Poly(2-(dimethylamino)ethyl methacrylate) Brushes with Incorporated Nanoparticles as a SERS Active Sensing Layer

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A simple, fast, and versatile approach to the fabrication of outstanding surface enhanced Raman spectroscopy (SERS) substrates by exploiting the optical properties of the Ag nanoparticles and functional as well as organizational characteristics of the polymer brushes is reported. First, poly(2-(dimethylamino)ethyl methacrylate) brushes are synthesized directly on glassy carbon by self-initiated photografting and photopolymerization and thoroughly characterized in terms of their thickness, wettability, morphology, and chemical structure by means of ellipsometry, contact angle, AFM, and XPS, respectively. Second, Ag nanoparticles are homogeneously immobilized into the brush layer, resulting in a sensor platform for the detection of organic molecules by SERS. The surface enhancement factor (SEF) as determined by the detection of Rhodamine 6G is calculated as 6×10^6.

1. Introduction

Since the pioneering work of Jeanmaire and Van Duyne,[1] surface enhanced Raman spectroscopy (SERS) has garnered ever-increasing scientific interest and emerged as a potentially powerful platform for the fabrication of the nanosensors for ultrasensitive chemical and biological detections. The ''fingerprinting'' property, high sensitivity, and limited influence of water are some fascinating characteristics of SERS, which make it a very attractive technique for the characterization and detection of a variety of chemical and biological molecules and molecular structures. In spite of recent popularity, SERS does have limitations, including strict requirements that must be met in order to achieve optimal enhancement. One of the critical aspects of the technique involves the need for producing an ideal surface morphology on the SERS substrate for maximum enhancement, a requirement that is predicted from long-range classical electromagnetic theory.[2] So far, a wide range of strategies have been proposed to the fabrication of SERS substrates based on aggregated noble metal colloids,[3] anisotropic metal nanoparticles (NPs),[4] metal island films,[5] metal film over nanospheres,[6] particles grafted on silanized glasses,[7] regular holes in thin noble metal films,[8] and regular NP arrays[9] to name only a few. Recent studies suggest that performance of fabricated SERS substrates depend on a variety of structural parameters including the size,[10] shape,[11] type of noble metal,[12] and aggregation properties,[13] which are far from straightforward to control. Based on the previous studies, it appears that tailored organization of metal NPs on macroscopic surfaces with an effective control over above-mentioned parameters is of pivotal importance in the context of fabrication of highly efficient SERS substrates.

In recent years, a wide range of the strategies have been employed for a tailored stabilization of inorganic NPs on macroscopic surfaces and interfaces.[14] However, polymer brushes have emerged as an effective mean to the controlled organization of metal NPs on macroscopic surfaces.[15] Polymer brushes are nanoscale assemblies of macromolecules, tethered by one end to a surface or interface in such a way that the distance between two grafted chains is significantly smaller than the radius of the gyration of a polymer chain.[16,17] Most of the previously reported studies employ either ''grafting to'' or ''grafting from'' approach to grow the polymer brushes on an underlining substrate. The first approach involves attachment of the end-functionalized polymer chains on solid substrates by exploiting the surface chemistry[18] and the latter uses polymerization of the monomer of interest from initiator grafted on the interface. Recently, we have demonstrated an alternative route,

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that is, self-initiated photografting and photopolymerization (SIPGP), for the fabrication of polymer brushes with an effective control on their structural parameters. SIPGP is a simple, fast, facile, and versatile approach because functionalization of the surfaces with self-assembled monolayers (SAMs), anchoring layers, or initiators is no longer required and direct brush grafting on surfaces can be realized in a one-step reaction at room temperature under UV-irradiation.[19–22] In addition, it can be realized on a wide range of substrates including silicon oxide, glassy carbon (GC),[21] diamond,[19] and, by carbon templating,[22] virtually any inorganic substrate.

