

Electrochemical Synthesis of CdSe Quantum-Dot Arrays on a Graphene Basal Plane Using Mesoporous Silica Thin-Film Templates

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Since the discovery of microscale single-layer graphene in 2004,^[1] graphene and related materials^[2] have received intensive attention as promising materials for nanoelectronics because of their fascinating electrical,^[3] mechanical,^[4] and chemical properties.^[5,6] In addition, the recent large-scale synthesis of high-quality graphene films enables their use in bendable and/or stretchable transparent electrodes^[7] for solar cells, sensors, and displays. Surface grafting on graphene of functional materials will be an indispensable technique for these applications. This, however, requires the problems arising from the lack of reactivity of the graphene basal plane to be resolved. A perfect graphene structure does not have dangling bonds on the basal plane for chemical-bond formation. The chemical potential of the basal plane is lower than that at the edges or defects. Therefore, deposition occurring directly on a graphene structure usually results in grafting on the edges and defects only.^[8] Using vacuum-deposition techniques, this problem may be solved by modifying the graphene surface by, for instance, ozone treatment, forming a metal underlayer, or attaching organic molecules with functional groups.^[9] Thus far, however, there has been no reports on grafting on the graphene basal plane using electrochemical techniques. Sundaram et al. reported that varying the potential during the electrochemical deposition of Pd did influence the number density of the Pd nanoparticles,^[10] but the site of deposition was still restricted to the edges only. None of the surface-modification methods used in vacuum deposition seem to be appropriate for electrochemical deposition because they cannot change the potential difference between the basal plane and the edges/defects.

Here, we demonstrate that the use of a nanoporous mask can be a viable means to form a uniform nanostructured film on the graphene basal plane. We applied a mesoporous silica thin film

whose pore structure is composed of about 8-nm sized vertical channels in a hexagonal symmetry (denoted as SKU-1 in a previous report)^[11] on the graphene surface as a nanoporous mask. The nanochannels exert resistance against the diffusion of electrolytes and, thus, function as a potential-equalizer to suppress the preference for the edge and defect sites. By depositing CdSe particles, we were able to form CdSe quantum dots into a hexagonal array structure. The synthesis procedure of the present study is outlined in Figure 1.

The graphene electrodes were synthesized by chemical vapor deposition of methane on thin Ni layers formed on SiO₂/Si substrates.^[7] The Raman spectra show that the graphene films are composed of individual graphene sheets of 1 to 5 layers (Supporting Information). A mesoporous silica film was formed on top of this graphene/Ni bi-layer by spin-coating a precursor solution composed of tetraethoxyorthosilicate (TEOS) and a triblock non-ionic surfactant F-127 (EO₁₀₆PO₇₀EO₁₀₆, EO = ethylene oxide, PO = propylene oxide), followed by aging at 80 °C, and calcination at 400 °C.^[11] The pore morphology of these mesoporous silica films, as characterized by scanning electron microscopy (SEM), showed arrayed pores on the film surface, a feature expected for the SKU-1 film (Supporting Information). By using the SKU-1-coated graphene as a working electrode, CdSe was deposited under a constant potential of -0.7 V at 50 °C. After the deposition, the SKU-1 template was removed by dissolving in an aqueous HF solution. We also prepared a CdSe film grown on a graphene/Ni bi-layer without the SKU-1 coating following the same procedure except for the formation of SKU-1. The energy-dispersive X-ray spectroscopy (EDS) data on these samples show the presence of Cd and Se for both samples (see Supporting Information).

Figure 2 shows the morphologies of the two CdSe films. The atomic force microscopy (AFM) image of the film without the SKU-1 template (Fig. 2a) shows that CdSe was deposited into lines forming closed loops enclosing domains of various areas from $0.3 \mu\text{m} \times 0.3 \mu\text{m}$ to $1.5 \mu\text{m} \times 1.5 \mu\text{m}$. Based on the literature data on graphenes, these loops are probably the edges around the multiple layered graphene sheets.^[7] The height of the CdSe deposits varied from 7 to 9 nm as determined by AFM height scans. The SEM images on this sample with a higher magnification (Fig. 2b) reveal that the loops are composed of small CdSe particles and that there are also CdSe deposits on the basal plane, probably at the defect sites. Compared to literature data on the electrochemical deposition of Pd on graphene,^[10] our data shows a much higher density. Probably, the Ni underlayer present in our samples provides conduction paths, thus, circumventing the problem of high resistance of the graphene basal plane.

