

Quantum Dot Modification of Large Area Graphene Surfaces via Amide Bonding

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Large-area graphene grown by chemical vapor deposition is functionalized by *p*-aminophenyl groups via the diazonium-route. Subsequently, carboxylic acid-modified CdS_xSe_{1-x}/ZnS dots (QDs) with maximum emission wavelengths of 540 nm and 630 nm are immobilized via amidation reaction to the amino-functionalized graphene on the copper growth substrate forming stable covalent bonds in all functionalization steps. After immobilization of the QDs, the functional QD/graphene stack is available for transfer from the growth substrate onto any other substrate. In this study, the QD-modified graphene is transferred to a Si wafer with surface oxide without losing the QD modification. The successful binding of the QDs onto the functionalized graphene is characterized by their vibrational signature using Raman backscattering and infrared-spectroscopic ellipsometry and by their specific light emission as measured by photoluminescence (PL) spectroscopy.

1. Introduction

The functionalization of surfaces and immobilization of biological macromolecules like enzymes/antibodies or semiconducting quantum dots (QDs) is of great interest in biosensing^[1-8] or photocatalytic applications^[9-12] where such molecules serve as active elements. Among potential applications, the use of graphene

as a substrate in chemical (bio-)sensors or other devices is very promising^[13-15] as graphene can be functionalized and transferred to any other substrate without loss of functionality and with only little reduction in conductivity.^[16] So far, nanocomposites of graphene or graphene oxide and QD material (mostly CdS, Zn_xCd_(1-x)S) have been investigated where the QDs are not covalently bound to the graphene sheets.^[10-12] Recently, paper tissue was modified by grafting cellulose fibers with imidazole and dithiol, or by aminosilanization to immobilize QDs and Au/Pt-nanoparticles by interaction of free electron pairs of nitrogen and sulfur atoms with the adsorbates.^[17] As reported earlier, the transfer of graphene, which has

been functionalized on its growth substrate, represents a facile way to modify any kind of surface with thin films of macromolecules immobilized via maleimido-functionalized graphene.^[18]

The 2D-carbon material graphene, consisting of only a single atomic layer of sp²-hybridized carbon, has been at the center of research during the past years. Graphene is highly sensitive to chemical changes in the vicinity of its surface, which leads to doping effects and hence, a shift of the Fermi energy. However, this versatile sensitivity to almost every analyte comes at the price of selectivity,^[19-21] an issue that can be solved by the aforementioned immobilization of selective receptors. To achieve homogeneously distributed and controllable immobilization, anchor layers providing functional groups for linking reactions are necessary. Different approaches are known to deposit such linkers, mainly separated by the kind of interaction enabling the immobilization. Among those, the electrochemical reduction of aryl diazonium salts is a common method to introduce covalently bound functional groups.^[22-27,28] Major advantages of this kind of functionalization are the vast number of functional groups to select from, the low thickness of the functional layer, which is typically equivalent to a range of one to five molecular layers, as well as the covalent nature of the formed bond between the graphene lattice and the aryl residue. The latter is often considered a compromise, as the strong bonding is accompanied by the formation of sp³-defects in the graphene lattice.^[28]

In this paper, a route is described that shows how graphene is modified by covalently binding QDs with a diameter of ≈6 nm to its surface. Subsequently, these layers are transferred to a desired substrate while preserving the light-emitting properties of

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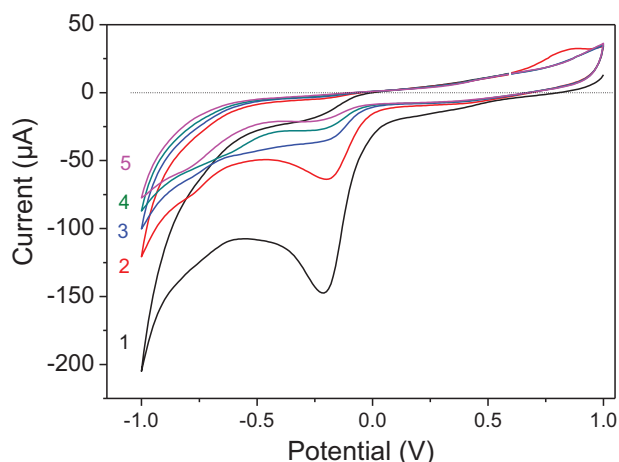