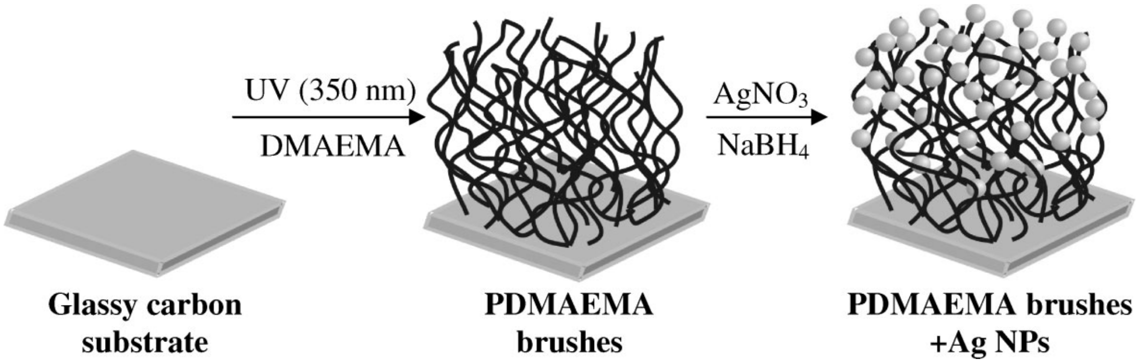
Herein, we demonstrate the fabrication of excellent SERS substrates by immobilizing Ag NPs on macroscopic surfaces modified with poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) polymer brushes. For the first time, fabrication of PDMAEMA brushes onto GC substrates is demonstrated. PDMAEMA is known to have a unique combination of temperature- and pH-sensitivity along with biocompatibility.[23] In addition, GC has been reported as a suitable material for implants and is considered as a biocompatible material.[24] Thus, fabrication of the SERS substrates based onto the GC modified with biocompatible polymer brushes such as PDMAEMA may open a new field of applications for the biosensing and biomedical applications. A schematic illustration of the fabrication of PDMAEMA–Ag NPs nanoassemblies is shown in Scheme 1.

2. Results

PDMAEMA brushes were grown on GC substrates by SIPGP with UV-light of a spectral distribution between 300 and 400 nm ($\lambda_{\mathrm{max}} = 350$ nm). The prerequisite for realizing the photografting of PDMAEMA brushes on macroscopic surfaces is the possibility of hydrogen abstraction by a radical mechanism under the UV-illumination. Earlier studies demonstrate that polishing of the GC causes the partial oxidation resulting in the generation of the C–OH surface functionalities.[21,25] These groups are exploited for growing the PDMAEMA brushes by means of SIPGP. In addition, it has also been observed that polished GC substrates are covered with up to 10% of aromatic –OH groups.[26] Underlying the low bond dissociation energy of phenolic moieties,[27] it is quite reasonable to assume that hydrogen atoms are also abstracted radically from surface –OH functionalities during the SIPGP process. The thickness of the resulting dried PDMAEMA brushes has been measured as $h_{\mathrm{d}} = 140 \pm 6$ nm by ellipsometry. In situ immobilization of Ag NPs on PDMAEMA brushes has been realized by incubating the brush surface with an aqueous solution of the $AgNO_3$, which led to the adsorption of electron-deficient Ag^+ along the PDMAEMA chains by electrostatic interaction. Subsequently, reduction of coordinated Ag^+ in aqueous $NaBH_4$ solution resulted into the formation of Ag NPs in the PDMAEMA brushes.

Figure 1 shows atomic force microscopy (AFM) scans of PDMAEMA brushes taken before and after the immobilization of Ag NPs. While the bare polymer brush surface appears homogeneous and smooth, the surface morphology changes significantly after formation of the Ag NPs within the brush layer. The root-mean-square (rms) roughness of the bare polymer brushes has been measured as ~1.12 nm, and increases significantly to ~8.80 nm for PDMAEMA–Ag NPs due to the incorporation of NPs. Figure 1b reveals a nearly homogenous distribution of immobilized Ag NPs in the PDMAEMA brushes, suggesting that fabricated brushes can serve as effective adhesion promoters for the immobilization of NPs onto the macroscopic surfaces. In comparison to previously reported studies on the fabrication of SERS substrates, the presented approach offers immobilization of relatively smaller size of the Ag NPs having a much narrower size distribution on an underlying substrate.[28] An increase in advancing water contact angle from $51^\circ \pm 1.5^\circ$ for bare PDMAEMA brushes to $79^\circ \pm 1.7^\circ$ for PDMAEMA–Ag NPs further indicates the increase in roughness of the brush surfaces due to the presence of Ag NPs on the later ones.[29]