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The images of the SKU-1-templated CdSe film show that the template brings about quite a dramatic effect. The wide-area AFM image (Fig. 2c) shows that the loop-like structure seen in Figure 2a on the CdSe film formed without SKU-1 template has

disappeared. Instead, the whole surface of graphene is covered with a very fine structured film. The height variation plot across the image shows that the film is composed of even-sized particles of about 5–12 nm in height. The SEM image (Fig. 2d) shows that arrays of dots are arranged into a hexagonal symmetry and the dot-to-dot distance is measured to be 14 nm. These morphological characteristics agree well with the pore structure of the SKU-1 template.

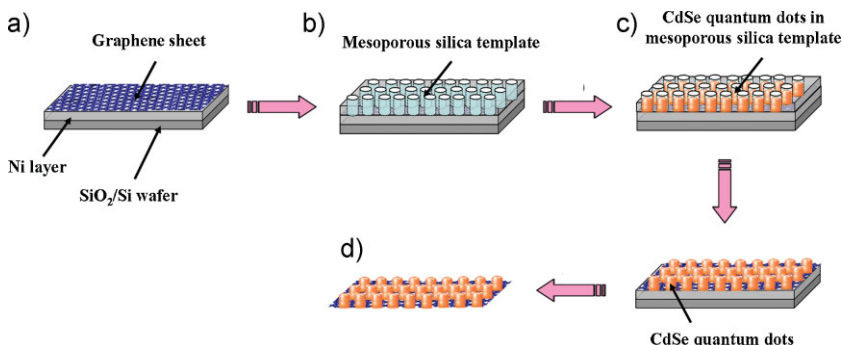


Figure 1. Procedure to synthesize a CdSe quantum dot array on the basal plane of a graphene sheet using a mesoporous silica thin film as a template: a) Formation of a mesoporous silica film on the graphene surface by spin-casting, aging, and calcination, b) electrochemical deposition of CdSe onto the graphene surface through the pores of the mesoporous silica film template, c) removal of the mesoporous silica template, and d) removal of the Ni layer underneath the graphene sheet.

Figure 3 shows the transmission electron microscopy (TEM) images of the CdSe quantum-dot array grown using the SKU-1 template. The TEM sample was prepared by removing the Ni underlayer by treating with a FeCl_3 solution.^[7] These images clearly show that this film is composed of nanoparticles in a hexagonal array structure. The dot size was measured to be 10 nm and the dot-to-dot separation 14 nm, confirming the above AFM and SEM results. The selected-area electron diffraction (SAED) pattern of this sample (Fig. 3c) shows a ring pattern with $d = 0.26$, 0.22, and 0.18 nm matching the (102), (110), and (112) peaks of the hexagonal form of CdSe. The magnified image in Figure 3b also shows lattice fringes that are indicative of the CdSe lattice.

Our data clearly show that the combination of i) the use of graphene with a Ni underlayer and ii) the use of SKU-1 as a nanoporous mask makes it possible to synthesize CdSe quantum dots into an array structure on the graphene basal plane. The effects of these two measures can be explained as a decrease in the difference between the resistance at the edge/defect sites and that of the basal plane. The Ni underlayer provides conduction paths so that it can reduce the resistance on the basal plane. The nanoporous SKU-1 mask functions as a diffusion barrier for the incoming ions in the electrolyte solution, which overrides the conductivity difference between the edges/defects and the basal plane. Furthermore, the regular pore structure of SKU-1 functions as a template to deposit quantum dots into an array structure.

