We present an economical route to achieve an all-solution and vacuum-deposition free device for fabrication of both the photoactive layer and the electrode. This low cost strategy offers a wide range of possibilities in terms of chemical and physical properties for the fabrication of tailor-made materials and their devices.

Solution-based fabrication is a key to unlock the potential of low-cost, flexible and light organic electronic devices, such as solar cells,\(^1\) photodetectors,\(^2\) light-emitting diodes (LEDs),\(^3\) and field-effect transistors (FETs).\(^4\) In a typical optoelectronic device, an organic active layer and electrodes are key components. To date, vacuum-evaporated metals (e.g. aluminum and silver) and indium-tin oxide (ITO) have been extensively used as top and bottom electrodes in many types of devices, where the organic active layers are often prepared by a wet coating or a vacuum-deposition process. However, the ITO electrode tends to have a poor interfacial contact with the organic active layer and is made using large sputtering equipment with a high-energy cost. In recent years, the solution-processable electrodes have been actively exploited in order to replace the ITO electrodes. Several electrode candidates have been reported, including poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) with metal grids,\(^5\) carbon nanotubes,\(^6\) graphene,\(^7\) and silver nanowires.\(^8\) For these devices, a top counter electrode still needs to be applied by the vacuum deposition process. Thus, for practical applications, all-solution-processed fabrication of both the active layer and the electrode is urgently needed.

Currently, we have developed an electrochemical coupling layer-by-layer (LbL) assembly method\(^9\) to integrate different building blocks into a film with the preservation of their intrinsic physicochemical properties.\(^10\) The organic layer can fully cover the electrode surface to form uniform morphology because the bare area of an electrode surface has higher current density for the fast assembly process compared to the film covered area. This film has good interfacial interaction with the ITO surface without using any pre-treatment and its device can reach high performance compared to the device fabricated using conventional spin-coating films.\(^11\) The resulting film is highly stable and useful for further fabrication of additional functionalized building blocks in desirable area.\(^12\) In this communication, we report the use of gold nanoparticles as the economical route to achieve an all-solution, vacuum-deposition free device under normal atmospheric pressure for fabrication of the photoactive layer and the electrode by using one type of electrochemical process. In contrast to the previous reports for the organic–inorganic composites, we have demonstrated that this process can easily control the gold nanoparticle distribution in the multilayer film.

For the fabrication of distribution-controllable multilayers (Scheme 1B), we have designed and synthesized electrochemically active organic fluorescent small molecule 9,9′-spirobiﬂuorene derivatives (F-Cz) and carbazole-coated gold nanoparticles (Au-Cz, diameter of 2–3 nm, Fig. S1, ESI†) (Scheme 1A). These materials have shown successful applications in the fields of optoelectronics and biomedicals.\(^9\),\(^11\),\(^13\) As an organic–inorganic hybrid material, the electrochemical LbL assembly of the Au-Cz film (WE: indium tin oxide (ITO) in CH2Cl2 solution, c: 2 mg mL\(^{-1}\)) was successfully obtained through cyclic voltammetry (CV) by sweeping the potential between −0.6 and 1.1 V vs. Ag/Ag\(^+\) at 200 mV s\(^{-1}\).\(^14\) This experiment resulted in a regular growth (LbL) of the Au-Cz film as demonstrated by UV-vis spectroscopy (Fig. 1A; the layer dependence is shown in Fig. 1B) and CV (Fig. 1C; the layer dependence is shown in Fig. 1D). The main peaks (420–450 nm) and their shoulders (～550 nm) are relative to radical cations of the carbazole dimer and the plasma effect of gold nanoparticles, respectively (Fig. S1, ESI†). The successive
increase of current in the reversible redox waves can be attributed to the redox behavior of the dicarbazole. There may be two kinds of electrochemical coupling reactions of alkylcarbazole for inter-Au-Cz (Fig. 1E-a) and intra-Au-Cz (Fig. 1E-b), but the reaction of intra-Au-Cz could be negligible because the nanoparticles are strongly aggregated.