In order to confirm the chemical structure of the prepared PDMAEMA brushes, samples were analyzed with X-ray photoelectron spectroscopy (XPS). Figure 2a shows the wide scan spectrum of PDMAEMA brushes, revealing the peaks corresponding to carbon, oxygen, and nitrogen atoms at characteristic binding energies. Figure 2b illustrates a C1s core level spectra of the same sample, which has been deconvoluted into five component peaks (*A*, *B*, *C*, *D*, and *E* as shown in Fig. 2b and c). The intensity ratios of these deconvoluted peaks are in good agreement with the stoichiometric ratio of the corresponding carbon atoms in chemical structure of PDMAEMA as $[B]:[C]:[D]:[E] = 1:3:1:1$. These results strongly confirm that the grafted polymer brush



Scheme 1. Schematic illustration of the fabrication of PDMAEMA brushes by SIPGP and immobilization of Ag NPs.

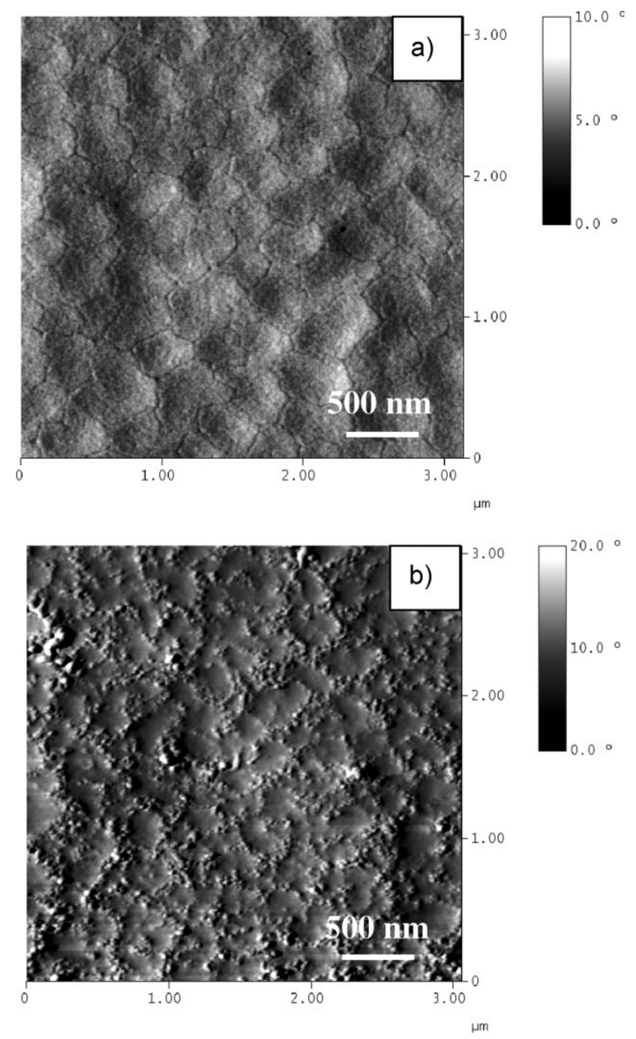


Figure 1. Tapping mode AFM scans (3 × 3 μm^2, phase) of the PDMAEMA brushes a) before and b) after the immobilization of Ag NPs.

layer on GC surfaces is composed of PDMAEMA chains. The presence of Ag NPs in the PDMAEMA brushes is further evidenced by XPS analysis and the results are shown in Figure 3. Figure 3b illustrates the Ag3d core level spectrum of the PDMAEMA–Ag NPs sample, revealing the presence of Ag $3d_{3/2}$ and Ag $3d_{5/2}$ component peaks at 374.2 and 368.2 eV, respectively, along with bulk plasmon satellite peaks. The difference in the binding energies of the Ag $3d_{3/2}$ and Ag $3d_{5/2}$ peaks has been found as $\Delta BE = |BE(Ag\ 3d_{3/2}) - BE(Ag\ 3d_{5/2})| = 6.00$ eV, which is in good agreement with literature values.[30] These results indicate the metallic silver (Ag^0) nature of the immobilized NPs and unambiguously confirm the presence of Ag NPs in the PDMAEMA brushes.