Figure 1. Current-voltage scans of graphene covered copper foil in 1 mM *p*-aminophenyl diazonium tetrafluoroborate (*p*-APDT) solved in acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate as conducting salt. The scan rate was 100 mVs⁻¹.

the QDs. First, we demonstrate the immobilization of QDs on graphene, which previously had been functionalized with amino groups via the deposition of *p*-aminophenyl residues derived from the corresponding *p*-aminophenyl diazonium cation. The deposited *p*-aminophenyl residues are used as anchoring groups in an amide bond formation reaction^[29] introducing two different kinds of QDs on the surface. The immobilization of the QDs was achieved by crosslinking the surface-bound amino groups and the QD surrounding carboxylic acid-containing polymer matrix. This represents a similarity to proteins, which may have a lot of carboxylic acid groups available in their shell due to the amino acid. The resulting surfaces were investigated by photoluminescence (PL) spectroscopy, while the deposited amino functionalities as well as the bond formation between the functionalized graphene surface and QDs were analyzed using infrared-spectroscopic ellipsometry (IRSE).

2. Results and Discussion

Graphene was functionalized by cycling the potential five times between +1 V and -1 V at a scan rate of 100 mVs⁻¹ in the *p*-APDT containing solution. The corresponding current-voltage scans are presented in **Figure 1**. The reductive current ≈ -0.2 V is reduced with every potential scan pointing to the formation of a passivating layer of *p*-AP as sketched in **Figure 2**.^[29,30]

Figure 2 shows a scheme of the activation of the carboxylic acid-modified QDs by EDC-HCl and their binding via amide bonding onto the *p*-aminophenyl modified graphene (*p*-AP/Gr).

The functionalization of the graphene layer by *p*-AP groups and the subsequent covalent bonding of the carboxylic acid-modified QD-shells to the *p*-AP-functionality were confirmed using Raman backscattering and IRSE.

The Raman spectrum in **Figure 3a** shows a spectrum of the pristine graphene with the G-band (at ≈ 1584 cm⁻¹) and only little contribution of the D-band (at 1353 cm⁻¹) due to distortion of the graphene sp²-hybridization. The spectrum in **Figure 3b** reflects the *p*-AP functionalized graphene with a lowering of the G-band

amplitude and a more pronounced D-band (shifted to slightly higher energy of 1364 cm⁻¹) as a result of the binding of *p*-AP molecules to the graphene that leads to a partly sp³-hybridization. This is also supported by the formation of the D'-band visible as a shoulder at the higher energy part of the G-band (at 1620 cm⁻¹). The analysis of the intensities of the D/G band ratio (I_D/I_G) after fitting of baseline corrected Raman-spectra according to Wang et al.^[31] for diazonium functionalized graphene leads to a defect density of $N_D = 1.1 \times 10^{13}$ cm⁻² within the graphene lattice using $N_D = 1 / L_D^2$ with the distance between covalent reaction sides of $L_D = 3.1$ nm, as derived from the I_D/I_G ratio of 1.31 of the functionalized graphene.^[31]

Figure 4 shows normalized tan Ψ spectra of a dried droplet of the carboxylic acid modified QDs on c-Si (a), of the *p*-AP-functionalized graphene (b), and of the QDs bound to the *p*-AP-functionalized graphene (c). Reference spectra were measured on c-Si covered with a native oxide layer (a), non-functionalized graphene on Cu foil (b), and the *p*-AP-functionalized graphene on Cu foil (c). The sketch on the right side of **Figure 4** depicts the measured species. The QDs show a pronounced band ≈ 1600 cm⁻¹ that relates to a high amount of deprotonated carboxylic acid groups (COO⁻). A weaker band at ≈ 1720 cm⁻¹ is due to a minor number of COOH groups of the QDs (see dashed line in **Figure 4a** that is the red solid spectrum magnified by 20). This phenomenon seems to be a result of the preparation process of the carboxylic acid functionalization performed in alkaline solution as typically used for CdSe-QDs.^[32]

