Supplementary for

Laser-Activated Area-Selective Atomic and Molecular Layer Deposition on 2D Materials

Recently, we proposed a way to overcome the chemical inertness of graphene to ALD precursors by locally activating the surface using direct femtosecond laser (fs-laser) two-photon oxidation (TPO) for area-selective ZnO deposition (*DOI: 10.1002/admi.202201110*). This method photochemically attaches oxygen-containing groups to graphene by exposing it to ultrafast laser pulses under an ambient atmosphere. As a result, epoxy and hydroxyl groups form on the graphene surface with moderate laser exposure, while carbonyl and carboxyl groups appear at higher irradiation doses, closer to the ablation threshold. TPO provides precise control over the oxidation level of graphene and enables the patterning of complex structures with high spatial resolution (~300 nm), with the potential to achieve below 20 nm resolution using tip-enhanced techniques. Additionally, this is a simple, resist-free ultrafast direct laser writing (UDLW) method, and the oxidized graphene surface can be restored to its initial state through thermal annealing in an inert atmosphere.

Here, for the first time, we perform area-selective ALD/MLD on the 2D materials surface with sub-micron resolution in a controllable manner, utilizing the chemical interactions of precursors with the TPO surface and restoring graphene to its initial state. Europium-organic thin films deposited via ALD/MLD show interesting photoluminescence properties, which are difficult to achieve using typical ALD of europium oxide. We combined UDLW and area-selective deposition to develop luminescent graphene/Eu-BDC heterostructures in predefined areas using TPO (see Figure 1). We achieved high homogeneity and over 90% selectivity in locally activated graphene regions for Eu-organic films up to 11 nm. The fabricated graphene/Eu-organic thin films exhibited high photoluminescence emission even when excited with a continuous wave 532 nm laser, while Eu^{3+} ions typically require UV excitation. These ALD/MLD films can also act as inhibitors for subsequent depositions, allowing for the addition of new functionalities to graphene-based heterostructure devices.

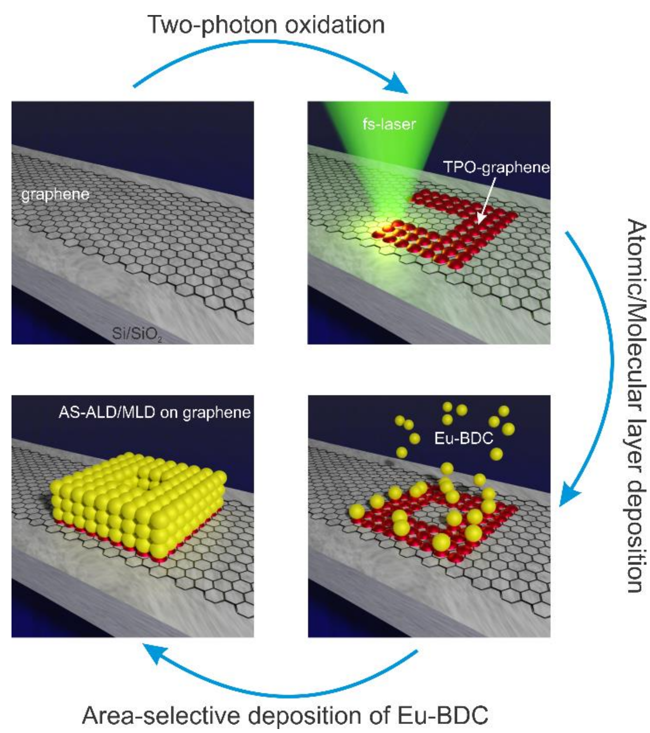

Figure 1. Process flow for ALD/MLD of Eu-BDC thin films on graphene using UDLW.