The Raman spectroscopy data in Figure 4 show that the CdSe quantum dots induce red-shifts of the G and 2D bands of graphene by 5 and 9 cm^{-1} , respectively. In order to verify that these changes are indeed induced by the CdSe quantum dots, we treated graphene films in various ways similar to the method used to form CdSe quantum dots but without the deposition of CdSe and measured their Raman spectra (Supporting Information). None of these manipulated graphene films produced similar changes both in direction and magnitude of the Raman peaks, which leads us to conclude that the large red-shifts are related to

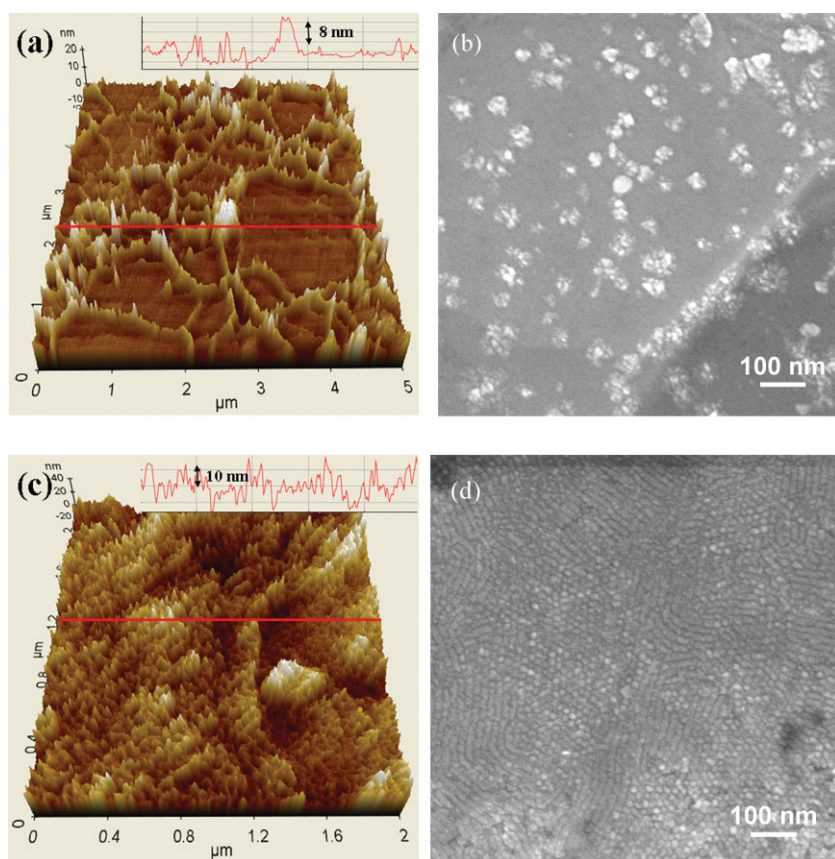


Figure 2. a) AFM and b) SEM images of CdSe grown on a pristine graphene sheet without a mesoporous silica film template, c) AFM and d) SEM images of a CdSe quantum-dot array grown on a graphene sheet by using a mesoporous silica film template. The insets in (a) and (c) are the height profiles taken along the red lines marked in the corresponding AFM images.