Immobilization of Ag NPs onto the PDMAEMA brushes has been further shown by UV-vis absorption spectroscopy (Fig. 4). In contrast to the bare PDMAEMA brushes, Ag NPs immobilized polymer brushes reveal a strong and symmetric absorption band in the range of 420–432 nm, characteristic for the surface plasmon resonance of the immobilized Ag NPs.[31,32]

In order to demonstrate the application of fabricated PDMAEMA–Ag NP nanoassemblies, we investigated their use as a sensor platform for SERS to detect organic molecules. We chose the Rhodamine 6G (R6G) as model analyte. A representative SERS spectrum of R6G adsorbed on PDMAEMA–Ag NP modified substrates is presented in Figure 5. For comparison, Raman spectra of R6G molecules adsorbed on unmodified and PDMAEMA-only modified GC substrates are also shown in Figure 5. It should be noted that a small peak visible at 500 nm^{-1} in Raman spectra of R6G molecules both in bulk (see Supporting Information 1) and absorbed on PDMAEMA brushes is an artifact that can be attributed to stray light. It is clear from these results that both fluorescence and the SERS intensity increases dramatically for spectra recorded with the aid of the PDMAEMA–Ag NP surface. This can be attributed to the near-field-mediated surface plasmon interaction of the Ag NPs with the adsorbed R6G dye.[33] Usually, the SERS surface enhancement factor (SEF) is calculated according to (SEF) is calculated according to $SEF = (I_{surf}/C_{surf})/(I_{bulk}/C_{bulk})$. In this expression, I_{surf} and I_{bulk} denote the integrated intensities for band of the R6G molecules adsorbed on the PDMAEMA-Ag NPs and those of dissolved in solution, respectively; whereas C_{surf} and C_{bulk} represent the corresponding concentrations of R6G molecules excited by the laser beam.

The SEF for the vibration of aromatic C—C stretching band at 1375 cm^{-1} can be estimated from our measurements: the height of the Raman peak is taken directly from Figure 5 ($I_{surf} = 12000$ counts). Contrarily, the luminescence of an aqueous droplet of R6G is dominated by fluorescence, and hence no proper value can be assigned to the Raman signal I_{bulk}. Therefore, we assume a maximum value of I_{bulk} in the range of the detector noise of 200 counts. (A Raman spectrum of R6G in water (1×10^{-1} M) is shown in Supporting Information 1). As mentioned above, R6G solutions at concentrations of 1.0×10^{-1} and 1.0×10^{-6} M were used for the bulk Raman and SERS experiments, respectively. This calculates to a SEF of 6×10^6. In order to further confirm such a high SEF and exclude any doubts pertaining to the employed experimental parameters, we performed another set of the experiments. After depositing R6G on PDMAEMA–Ag NP modified substrates, we washed the samples with an excess of ethanol and scanned the Raman spectra of remained dye. As expected, we observed the similar SERS signals as shown in Figure 5. However, as large portions of the dye are simply washed away, the absolute signal is observed about one order of magnitude smaller. This further corroborates that our material is suitable for detection of small amounts of dye molecules by SERS.

It should be noted that the observed SEF for the PDMAEMA–Ag NP surface is significantly higher than those obtained previously on the fabrication of SERS substrates by vapor deposition,[34] Ag NP conjugated polymer brushes,[28] defined NP cluster arrays on thin gold film,[35] and even for some nanolithographic structures.[36] The SEF obtained here is comparable to the highest SERS enhancements reported so far for substrates prepared by sophisticated nanolithographic procedures.[37,38] These SERS substrates have small interparticle distances in common. This allows for near-field coupling, which in turn may produce high local excitation fields.[39,40]

