (TiO_2) nanoparticles with chemical vapour deposited graphene sheets transferred on glass substrates is investigated by using atomic force microscopy, Raman spectroscopy and imaging. Significant electronic interactions between the nanoparticles of TiO₂ and graphene were found. The changes in the graphene Raman peak positions and intensity ratios indicate that charge transfer between graphene and TiO₂ nanoparticles occurred, increasing the Raman signal of the TiO₂ nanoparticles up to five times. The normalized Raman intensity of TiO₂ nanoparticles per their volume increased with the disorder of the graphene structure. The complementary reason for the observed enhancement is that due to the higher density of states in the defect sites of graphene, a higher electron transfer occurs from the graphene to the anatase TiO₂ nanoparticles.

S Online supplementary data available from stacks.iop.org/Nano/23/465703/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Several qualitative techniques are available for the physicochemical characterization of nanoparticles. Raman spectroscopy is a standard tool for chemical analysis, but the low cross-section of Raman scattering and the weak intensity of Raman signals result in low sensitivity and often limit its applicability in the analysis of nanoparticles or nanomaterials [1]. In spite of this, Raman spectroscopy is a sensitive method for the characterization of carbon-based materials [2], particularly graphene, a two-dimensional monolayer of sp² bonded carbon atoms [3, 4]. In addition to various excellent material properties [5], graphene can be used as a substrate for the enhancement of the Raman signal [6, 7].

A few methods are commonly used to enhance the Raman response: resonant Raman scattering [8], surface-enhanced Raman scattering (SERS) [9] and tip-enhanced Raman scattering [10]. Because of strong attendant fluorescence in the case of resonant Raman scattering [8] or technical

difficulties of tip fabrication for tip-enhanced Raman scattering [11], SERS is mostly used for the investigation of the molecular monolayers, nanoparticles etc [9, 12]. Noble metals such as gold and silver are used as SERS substrates. Despite numerous experimental and theoretical studies the SERS-specific mechanism of the enhancement process is not still fully understood. Based on the current research, two overlapped enhancement mechanisms are accepted, namely, an electromagnetic (EM) and a chemical mechanism (CM) [9]. The EM effect is based on the enhancement of the local electromagnetic field due to excitation of local plasmons on the nanostructured elements of the metal surfaces or isolated metallic nanoparticles resulting in a significant increase in the cross-section of Raman scattering of the characterized molecules. The enhancement value of EM reaches 10^8 [9, 12]. CM is based on a charge transfer between the noble metal surface and the molecules under investigation. In this case, the positive or negative charge induces changes in the position of the nuclei of the atoms in the molecule. Consequently, the molecular polarizability is increased, leading to an increase in the Raman scattering cross-section [13]. The enhancement factor of the CM can be up to 10^2 [9]. The difficulty in understanding the complex mechanism of SERS on rough metallic structures is that the EM and CM are always coexistent, when visible wavelength range lasers are used in the experiment. The large enhancement, based on EM, always obscures the enhancement due to the CM, making it difficult to study CM, which is based on the charge transfer between the surface and examined molecules or nanoparticles.

The main advantage of graphene as a SERS substrate is that the plasmon resonance in graphene is located in the terahertz frequency region, and cannot be excited by the Raman spectroscopy operating frequencies, which are usually in the visible range [14], and therefore only the CM enhancement of the Raman scattering is possible on graphene substrates. Most studies on the effect of SERS on graphene have been devoted to the interactions of organic aromatic molecules with graphene flakes [6, 7, 15, 16], where charge transfer suppresses photoluminescence [16] or enhances the Raman signal (graphene-enhanced Raman scattering, GERS) [6, 7]. However, the influence of graphene properties on the mechanism of Raman scattering enhancement is still under discussion.

In this work, we report on the potential of using chemical vapour deposited (CVD) graphene as a template for the Raman spectroscopy of inorganic nanoparticles: the relationship between graphene properties and the GERS signal from titanium dioxide (TiO₂) nanoparticles (NPs), as well as the correlation of the enhancement effect with the NP cluster form and size. CVD fabricated graphene has high-quality single-layer graphene regions on areas of a few hundred μm^2 , as compared to mechanically exfoliated graphene flakes [17, 18]. TiO₂ is a material of great interest in many fields, e.g., photocatalysis, solar cell devices, gas sensors, and biotechnology [19]. However, only a few works have described the interaction of TiO₂ nanoparticles with graphene oxide or graphene flakes [20, 21], and, according to our knowledge, no works have reported on the influence of CVD graphene on the Raman scattering of TiO₂ nanoparticles.