The *p*-AP-functionalized graphene on Cu foil (**Figure 4b**) shows no pronounced vibrational bands in this spectral range. Finally, the presence of the amide I vibrational band at ≈ 1660 cm⁻¹ confirms the covalent bonding of the QDs to the *p*-AP functionalized graphene (**Figure 4c**). Furthermore, a band due to absorptions of C=O vibrations of the COOH and/or the NHS groups of the coupled QDs emerge ≈ 1736 cm⁻¹. Handling of the QDs in aqueous, slightly acidic solution should lead to protonation of non-bonded carboxylic acid groups in the shell of the QDs. The acidity of the solution is caused by HCl that originates from EDC. Additionally, a weak contribution due to vibrations of residual COO⁻ groups of the QDs at ≈ 1600 cm⁻¹ is visible as a shoulder in **Figure 4c**. Characterization by IRSE reveals the successful immobilization of the QDs on *p*-AP/graphene via amidation on the copper growth substrate of the graphene. In the next step, graphene modified with QDs is transferred to another substrate without loss of the functional properties. To demonstrate this, the presence of both types of QDs was examined via their most outstanding property, exhibiting an intense PL after transfer to another substrate. **Figure 5** shows PL spectra of solutions of the pure QDs emitting at 540 and 630 nm (dashed lines), and the respective QD-modified *p*-AP/Graphene stacks after transfer to a SiO₂-coated silicon wafer (solid lines). The QD concentration in acetonitrile was 100 μ g mL⁻¹. Both QDs show a strong PL signal with a maximum at the desired wavelength of ≈ 540 and 630 nm.

The QDs that bind to the *p*-AP-functionalized graphene show a much broader PL emission than those in solution. Moreover, the emission peaks show a blue shift. The spectra of the QD⁵⁴⁰/*p*-AP/Graphene and QD⁶³⁰/*p*-AP/Graphene stacks are magnified by a factor of 40 compared to the spectra measured on QDs in solution. This very weak PL intensity is a result of the extremely thin layer of QDs on the *p*-AP-functionalized graphene

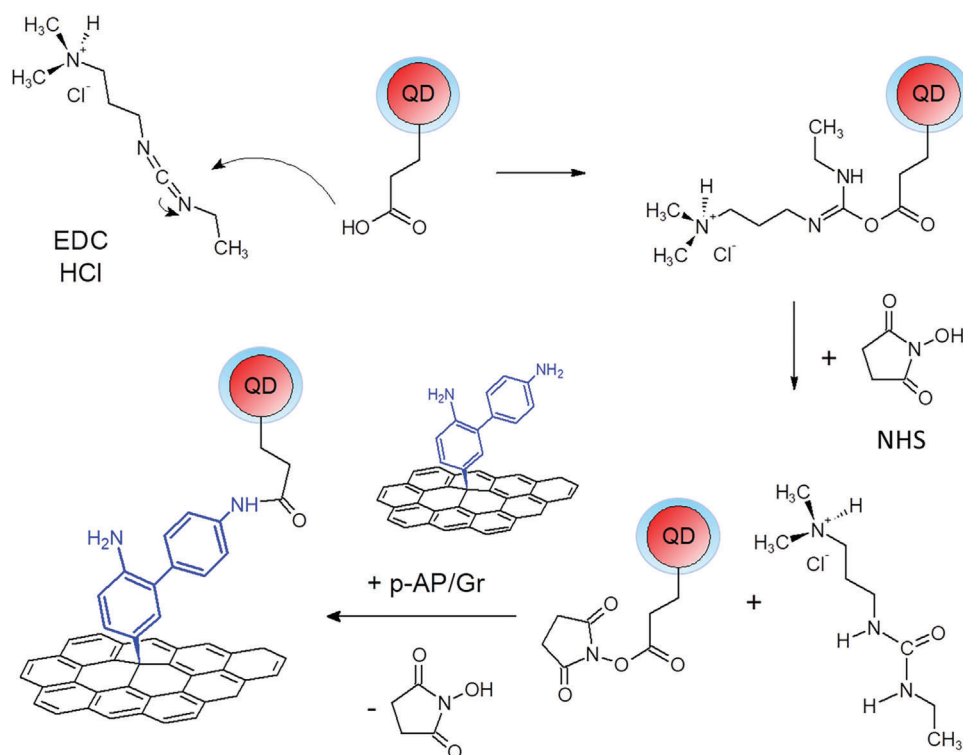


Figure 2. Activation of the carboxylic acid modified QDs via EDC·HCl and NHS and the bonding to *p*-AP-functionalized Graphene (*p*-AP/Gr) via amidation reaction. The arrows indicate the different steps of the functionalization process.