Moreover, one can observe that the contrast between Raman signal and fluorescence is improved substantially from unmodified or PDMAEMA-only modified substrates to PDMAEMA–Ag

NP ones. One might expect that if the plasmon-related near-fields enhance the Raman scattering by a factor 6×10^6, fluorescence should also be enhanced by a similar factor. Due to fluorescence quenching, this is not the case for most configurations of dye molecules in the vicinity of metallic nanospheres.[33] This quenching effect reduces the fluorescence to a remainder of only 1%. Consequently, the R6G-specific Raman signature becomes clearly visible. These results succinctly demonstrate that fabricated PDMAEMA–Ag NP brushes can readily be used as a sensing layer for a minute amount of the organic molecules.

3. Discussion

A facile approach to the fabrication of outstanding SERS substrates based on the PDMAEMA–Ag nanoassemblies has been demonstrated. Fabricated composite nanoassemblies have been found to show the surface enhancement factor of 6×10^6 for the detection of R6G by SERS. Because of the facile preparation, the biocompatible nature of the substrate, and the polymer brush, the nanocomposite layer is suitable for the development of a highly sensitive but robust (bio)sensor or other optoelectronic devices to be integrated into living matter. The pH and thermo-responsive properties of the PDMAEMA brush hosting the Ag NPs adds an exciting possibility for the development of switchable devices. The advantages of presented approach over the previously reported ones on polymer brushes include the following. 1) Unlike to the tedious and time consuming approaches,[41–43] the employed method offers an easy and fast way to the fabrication of polymer brushes with as much thickness as 145 nm. The high brush thickness offers a relatively large number of binding sites for NPs along the polymer chains. In addition, an immobilized amount of the Ag NPs can readily be modulated by tailoring the polymer brush thickness by changing the employed reaction parameters. 2) No modification of the substrates prior to the fabrication of polymer brushes is required. Moreover, apart from silicon dioxide, which is considered as the conventional underlined substrate for growing the polymer brushes, the presented approach can be extended to other substrates also such as GCs. 3) As PDMAEMA brushes are directly grafted to the substrates and not via an anchoring layer, they are relatively stable and can be used in robust conditions, where polymer brushes with labile anchoring layers such as silanes/thiols cannot be used.[44,45] 4) Immobilized Ag NPs are relatively smaller in size and nearly homogeneously distributed onto the substrates, which offers a large surface area for

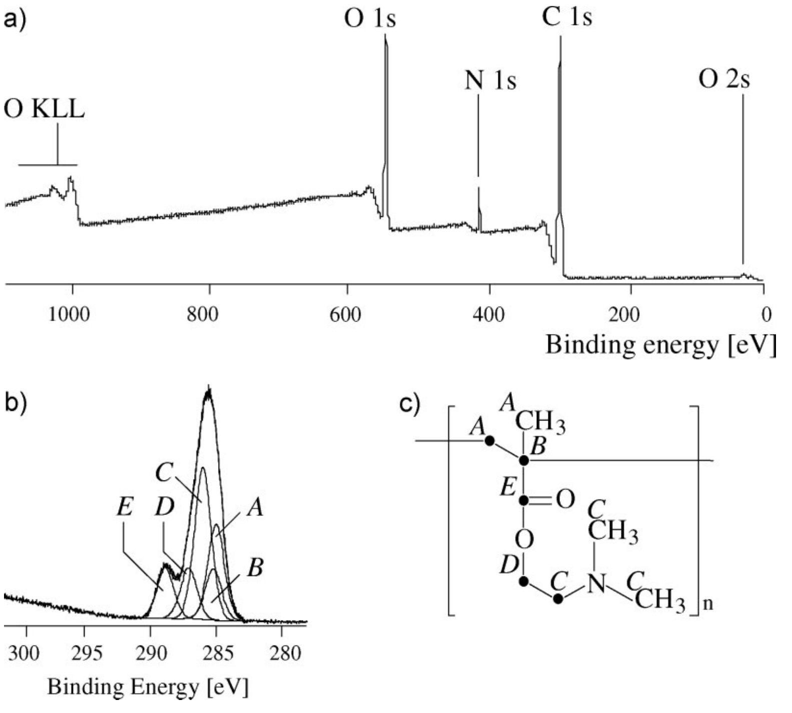


Figure 2. a) XPS survey spectrum and b) C1s core level spectrum of PDMAEMA brushes grafted on GC by means of SIPGP and c) labeling of the different carbon moieties in a PDMAEMA molecule.