2. Experimental details

2.1. Materials

CVD graphene was grown on a copper foil (Alfa Aesar, 99.8%) in a CH₄:H₂ 3:1 gas mixture, at 970 °C and 7 Torr, and transferred to a glass substrate using a sacrificial PMMA support layer. The TiO₂ NP water colloid solution was prepared by dispersing 1 mg of commercial TiO₂ NP powder (Nanostructured and Amorphous Materials, Inc.) in 10 ml deionized water.

2.2. Sample preparation

The TiO_2 water solution was sonicated and then filtered through a 200 nm pore polyethersulfone membrane (Chro-

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mafil PES-20/25, Macherey-Nagel) to remove large NP agglomerates and a 5 μ l drop was dispensed onto a graphene–glass support and dried.

2.3. Instruments and measurements

The Raman and AFM measurements were undertaken using an NTEGRA Spectra system (NT-MDT Inc.) in an upright configuration. The excitation wavelength was 632.8 nm (He-Ne laser, Melles Griot 25-LHP-928-230) and the controlling laser power 1 mW, with a spectral resolution of $1-3 \text{ cm}^{-1}$ for various diffraction gratings. The instrument was equipped with a 100 \times 0.7 NA objective, resulting in spot diameter of 0.5 μ m at the laser focus, and CCD camera TE-cooled to -60 °C (DV401-BV, Andor Technology). The beam is focused on the sample, which rests on a controlled XYZ piezostage capable of scanning samples over a 100 μ m × 100 μ m × 7 μ m. AFM measurements were carried out in intermittent contact mode using commercial silicon cantilevers NSG11 with a tip curvature radius of 10 nm and force constant of 5 N m⁻¹ at a scan rate of typically 0.75–1 Hz.

For TiO₂ nanoparticles Raman imaging, the acquisition time was chosen to be 10 s for each 344 nm pixel as an optimum of the imaging time and detected Raman signal, in a scan area of 33 μ m × 33 μ m (96 pixels × 96 pixels). Full Raman spectra in the wavenumber range of 100–3000 cm⁻¹ were measured to image TiO₂ on the graphene/glass support together with the graphene characteristic bands.

The volume of TiO_2 nanoparticles was calculated using the grain analysis procedure of the standard NT-MDT software (Nova 1.0.26).

3. Results and discussion

3.1. Enhanced Raman scattering of TiO_2 nanoparticles on CVD graphene

TiO₂ exists in three forms, anatase, brookite and rutile, with different physical and chemical properties [19]. Figure 1 shows the typical Raman spectra of anatase TiO₂ nanoparticles on CVD graphene and glass substrates measured at the same laser power and acquisition time of Raman signal. The 3-fold enhancement of the Raman signal of TiO₂ NPs on CVD graphene was observed for the peaks located at 145 and 640 cm⁻¹, with weak enhancement at 197 cm⁻¹. The anatase TiO₂ spectra have six Raman-active fundamentals in the vibrational spectrum: three Eg modes centred around 144, 197, and 639 $\mbox{cm}^{-1},$ two B_{1g} modes at 399 and 519 cm⁻¹, and an A_{1g} mode at 513 cm⁻¹ [22]. Thus, only Eg bands of TiO2 were enhanced by CVD graphene (figure 1). This can be explained by the large contribution of (101)-orientation to the total surface area of the TiO_2 NPs [19], leading to the spatial orientation of adsorbed NPs onto CVD graphene surface. Because of the low intensity of the $E_{g(2)}$ and $E_{g(3)}$ modes, only the $E_{g(1)}$ band with a maximal intensity will be considered and analysed further in the identification of TiO₂ NPs on



Figure 1. Raman spectra of TiO₂ NPs on CVD graphene and glass substrates measured at 1 mW laser power and 30 s acquisition time. The characteristic bands of graphene (D, G, 2D) and TiO₂ E_g bands are marked. The inset shows the fitting of the 2D peak by a Lorentz curve.

the graphene surface and the interpretation of enhancement mechanisms (sections 3.2–3.4). The XRD pattern of TiO₂ powder demonstrates the presence of the rutile form of TiO₂ (figure S1(a), supplementary data available at stacks.iop.org/Nano/23/465703/mmedia). The Rietveld method indicates that anatase TiO₂ NPs represent 94.2% of the sample (figure S1(b) available at stacks.iop.org/Nano/23/465703/mmedia), and their size is 43.6 \pm 0.8 nm.

