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Electrochemical Coupling Layer-by-layer (ECC-LbL) Assembly in Patterning Mode

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Functional building blocks (fullerene and fluorene) were integrated into multilayers by utilizing electrochemical coupling layer-by-layer (ECC-LbL) assembly driven by the covalent carbon–carbon coupling reaction of pendant alkylcarbazoyl groups. The ECC-LbL assembly in patterning mode can be used to locally immobilize functional units and has been demonstrated here in a patterned fluorescent display. ECC-LbL is a versatile method for surface fabrication with promising potential in many applications.

Layer-by-layer (LbL) assembly is a highly versatile technique for preparation of nanosized thin films on both flat surfaces and the surfaces of microscopic colloids.[1] Fabrication, functionalization, and applications of LbL assemblies have been intensively investigated in a wide range of science and technology fields including physics,[2] chemistry,[3] biology,[4] nanotechnology,[5] medical science,[6] and eco-energy technology.[7] LbL assembly can be performed by using a variety of driving forces including electrostatic interactions,[8] hydrogen bonding,[9] metal coordination,[10] stereocomplex formation,[11] charge transfer,[12] biospecific recognition,[13] supramolecular inclusion,[14] and covalent bonding.[15] Such assemblies occur by spontaneous interactions between the components and cannot be stimulated or influenced by signals from the underlying substrate. Therefore, existing LbL methods are not always appropriate for thin film preparation at selected positions (or areas) at particular time intervals, which is necessary for on-demand surface patterning of functional units.

As a new concept of LbL assembly involving triggering by stimuli from the underlying solid substrates, we have recently developed electrochemical coupling layer-by-layer (ECC-LbL) assembly based on a reagentless clean process of the electrochemical oxidative coupling reaction of *N*-alkylcarbazole.[16] This can be initiated by an electrochemical stimulus from an electrode surface at the underside of the films without the use of additional reactants. Because *N*-alkylcarbazole and its dimer have large hole-transport mobilities,[17] electrochemical signals can be transmitted to the top layers of their films. Unlike other electropolymerizable precursors such as aniline and thiophene the resulting *N*-alkyldicarbazole is transparent in the visible light absorption region[18] and so does not impair the optical or electrical properties of the active moieties in the film. Simply by introducing *N*-alkylcarbazole substituents to functional units enables their immobilization in layered films without causing any structural perturbations of the functional units. In fact, in our preliminary report we successfully prepared assemblies of porphyrin, fullerene, and fluorene units within variously layered films.[16]

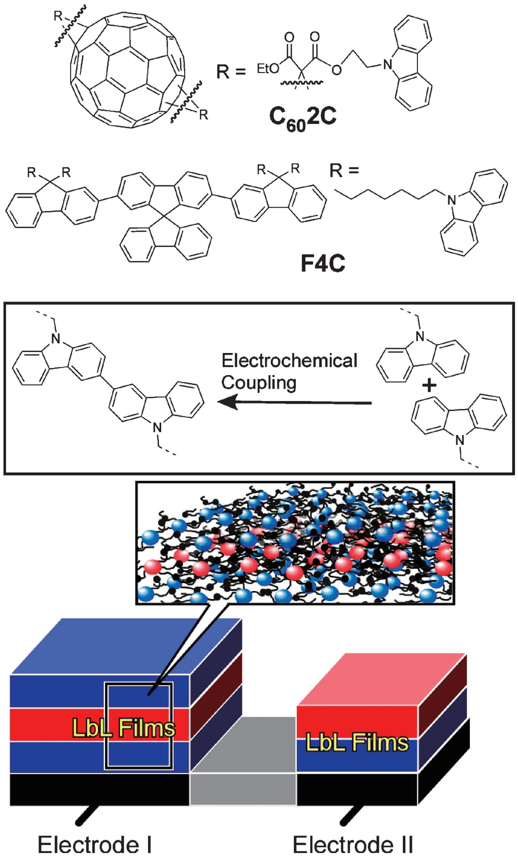

Figure 1. Component molecules used for electrochemical coupling layer-by-layer (ECC-LbL) assembly in patterning mode through crosslinking of the peripheral *N*-alkylcarbazole units.

However, the previous example of ECC-LbL assembly is insufficient to demonstrate the great potential of this method. For example, this technique should be also useful for patterned surface fabrication through area-selective covalent assembly. Here, we present ECC-LbL assembly in patterning mode to further illustrate the important potential of ECC-LbL as shown in Figure 1. In one possible application, a two-dimensionally selectively fluorescent display is demonstrated.