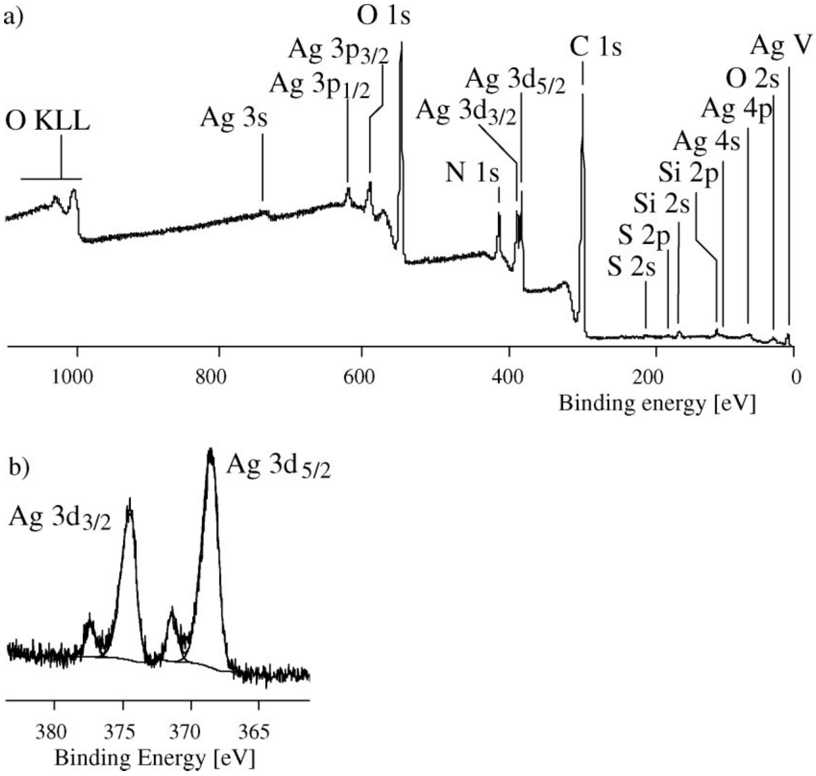


Figure 3. a) XPS survey spectrum and b) Ag3d core level spectrum of PDMAEMA brushes immobilized with Ag NPs.

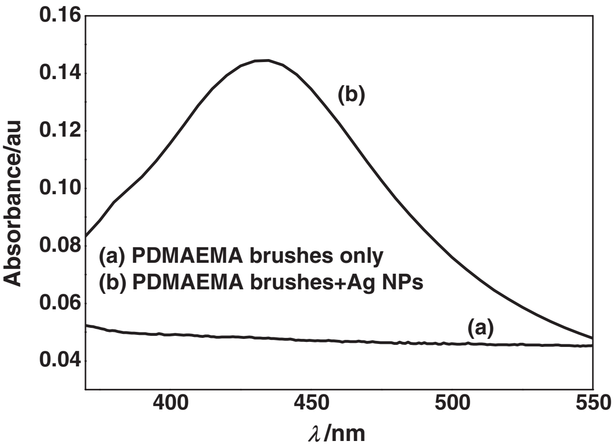


Figure 4. UV-vis spectra of PDMAEMA brushes before and after the immobilization of Ag NPs.