The graphene spectrum (figure 1) exhibits all the characteristic bands of graphene (D, G, 2D). The graphene G-band at 1600 cm⁻¹ wavenumber arises from the stretching of the C-C bond in graphitic materials, and is common to all sp² carbon systems. The G peak corresponds to the E_{2g} phonon at the Brillouin zone centre, its relative intensity increases with the number of layers [23, 24]. The D-band at 1300 cm^{-1} wavenumber is due to the breathing modes of sp² atoms and requires a defect for its activation [25]. The 2D-band at 2700 cm^{-1} wavenumber represents the second-order zone-boundary phonons [2, 3]. It is always seen, even when no D peak is present. The shape and position of the 2D peak distinguish single and multilayer samples, and this peak is also sensitive to doping. Single-layer graphene has a sharp, single 2D peak (as inset in figure 1(b)), in contrast to graphite and few-layers graphene [3]. The presence of a relatively big area of CVD graphene transferred onto the glass substrate opens the way for direct chemical imaging of the surface structures.

3.2. Raman imaging of TiO₂ NPs on CVD graphene/glass supports

Raman imaging of TiO₂ NPs on CVD graphene is shown in figures 2(a) and (b), where the strongest band of anatase TiO₂ ($E_{g(1)}$ mode around 145 cm⁻¹) was selected as the TiO₂ NP fingerprint [22].

Data presented in figure 2(a) show that TiO₂ NPs can agglomerate in large clusters both on glass and graphene due to relatively high surface energy of TiO₂ in the anatase form [26]. Figure 2(c) shows the distributions of TiO₂ NP absolute Raman signals without a regard for NP volume,

demonstrating only a 30% mean enhancement on CVD graphene. Moreover, it was found that not all of the optically imaged TiO₂ NPs (figure 2(a)) give a measurable Raman response (15 counts in figure 2(b)). It can be explained (i) by too short acquisition time of Raman signal (10 s), (ii) by the impurities in TiO₂ powder or rutile-based NPs (figure S1(a) available at stacks.iop.org/Nano/23/465703/mmedia), known to have low intensity at the 145 cm⁻¹ band [22] or (iii) because some structural defects on CVD graphene were misinterpreted as NP agglomerates (black circle on figure 2(b), bottom part).

The 'dark' regions on the graphene surface (figure 2(a)) have a lower reflectivity at the 632.8 nm wavelength and a significant increase of Raman signal for all the characteristic bands of graphene (figure S2 available at stacks.iop.org/Nano/23/465703/mmedia). They are characterized by a larger G/2D ratio of graphene bands as well (figure S2 available at stacks. iop.org/Nano/23/465703/mmedia). It means that these regions correspond to multilayer graphene, formed during the CVD reaction on the defects and edges of crystal planes of the copper foil before the transfer of graphene onto the glass [17, 18].

The NP agglomeration (figure 2(a)), even using a filtering procedure, complicates an evaluation of the real Raman enhancement because of an obvious correlation between the NP agglomerate volume and the Raman signal intensity. To clarify the role of agglomeration on the enhancement, AFM measurements of adsorbed NPs on graphene/glass supports were performed.

3.3. AFM characterization of TiO₂ NPs

AFM measurements (figures 3 and S3 available at stacks. iop.org/Nano/23/465703/mmedia) show that the most Ramanactive NPs are TiO₂ NP agglomerates, giving a detectable Raman signal (15 counts in figure 2(b)) at 10 s acquisition time. The typical height histograms of glass and CVD graphene surfaces before NP adsorption have similar parameters (figure S3(c) available at stacks.iop.org/Nano/ 23/465703/mmedia), indicating that the graphene covers



Figure 2. (a) A 33 μ m × 33 μ m confocal laser scanning microscopy image of TiO₂ NPs (most of the white spots) on the CVD graphene/glass substrate. (b) 96 pixel × 96 pixel Raman imaging of TiO₂ NPs on the CVD graphene/glass substrate (33 μ m × 33 μ m, acquisition time is 10 s for each point, 1 mW laser power). The TiO₂ E_{g(1)} band at 145 cm⁻¹ (figure 1) was selected as the NP 'fingerprint'. The D-band of graphene indicates the graphene border. (c) Statistical characterization of TiO₂ NPs Raman signal on graphene and glass substrates, indicating a mean enhancement of 30% on CVD graphene.