surface in comparison to the QD solutions, which were measured in cuvettes with an optical pathlength of 1 cm. These observations may be due to close interaction of the QDs with the covalently modified, but still conductive graphene or the substrate surface, partial damaging of the QD shell during the activation with EDC/NHS, or the presence of residual NHS groups at the shell from the activation process.^[33–35] The observed pho-

toemission of the covalently immobilized monolayer of QDs is, however, impressive. To further improve the response, especially with respect to the broadening of the photoemission, the stability of the QDs' shell has to be enhanced. Furthermore, by increasing the distance between the graphene and the QDs, e.g. by increasing the length of the carbon chain in between the two, a narrower response should be observed as well.

The detected photoemission underlines the successful transfer of the *p*-AP functionalized graphene subsequent to QD-immobilization via amidation. The layer of QDs on graphene is extremely thin. Assuming a diameter of 6 nm and using a surface area of $6 \times 6 \text{ nm}^2$ per QD (quadrat instead of circle as the QD is surrounded by carbon chains with -COOH groups) one gets 2.8×10^{12} QDs per cm^2 as maximum density on the surface of the graphene. This is ≈ 4 -times less than the defect density of $1.1 \times 10^{13} \text{ cm}^{-2}$ as obtained from the analysis of the I_D/I_G ratio of the Raman investigation of the *p*-AP functionalized graphene (see Figure 3). The transfer is a process involving a sequence of steps imposing mechanical and chemical stress for the functionalized graphene (polymer coating, copper etching, solvent cleaning, drying in stream of N_2 , etc.). However, the QDs keep their light-emitting properties after the processing, which can be detected despite of all the treatments and the extremely small layer thickness. This underlines the exceptional persistence and stability of the covalent modification approach. Furthermore, this carries potential for applications of such QD-graphene layers on its own, and also shows the high potential for specific covalent immobilization.

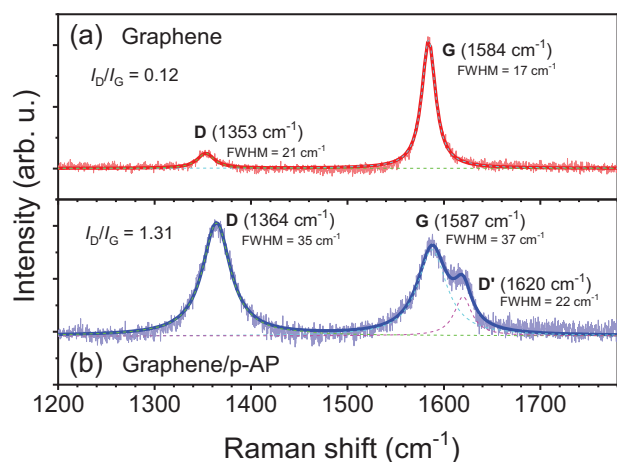


Figure 3. Background corrected Raman spectra of pristine graphene (a) and the *p*-AP functionalized graphene (b). The D, G and D' peaks are fitted with Lorentzians. The position and FWHM of each peak are indicated along with the I_D/I_G ratio used for the determination of the defect density.