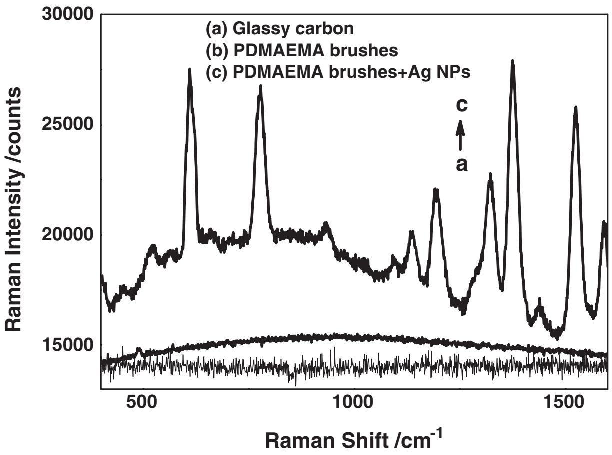


Figure 5. SERS spectra of R6G adsorbed on unmodified, PDMAEMA, and PDMAEMA–Ag NP modified GC substrates.

the adsorbed model analyte resulting into the relatively higher surface enhancement factor. 5) Unlike previously reported studies,[46] immobilized Ag NPs are not covered with any protective shell, which may inhibit the surface plasmon interaction of the Ag NPs with analyte molecules. 6) The employed methodology generates a dense collection of Ag NPs because they are attached at several points on polymer chain and hence SERS can be recorded over the whole surface area but not limited to only few hotspots as reported elsewhere.[47]

4. Experimental

Materials: 2-(Dimethylamino)ethyl methacrylate (DMAEMA >98%) was purchased from Aldrich and passed through basic alumina column before use. Polished GC substrates (SIGRADUR G) were purchased from Hochtemperatur-Werkstoffe GmbH (Germany). Silver nitrate (99.99%), sodium borohydride (99%), and R6G (99%) were purchased from Aldrich and used as received. Toluene, ethanol, and ethyl acetate of analytical grade were obtained from Aldrich and used as received. Millipore water was employed throughout the experiments.

Characterization: Thickness and grafted amount of polymer layers were measured at $\lambda = 632$ nm and at an incidence angle of 70° with a SENTECH SE-402 scanning microfocus ellipsometer equipped with an XY-positioning table for mapping the sample surface. The refractive indices used for the calculations were 1.8689 – i0.7205 and 1.5171 for GC substrate and PDMAEMA brushes, respectively. The advancing water contact angle was measured on a ''DSA-10'' Krüss (Germany) contact angle goniometer. XPS experiments were performed with an AXISULTRA spectrometer (Kratos Analytical, U.K.) equipped with a monochromized Al Kα X-ray source of 300 W at 20 mA. The survey spectra and high-resolution spectra were obtained at analyzer's pass energy set value of 160 and 20 eV, respectively. For UV-vis measurements, samples were prepared on a glass substrate using the same procedure as employed for GC and spectra were recorded with a Perkin Elmer spectrophotometer using substrates without NPs for the base line correction. AFM was performed on a Dimension 3100 (Digital Instruments, Inc., Santa Barbara, CA) microscope. SERS spectra of the samples were acquired with a home-built Raman microscope based on a Zeiss Axiovert 200 microscope and a TII Solar 7504 spectrometer equipped with an Andor DU440 camera.

Preparation of PDMAEMA Brushes: Polished GC substrates were cleaned by sequential ultrasonification in toluene, ethanol, and ethyl acetate before use. Substrates were submerged in the degassed monomer, taken in a polymerization tube, which was tightly sealed and subsequently irradiated with UV light ($\lambda_{max} = 350$ nm) for 1 h at 23 °C. After photopolymerization, the samples were cleaned by ultrasonification for 5 min in each water and ethanol, respectively.

Immobilization of Ag NPs in PDMAEMA Brushes: PDMAEMA-brush-modified GC substrates were stirred in an aqueous $AgNO_3$ solution (0.01 M) for 1 h under argon flow. Subsequently, samples were quickly dipped and stirred into the aqueous $NaBH_4$ solution (0.2 M) for 5 min. Finally, substrates were washed several times with water, dried under argon, and used for further characterizations.

Raman Spectroscopy Measurements: A drop of the aqueous solution of R6G (1×10^{-6} M) was dried under ambient conditions onto the unmodified and PDMAEMA–Ag NP modified GC substrates. Samples were excited with laser light of 532 nm wavelength and 2 mW input power. The diameter of the focused laser spot on the sample was 1 ± 0.1 µm and the integration time of Raman spectrum was 10 s.

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