Syntheses of the component molecules and detailed descriptions of the assembly procedures are given in the Supporting Information[19] and our previous report.[16] Since the ECC-LbL films are stable against dissolution (being insoluble in most solvents, e.g., in CH_2Cl_2) owing to crosslinking of their

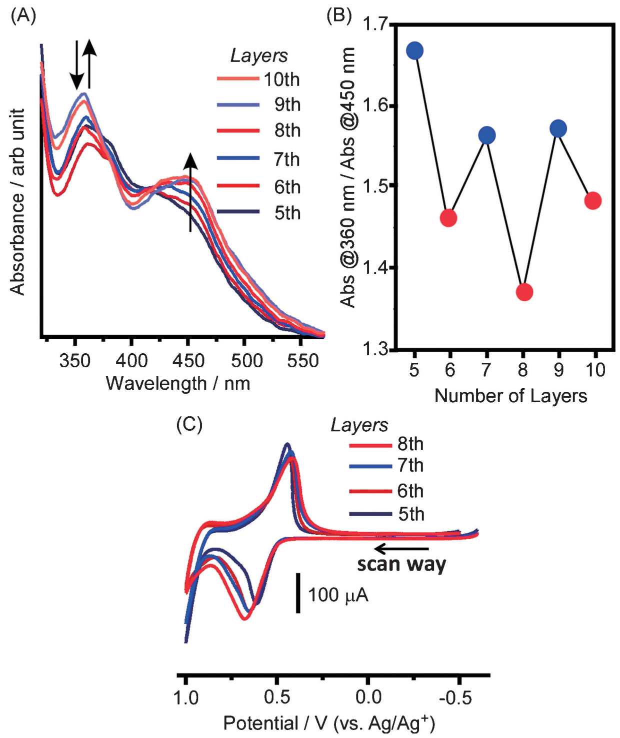

Figure 2. ECC-LbL assembly of **F4C** (odd layer) and **C_{60}2C** (even layer): (A) UV–vis spectra, (B) ratios of absorbance values at 360 and 450 nm as a function of number of layers, and (C) cyclic voltammograms of films with different numbers of layers.

alkylcarbazole moieties, ECC-LbL can be applied in the construction of multilayer assemblies of **F4C** (trifluorene) and **C_{60}2C** (fullerene). Alternating layers of **F4C** and **C_{60}2C** were prepared by applying a command signal from the substrate surface, i.e., cyclic voltammetric (CV) sweeping between −0.6 and 1.0 V at 200 mV s^{-1} for 2 cycles for each layer of **F4C** and **C_{60}2C** films with an intervening CH_2Cl_2 washing. **F4C** and **C_{60}2C** layers were successively and alternately prepared by respectively alternating with solutions containing **F4C** and **C_{60}2C**.

During film preparation by the layer-by-layer processes, constant film growth was confirmed by UV–vis spectroscopy (Figure 2A).[16] Absorption peaks at 360 and 450 nm are due to trifluorene and fullerene, respectively. With increasing layer number, absorption peaks at 450 nm grew continuously, while those at 360 nm alternately increased and decreased, before and after **C_{60}2C** was assembled on the **F4C** layer surface. The latter switching behavior is also exhibited by the ratio of absorbance at 360 and 450 nm in Figure 2B. These results demonstrate that the alternate ECC-LbL assembly of **F4C** and **C_{60}2C** was achieved and reveal that **F4C** and **C_{60}2C** are electronically interacting as donors and acceptors between the pairs of layers.

Switching behavior of **F4C**/**C_{60}2C** assemblies was also observed by CV measurement (Figure 2C). Redox peaks for both **F4C** and **C_{60}2C** layers can be attributed to the redox reaction of dialkylcarbazole,[20] which is not easily distinguished from the **F4C** and **C_{60}2C** layers although the oxidation current at 1.0 V of carbazoles of **F4C** bearing four alkylcarbazole units (blue curves for 5th and 7th layers) is obviously higher than that of **C_{60}2C** bearing two carbazole units (red curves for 6th and 8th layers), where the oxidation currents at 1.0 V switch upon **C_{60}2C** assembly.