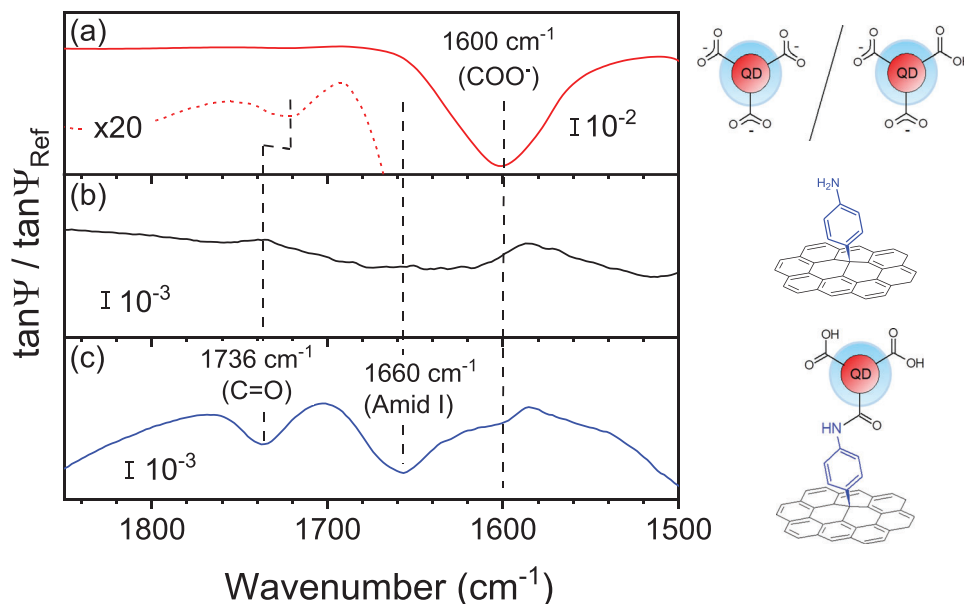


Figure 4. $\tan\Psi/\tan\Psi_{\text{Ref}}$ spectra of a dried droplet of carboxylic acid modified QDs on c-Si with native oxide (a), of *p*-AP-functionalized graphene on Cu (b), and of QDs bound to the *p*-AP-functionalized graphene on Cu (c). The spectra used as $\tan\Psi_{\text{Ref}}$ were measured on c-Si covered by native oxide for (a), the graphene on Cu foil for (b), and the *p*-AP-functionalized graphene on Cu foil for (c).

3. Conclusion

Graphene was functionalized by *p*-aminophenyl groups and bound carboxylic acid modified $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ QDs to these *p*-aminophenyl groups via amidation reaction. The bonding of the QDs was monitored by infrared spectroscopic ellipsometry and PL spectroscopy by verification of specific amide related vibrations and PL emission associated to the bandgap of the QDs. Furthermore, the QD-modified graphene sheets were transferred to silicon substrates without losing the respective QD-

modification. This process is not limited to silicon, any other kind of surface can be used. By selection of the respective carboxylic acid modified QD, an emission wavelength or a mix of different emission wavelengths of choice will be available. Moreover, our studies indicate that it is possible to covalently immobilize macromolecules with a size of several nanometers on aryl-functionalized graphene. As many applications involving graphene demand the deposition of such macromolecules, e.g. enzymes as receptors for biosensors, this method reveals a pathway for an easy and efficient way to provide functional graphene ready-to-transfer to a vast variety of substrates. However, depending on the used biomolecules, it might be necessary to choose different chemicals for support and solvents that have to be tested individually.

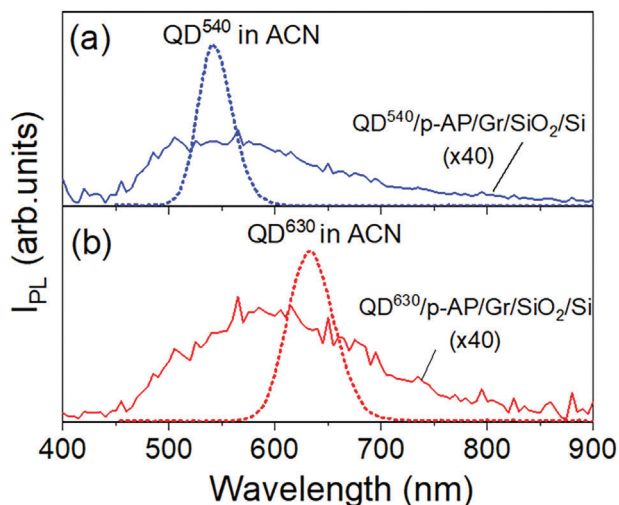


Figure 5. PL spectra of QD^{540} (a) and QD^{630} (b) in solution (dashed lines) and of QD-modified *p*-AP/Graphene on a 300 nm thick SiO_2 layer (solid lines). For both QDs, the concentration amounted to $100 \mu\text{g mL}^{-1}$ in solution. Note the spectra measured on the functionalized samples are multiplied by a factor of 40.