Figure 3. AFM topography of TiO_2 NPs and their agglomerates on CVD graphene (a) and glass substrate (b), corresponding to the marked regions on the middle insets: laser confocal (PMT) and Raman mapping images (full images are shown in figure 2). Blue and red circles, having the diameter of the laser spot, indicate one-layer TiO_2 agglomerates. The defect on CVD graphene is highlighted in black.

the glass uniformly after transferring from PMMA support layer. The density of TiO₂ NPs on graphene is 1.5 times higher than on the glass (figure S3(c) available at stacks. iop.org/Nano/23/465703/mmedia), which is due to an effect of electron and hole puddles, whereby the Dirac point deviates spatially, leading to the strong local reactivity of single-layer graphene sheets [27]. The mean size of single TiO₂ NPs, from AFM analysis on glass and graphene, is 41.9 ± 0.8 nm (figure S3(d) available at stacks.iop.org/ Nano/23/465703/mmedia), and corresponds very well to the XRD data, (figure S1(b) available at stacks.iop.org/Nano/23/ 465703/mmedia).

All the Raman-active TiO_2 agglomerates in figure 2(b) were evaluated with the aim of analysing the volume influence on the Raman signal. Such dependences for glass and CVD graphene are shown in figure 4(a), demonstrating the increase of absolute Raman signal with NP volume. The variability in the number of NPs in close proximity to the graphene surface will have influenced the Raman signal of the agglomerate, if the chemical-enhanced mechanism in GERS is effective only in close proximity to graphene, as generally assumed [7].



Figure 4. (a) The dependence of TiO₂ NP Raman intensities on their volume (in the units of single NP volume of 73.6×10^3 nm³) on CVD graphene (blue line and points) and glass substrate (red ones). The marked points b and c correspond to the AFM images of one-layer agglomerates on CVD graphene, consisting from 3 (b) and 15 (c) TiO₂ NPs. AFM cross-section of 15 NP agglomerate is also shown.

Thus, a higher slope in the case of CVD graphene (figure 4(a)) can be caused by the chemical enhancement. Moreover, only single NPs or one-layer agglomerates should be considered for the purposes of an enhancement mechanism on CVD graphene, and only isolated agglomerates in an area with the diameter of a laser spot of 500 nm (figures 4(b) and (c)) should be taken into account to avoid the input from a few agglomerates into the Raman signal. The summarized scheme for agglomerate selection is shown in figure S4 (available at stacks.iop.org/Nano/23/465703/mmedia).

As the unit for the *x*-axis in figure 4(a), a single NP volume $(41.9^3 \approx 73.6 \times 10^3 \text{ nm}^3)$ is chosen, using a packing density of 0.8 for higher agglomerates. The deviation from linearity can be explained by variability in the size or packing density of composed NPs. The threshold volume value of Raman detectable particles on the glass substrate is about 7 NPs (figure 4(a)), while for graphene this value can start with a single NP at the same acquisition time and laser power, demonstrating the GERS effect for inorganic NPs. The detailed analysis of agglomerates on both CVD graphene and glass substrate have shown that one-layer agglomerates formed from less than 20 NPs (figures 4(b) and (c)).

3.4. Charge-transfer between graphene and anatase TiO_2 NPs

Significant changes in the properties of graphene, in particular its phonon frequencies and electronic structure, occur when electrons or holes are added by electrochemical means [24]. It was also recently shown that GERS is mainly based on the charge-transfer mechanism and that the resonance conditions can be modulated by changing the Fermi level of graphene [28]. Charge transfer is a well known phenomenon in molecular systems [6, 7, 29-31]. The adsorption of molecules induces charge transfer between these molecules and graphene, which in turn greatly changes the electronic properties of graphene, in particular the characteristic Raman spectra of graphene. Charge transfer can be identified by monitoring the intensity and position of D-, G- or 2D-bands or their ratios [15, 29-31]. Figure 5 demonstrates the dependences of the normalized Raman signals of the TiO₂ one-layer agglomerates, using

the selection procedure (figure S4 available at stacks.iop. org/Nano/23/465703/mmedia), on the CVD graphene local properties and the distribution of the G-peak position before and after the adsorption of all the types of TiO₂ agglomerates. The respective Raman spectra were fitted by the sum of four Lorentz curves centred approximately at the TiO₂ $E_{g(1)}$ peak position, and the D, G, 2D-peaks of graphene, respectively. Then the normalized TiO₂ Raman signals were calculated as the height of the TiO₂ Lorentz curve divided by the volume of the one-layer agglomerate. The positions and intensities of the D, G, and 2D-peaks were also taken from the parameters of the fitted curves.