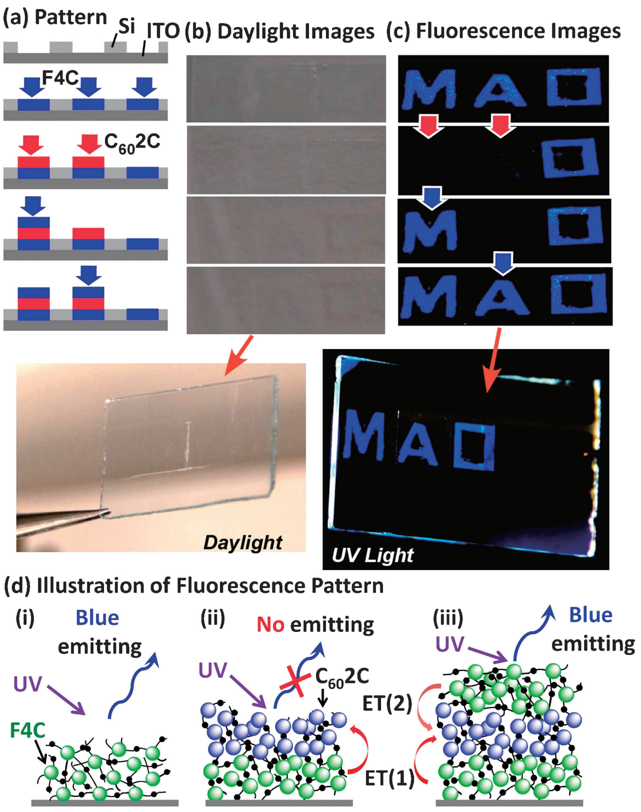

Figure 3. Area-selective ECC-LbL assembly in patterning mode: cross-sectional schematic diagram (a) of patterned assembly and vertical view photos of the films under day light (b) and UV light irradiation at 254 nm (c); (d) illustration of fluorescence display mechanism: (i) **F4C**; (ii) **C_{60}2C/F4C**, and (iii) **F4C/C_{60}2C/F4C** films.

In order to realize ECC-LbL in area-selective patterned mode, a nonconductive SiO_2 film of 200 nm thickness was sputtered onto a “MAO”-shaped masked ITO surface, and so patterned ITO was obtained. Three capital letters, M, A, and O, were positioned on different parts of the ITO of the same glass surface where ECC-LbL assembly can operate at different areas so that each of the ITO parts could be individually turned on by connection to a working electrode. Despite each character being assembled differently with either of **F4C** or **C_{60}2C**, as shown in Figure 3, all the characters on the plate appear almost transparent under observation in daylight. In sharp contrast, a patterned display could be demonstrated under irradiation with UV light (254 nm) in the dark.

In the first step, fluorescent **F4C** was assembled on all the characters, and the patterning areas, M, A, and O, could be displayed by fluorescence from **F4C** layer (Figure 3d(i)). Another nonfluorescent layer of **C_{60}2C** was area-selectively deposited only on M and A, inducing fluorescence quenching in that area and changing the message from MAO to ____O. However, the fluorescence could be recovered by further assembly of an **F4C** layer. The stepwise assembly on M then A made these characters visible in fluorescence mode, resulting in changes of messages from MAO, to ___O to M__O and finally to MAO. Quenching of fluorescence from the **F4C** (energy donor) layer by covering with the **C$_{60}$2C** (energy acceptor) layer is induced by efficiently energy transfer (ET(1)) at the interface of these two layers (Figure 3d(ii)). As shown in Figure 2, UV–vis absorption for fluorene units (energy donor) at 360 nm was effectively attenuated by coating with **C$_{60}$2C** (energy acceptor). The latter supports occurrence of energy transfer at the interfaces of **F4C** and **C$_{60}$2C**. After **F4C** was assembled on **C$_{60}$2C/F4C** as third layer shows fluorescence again, which is suggested that the fluorescent behavior from covering with the on **C$_{60}$2C** has too strong fluorescence intensity of outermost trifluorene units and overload energy transfer (ET(2)) of **C$_{60}$2C**; therefore, the film **F4C/C$_{60}$2C/F4C** still shows strong fluorescence (Figure 3d(iii) and Figure S1). The thickness of each layers is very useful to explain the energy transfer, for example, it is well-known that 10 nm is considered to be efficient energy-transfer distance. Actually, these films we prepared by ECC-LbL assembly are very thin (probably ca. 5 nm for each layer, ca. 10 nm for bulk layer), so it is very hard to precisely measure this thickness for such thin films.

These simple patterning examples suggest that ECC-LbL assembly can be employed on well-defined micro- and nano-sized conductive material surfaces of arbitrary topography for device and biorelated applications. We should note that area-selective ECC-LbL assembly in patterning mode can be performed by varying the spatial application of voltage. Therefore, we can prepare the desired patterns by using the ECC-LbL technique even if the whole substrate is immersed in solution. We expect that this methodology could be coupled with highly miniaturized integrated circuits.

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