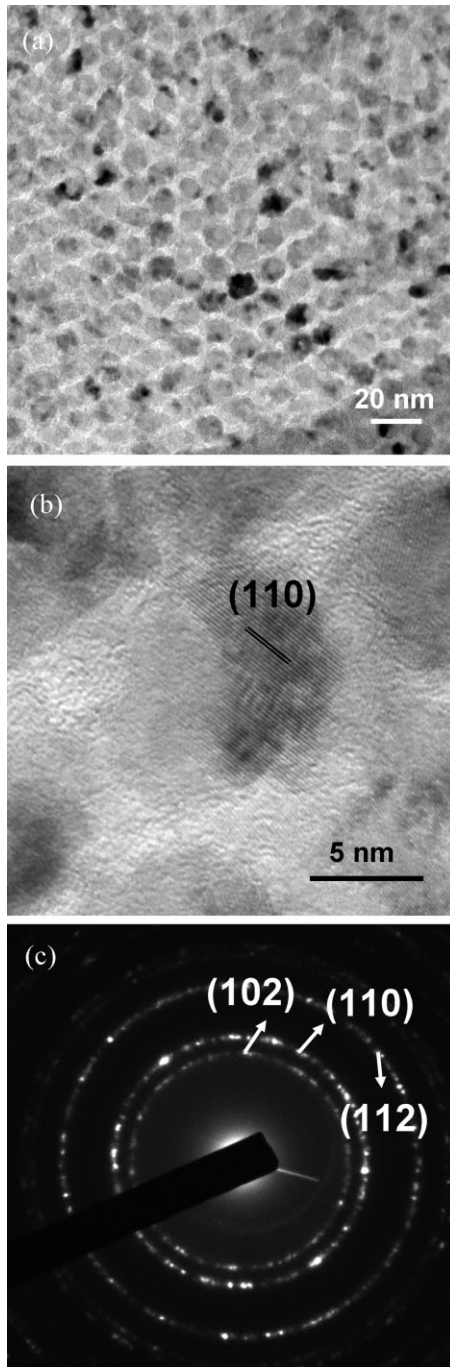


Figure 3. a) High-resolution TEM image of a CdSe quantum dot array, b) enlarged view of (a) to reveal the lattice fringe, and c) SAED pattern.

the CdSe quantum dots. The G and 2D band positions are known to be sensitive to electron or hole doping.^[12,13] The observed red-shifts imply that the graphene sheet is doped with electrons. From the magnitude of the G-band shift, the charge-carrier (electron) density is estimated to be $3.0 \times 10^{12} \text{ cm}^{-2}$, which corresponds to an up-shift of the Fermi level by around 100 meV compared to that of pure graphene. This level of n-doping is larger than that reported for viologen-modified carbon nanotubes

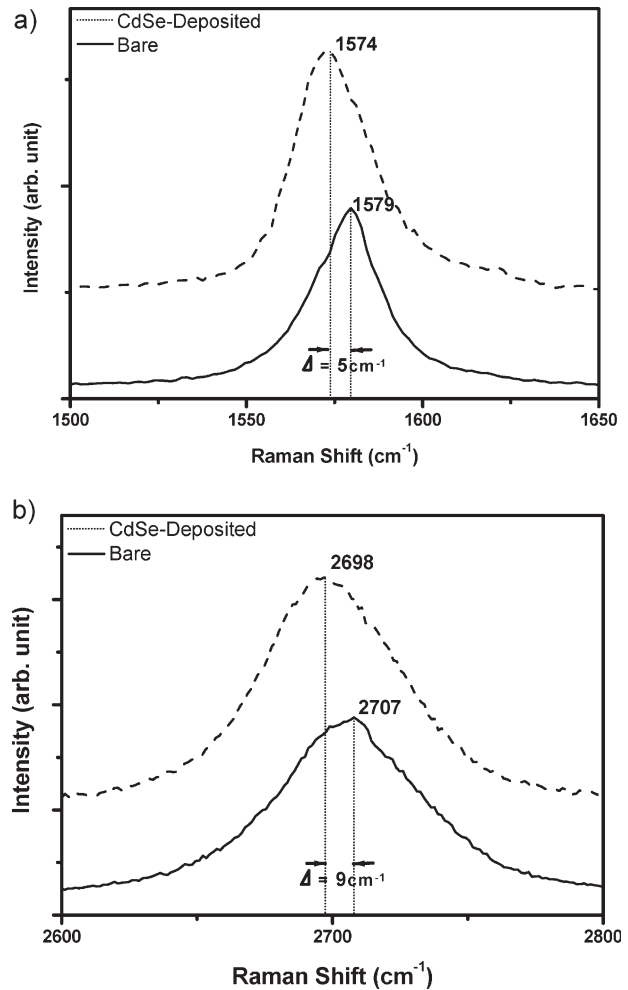


Figure 4. a) G-band and b) 2D-band Raman spectra of a graphene sheet with CdSe quantum dots deposited on the surface (dashed lines) and a bare graphene film (solid lines).

(CNTs), which showed a G-band shift of 2 cm^{-1} .^[14] These data are truly significant as most of the surface modifications of graphene in the literature result in p-doping.^[15,16] Therefore, the n-doping characteristics of the CdSe quantum-dot-modified graphene may find applications in engineering bandgap structures of graphene nanostructures for various electronic applications.