A steep linear dependence of the normalized TiO₂ Raman signal on the 2D/G ratio (figure 5(a)) is in agreement with a statement that the 2D/G value is a quite sensitive characteristic to monitor the doping of graphene [24]. The decrease of 2D/G value after the adsorption of all the types of TiO₂ agglomerates (figure S5(a) available at stacks. iop.org/Nano/23/465703/mmedia) corresponds to the doping of graphene, but such changes are the same for both electron and hole doping [24]. The G-peak position after the adsorption of all the types of TiO₂ agglomerates is up-shifted by 1 cm⁻¹ (figure 5(b)), corresponding to charge transfer between graphene and anatase TiO₂ NPs, where the electrons transfer from graphene to TiO₂ NPs [7, 15, 20]. However, any visible correlation between the normalized Raman signals and G-peak position has not been found (figure S5(b) available at stacks.iop.org/Nano/23/465703/ mmedia). No visible correlation was observed for the 2D-peak position either, in spite of higher values of up shift (up to 10 cm⁻¹, figure S5(c) available at stacks.iop.org/Nano/23/ 465703/mmedia), which corresponds to the hole doping of graphene or electron transfer to TiO₂ NPs [24]. It is therefore clear that the anatase TiO2 NPs interact with graphene as an electron acceptor, and there is a charge transfer between graphene and the TiO₂ NPs.

Figure 5(c) demonstrates the relation between the normalized TiO₂ Raman signal and the graphene D/G ratio, which is a characteristic of the disorder in the sp² carbon lattice [2, 25]. Recently, the authors in the work [32] have shown that a UV/ozone-based oxidation treatment of CVD



Figure 5. The dependences of the normalized Raman signals of TiO_2 one-layer agglomerates per their volumes on the 2D/G (a) and D/G ratios (c). (b) The distribution of CVD graphene G-peak position before (red) and after (blue) the adsorption of TiO_2 agglomerates.

graphene introduces structural disorder and defects in the graphene layer and this disorder resulted in an enhancement in the Raman signal based on a chemical mechanism from dye molecules on graphene. The intensity of the D/G ratio can be increased by adsorbed acceptor molecules on the surface of graphene, but the enhancement is weak (e.g. 0.185 in [27]). Therefore, the graphene defects with a high density of states and high D/G ratio values are more likely to be the cause for stronger charge transfer from graphene to anatase TiO_2 nanoparticles, and thus the reason for the higher enhancement of Raman signal.

The value of the normalized TiO₂ Raman signal per NP volume on the reference glass substrate was found about 2.5 (a slope of red line in figure 4(a)). In the case of a CVD graphene substrate this value reaches 12.5 (figure 5(c)), resulting in a five-fold enhancement factor of the Raman signal for a single TiO₂ NP of 42 nm size. The low factor is a result of the chemical mechanism of enhancement only, which is a short-range effect with the exponential r^{-10} dependence, where r is the distance between the probe molecule and the substrate [7, 9]. In spite of that, our results demonstrate that CVD graphene has potential as a substrate to enhance the Raman signal even for relatively large inorganic nanoparticles, and on the other hand that Raman spectromicroscopy is a powerful tool to investigate the photonic properties of nanoparticle–graphene interactions.

4. Conclusions

In this work, comprehensive AFM and Raman investigations of TiO₂ nanoparticles on glass and CVD graphene demonstrate the potential of using graphene as a template for enhanced Raman analysis of nanoparticles. In spite of the short-range nature of the chemical mechanism of Raman enhancement, a five-fold enhancement factor was observed for single TiO₂ nanoparticles of 42 nm size and their one-layer agglomerates. The up-shifts of graphene G- and 2D-bands together with a steep linear dependence of the normalized TiO₂ Raman intensity on the 2D/G ratio indicate that the observed phenomenon is based on surface interactions, i.e. on the charge transfer from graphene to anatase TiO₂ nanoparticles, increasing the TiO₂ nanoparticle Raman signal. The Raman intensity of TiO₂ nanoparticles was found to increase with an increasing local defect density of graphene (D/G ratio). The higher defect density areas of graphene produce a stronger charge transfer between the graphene and TiO_2 nanoparticles and as a consequence a stronger enhancement of the TiO_2 Raman signal. Based on the strong dependency between the TiO_2 Raman signal intensity and the D/G ratio of graphene, we make a conclusion that the Raman enhancement in the case of TiO_2 –graphene is strongly dependent on the defect density of graphene.

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