The transparent purple film (photo in Fig. S1, ESI†) of Au-Cz shows a very uniform surface modified with nearly mono-dispersed Au-Cz (Fig. 2A and B). The thin Au-Cz film (prepared using 2 cycles) (Fig. 2C) has a similar morphology to the ITO surface (Fig. 2D), but a thick film (20 cycles) shows completely different morphology (Fig. 2E), indicating that this assembly can be self-repaired for a 2D regular distribution of Au-Cz on ITO. The transparent Au-Cz film between ITO and Al electrodes shows a high conductivity value of $1.2 \times 10^2$ S cm$^{-1}$ (Fig. S2, ESI†). This value is better than that of the conventional chemically exfoliated and reduced graphene oxide and comparable to those of the carbon nanotubes.

Similarly, F-Cz can also electrochemically undergo LbL assembly on ITO and shows a smooth surface (Fig. 3A) for the next preparation of the Au-Cz LbL film. As Au-Cz film thickness increases, the texture of the F-Cz film transformed into the Au-Cz texture (Fig. 3B and C), demonstrating a vertical distribution of the Au-Cz film on an organic layer, while the F-Cz layer can be fully covered by the Au-Cz film (Fig. 3D and E). The fluorescence intensity of the F-Cz film quickly decreased (quenching process) indicating that the surface of the F-Cz film was partially covered by the Au-Cz film. This observation shows good electronic interactions between F-Cz and Au-Cz layers (Fig. S3, ESI†) and implies great potential application in organic–inorganic hybrid electronics. Multilayers of these films can be prepared by an alternative CV sweeping at 200 mV s$^{-1}$ for 2 cycles from their solutions with intervening CH$_2$Cl$_2$ washing. The film formation process uses cross-linking of the alkylcarbazole, therefore once film formation is complete it is insoluble and durable in CH$_2$Cl$_2$ and other similar solvents. The constant film growth (LbL process) can be confirmed by the successive enhancement of the absorption intensity at 510 nm (Fig. 3F and G) and the switching behavior of the cyclic voltammogram (Fig. S4-A, ESI†). The absorption intensity at 360 nm does not show good switching behavior probably due to the size and interface effect of Au-Cz nanoparticles and small molecular F-Cz.
multilayer preparation of F-Cz/Au-Cz hetero-assembly was completed, AFM was used to study its surface morphology (Fig. S4-B). The thickness of every individual layer (inside multilayers) can be quantitatively tailored by a number of CV cycles, so the distribution of Au-Cz nanoparticles is tunable for optoelectronic applications (Scheme 1C). Previously, such kinds of films were prepared using polar solvents (mainly H2O) with poor quality compared to those prepared using organic solvents. Achieving a controllable continuous percolation network between organic and inorganic materials with high repeatability and stability remains difficult. In particular, the co-assembly of inorganic and small organic building blocks into a hybrid film with homogeneous dispersion is very difficult due to the strong tendency of nanoparticles to irregularly distribute and agglomerate.

The transparent Au-Cz film is highly conductive, so the Au-Cz layer can work as an electrode in a device with the structure ITO/F-Cz/Au-Cz as a fully-solution-processable device model. Its work function of an electrode could be tailored by an additional electrochemical LbL assembly and electrochemical doping processes. Furthermore, different organic–inorganic hybrids can enhance the performance of the device made from one-pot solution-processing based on our previous study.

In summary, we have developed an economical route to achieve an all-solution and vacuum-deposition free device under normal atmospheric pressure for fabrication of both the photoactive layer and the electrode by using one type of electrochemical process. In this process, the gold nanoparticle distribution in the multilayer film can be easily controlled in contrast to the previous reports on organic–inorganic composites. This low cost strategy offers a wide range of possibilities in terms of chemical and physical properties for the fabrication of tailor-made materials and their devices. Next, the gold nanoparticle could be replaced by a cheaper copper nanoparticle or something else. This study is underway.

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Notes and references


14 Cyclic voltammetry (CV) was performed in order to precisely control the order thickness and their regular distribution of constituents, since continuous application of a constant potential leads to thickness control problems.
