Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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COMMUNICATION

Fabrication of Both Photoactive Layer and Electrode by Electrochemical Assembly: Towards Fully Solution-Processable Device

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We present an economical route to achieve an all-solution and vacuum-deposition free device for 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) are extensively used as top and bottom electrodes in many types of devices, where the organic active layers are often prepared by wet coating or vacuum-deposition process. However, the ITO electrode tends to have a poor interfacial contact with 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 electrode. 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 active layer and electrode is urgently needed.

Recently, we have developed an electrochemical coupling layer-by-layer assembly (LbL) 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 electrode surface to form uniform morphology because the bare area of an electrode surface has higher current density for 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 film.[11] The resulting film is highly stable and useful for further fabrication of additional functionalized building blocks on desirable area.[12] In this paper, we report the gold nanoparticles utilized as the economical

route to achieve an all-solution, vacuum-deposition free device under normal atmospheric pressure for 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.
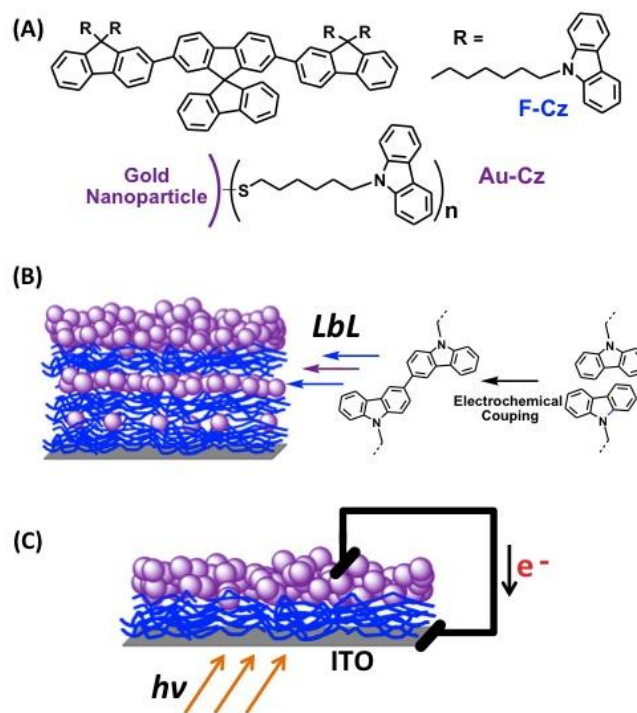
Scheme 1. (A) Small molecule F-Cz and Au-Cz used for dispersed-controllable (B) electrochemical LbL assembly through covalent carbon-carbon coupling reaction of the peripheral N-alkylcarbazole units for (C) fully solution-processable device.

For the fabrication of distribution-controllable multilayers (Scheme 1B), we have designed and synthesized electrochemically active small fluorescent 9, 9'-spirobifluorene derivative (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 optoelectronics and biomedicals.[9,11,13] As an inorganic-organic hybrid material, the electrochemical LbL assembly of Au-Cz film (WE: indium tin oxide (ITO) in CH_2Cl_2 solution, c: 2 mg/mL) was successfully obtained through cyclic voltammetry (CV) by sweeping the potential between -0.6 to 1.1 V vs. Ag/Ag^+ at 200 mV/s.[14] This experiment resulted in a regular growth (LbL) of Au-Cz film as demonstrated by the 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 its shoulders (~550 nm) are relative to radical cation of carbazole dimer and 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.[10a] 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.
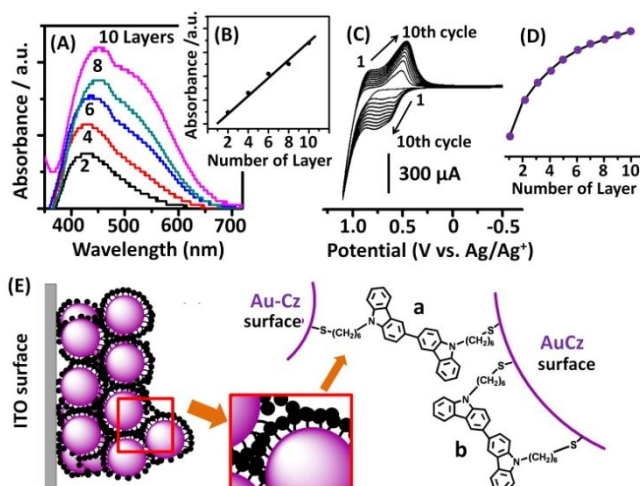

Fig. 1 Au-Cz homo-type LbL films: UV-vis spectra (A) and its absorption intensity at 510 nm (B); Cyclic voltammogram (C) and layer number dependence of the reduction current of dicarbazole (0.45 - 0.60 V) (D); Electrochemical coupling routes (E) of alkylcarbazole inter- and intra-Au-Cz (b).