The mechanism of n-doping by CdSe quantum dots is quite intriguing. Because the work function of graphite, reported to be 4.6–5.0 eV,^[17,18] is located at the HOMO–LUMO gap of CdSe,^[19] it is possible that electrons from the conduction band of CdSe quantum dots flow into graphene. Very recently, Farrow and Kamat reported that CdSe quantum dots on CNTs can inject electrons into the CNTs by this mechanism.^[20] On the other hand, Zhou et al. reported that an epitaxially grown graphene on a SiC substrate was n-doped and discussed that this was probably associated with the surface charges at the interface between graphene and SiC substrate,^[21] which might also be the case for our system. Alternatively, although bulk CdSe is known to be stoichiometric, with Cd/Se = 1:1, it is possible to make CdSe nanoparticles that have an excess of either Cd- or Se.^[22] Therefore,

if the CdSe quantum dots in our samples have an excess in Se and, thus, are n-doped, they may be able to cause the n-doping of the graphene. Further studies are required to better understand the effect of the CdSe quantum dots to the red-shifts of the Raman peaks.

In summary, we demonstrate, for the first time, a method that can produce a homogenous, nanostructured thin film with an ordered nanostructure on the basal plane of a graphene by electrochemistry. This method enables the direct contact between the CdSe quantum dots and the graphene film without intervening layers, possibly leading to the enhancement of the electrical and mechanical properties.^[23] With these functionalities, the present method is expected to open a new horizon for exploring graphene in many different fields.

Experimental

Synthesis of Graphene: The graphene/Ni bi-layer was synthesized by the chemical vapor deposition method reported before [7]. A thin layer of nickel (less than 300 nm) was formed on a SiO₂/Si substrate using an electron-beam evaporator and was placed in a quartz tube under an argon atmosphere. The temperature was raised to 1000 °C and a reaction gas mixture (CH₄/H₂/Ar = 550:65:200 standard cubic centimeters per minute) was allowed to flow through. Then the substrate was cooled to room temperature at a rate of about 10 °C s⁻¹. A graphene film was formed on top of the nickel layer.

Synthesis of Mesoporous Silica Thin Films: A stock solution for SKU-1 was prepared by dissolving TEOS (99.999%) and F-127 (EO₁₀₆PO₇₀EO₁₀₆, EO = ethylene oxide, PO = propylene oxide) in a mixed solution of diluted aqueous HCl and absolute ethanol to make the composition TEOS/F-127/HCl/H₂O/EtOH = 1: 6.60 × 10⁻³: 6.60 × 10⁻³: 4.62: 22.6 (molar ratio). The solution was stirred at 20–25 °C for 12–20 h under a controlled relative humidity of below 20% before use. The stock solution was spin-coated on the graphene/Ni bi-layer substrate, aged at 80 °C, and calcined at 400 °C to form a nanoporous silica thin film.

Electrochemical Synthesis of CdSe Quantum Dots: A corner of the SKU-1 film on the graphene/Ni bi-layer was etched out to reveal the graphene surface to make an electrical contact with a wire for the consecutive electrochemical deposition. Using a SKU-1-coated graphene as the working electrode, a Ag/AgCl reference, and a Pt counter electrode in a three-electrode cell, as well as an aqueous electrolyte solution (0.3 M CdSO₄, 0.003 M SeO₂), CdSe was deposited under a constant potential of -0.7 V at 50 °C [24]. After the deposition, the SKU-1 template was removed by dissolving in an aqueous 0.2 wt % HF solution. A CdSe film on a graphene/Ni bi-layer without the SKU-1 coating was also prepared following the same procedure except for the formation of SKU-1.

Characterization: SEM (JEOL 7100F, 5–10 kV), AFM (Park systems XE-NSOM; non-contact mode), and TEM (JEOL JEM 3010, 300 kV) were used to characterize the samples. Raman spectra were recorded with a Renishaw RM 1000-Invia by using a 514 nm excitation and a notch filter of 50 cm⁻¹. The spectral resolution is 0.2 cm⁻¹.

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