4. Experimental Section

Large-area graphene was grown by chemical vapor deposition (CVD) on a 25 μm thick copper foil using a gas mixture of methane (CH_4) and hydrogen with a flow ratio of 16:1. The total flow rate amounted to 12 sccm. The deposition temperature and gas pressure were set to 1050 $^\circ\text{C}$ and 0.5 mbar, respectively. For functionalization, the graphene covered copper foil was integrated as a working electrode (WE) into an electrochemical cell using a gold wire as counter electrode and an Ag/AgCl [sat. KCl] reference electrode (RE). *p*-Aminophenyl diazonium tetrafluoroborate (*p*-APDT) used for the electrografting of graphene with *p*-aminophenyl residues (*p*-AP) was synthesized according to Becker et al.^[36] The electrolyte consists of 1 mM *p*-APDT and 0.1 M tetrabutylammonium tetrafluoroborate as conducting salt dissolved in acetonitrile (ACN).

The modification of the amino-functionalized graphene with Trilite[®] QD was performed according to Zhang et al.^[29] using 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl) and N-hydroxy succinimide (NHS) as crosslinking agents. The QDs, functionalized by carboxylic acid groups, were purchased from Sigma-Aldrich. The $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ QDs had a diameter of 6 nm with a maximum wavelength emission at 540 nm or 630 nm, respectively. For transfer, the resulting

Table 1. Advantages and disadvantages of the functionalization of graphene before or after transfer to any substrate.

Functionalization	Advantage	Disadvantage
Before transfer	(a) More homogeneous layer due to very good electrical contact via Cu-substrate. (b) No need for the user to do surface functionalization and any chemistry (c) Functionalized graphene is prepared in advance and can be used at any time when needed	Dissolution of the supporting layer on the functionalized graphene may damage the functionality, this can be avoided by a proper choose of support/solvent combination.
After transfer	The user is more flexible by choosing the functional layer and can apply his/her own chemistry processing.	Possible inhomogeneous layer if the graphene is only contacted at one point/edge for the electrochemical functionalization.

QD-functionalized graphene was protected by a thin nitrocellulose-based polymer support prior to removal of the copper substrate in a solution of 0.1 M ammonium peroxodisulfate in deionized water at 50 °C. The support/QD/*p*-AP/graphene stack was free-floating on the liquid surface, transferred to deionized water for cleaning, and finally picked-up with a Si-wafer coated with 300 nm SiO₂. Subsequently, the nitrocellulose was removed with ethyl acetate and the resulting surface was dried in a nitrogen stream. All surfaces were rinsed multiple times with deionized water and ethanol and purged in dry air prior to spectroscopic characterization. Functionalization prior to the transfer is preferred, due to the advantages discussed in **Table 1**.

Infrared spectroscopic ellipsometry (IRSE) results were recorded using an ellipsometric set-up attached to a Fourier Transform-Infrared (FT-IR) spectrometer (TENSOR 37, Bruker, Germany). The spectra were obtained with a resolution of 4 cm⁻¹ using a mercury cadmium telluride detector cooled with liquid nitrogen. TanΨ is defined as the ratio of amplitudes of p- and s-polarized reflection components. The geometry of the experimental set-up can be found in the literature.^[37] Referenced tanΨ-spectra (tanΨ/tanΨ_{ref}) are used to visualize the relatively weak signals from the thin films. The PL spectra were obtained using a time-integrating Si photodetector that is connected to a prism-monochromator. For the excitation a pulsed laser with a repetition rate of 10 Hz and an excitation wavelength of 337 nm was used. The laser fluence amounted to 16 μJ.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

amide bonding, graphene, IRSE, quantum dots, surface functionalization

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