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-B). Thin Au-Cz film (prepared using 2 cycles) (Fig. 2C) has similar morphology to ITO surface (Fig. 2D), but thick film (20 cycles) shows completely different morphology (Fig. 2E), indicating this assembly can be self-repaired for a 2D regular distribution of Au-Cz on an ITO. The transparent Au-Cz film between ITO and Al electrodes shows a high conductivity value of 1.2×10^2 S·cm^{-1} (Fig. S2, ESI[†]). This value is better than the conventional chemically exfoliated and reduced grapheme oxide and comparable to the carbon nanotubes.[15]
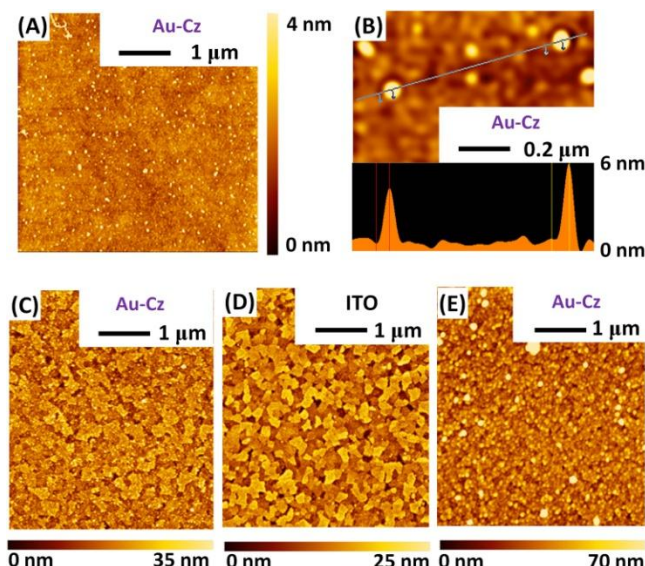

Fig. 2 AFM images of Au-Cz LbL assembly film on gold-coated glass prepared using 10 cycles (A) with nearly monodispersed Au-Cz on surface (B), thin Au-Cz film prepared using 2 cycles on ITO (C), ITO only (D) and thick Au-Cz film prepared using 20 cycles on ITO (E).
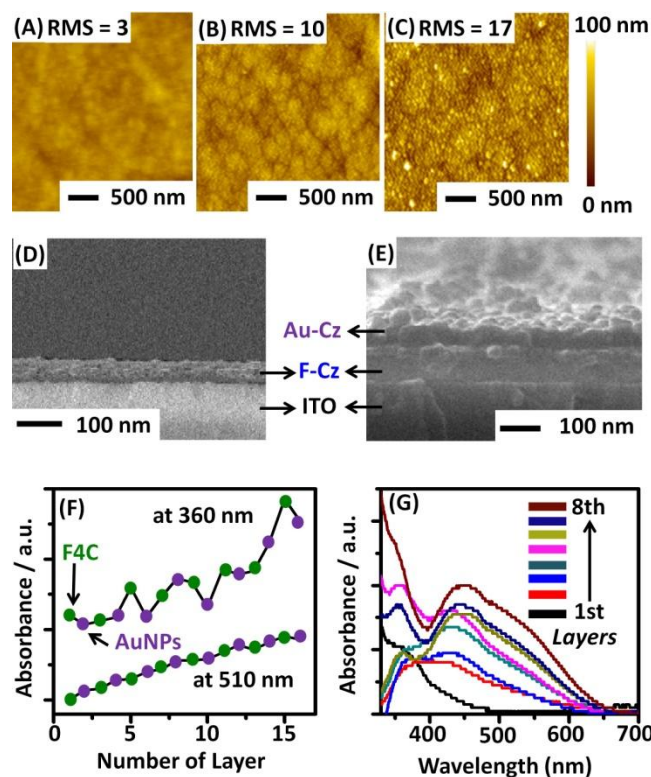

Fig. 3 AFM images of F-Cz LbL assembly film by 0 (A), 4 (B) and 10 (C) cycles prepared Au-Cz film covered. Cross-section SEM images of F-Cz (D) and Au-Cz/F-Cz (E) films; Absorbance values of multilayer Au-Cz/F-Cz film as function of number of layer (F) and its UV-vis spectra (G).

Similarly, F-Cz also can electrochemically undergo LbL assembly on an ITO and shows smooth surface (Fig. 3A) for next preparation of Au-Cz-LbL film. As Au-Cz film thickness increases, texture of F-Cz film transformed to the Au-Cz texture (Fig. 3B-C), demonstrating

a vertical distribution of Au-Cz film on an organic layer, while F-Cz layer can be fully covered by Au-Cz film (Fig. 3D-E). The fluorescence intensity of F-Cz film quickly decreased (quenching process) indicating that the surface of F-Cz film was partially covered by 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 for 2 cycles from their solutions with an intervening CH_2Cl_2 washing. The film formation process uses cross-linking of the alkylcarbazole, therefore once film formation is complete they are insoluble and durable in the CH_2Cl_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-G) and the switching behavior of 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. After the multilayer preparation of F-Cz/Au-Cz hetero-assembly was completed, AFM was used to study its surface morphology (Fig. S4-B, ESI[†]). Thickness of every individual layer (inside multilayers) can be quantitatively tailored by number of CV cycles, so the distribution of Au-Cz nanoparticles can be fabricated (Scheme 1B) for tunable structures for optoelectronic applications. Previously, such kinds of films were prepared using polar solvents, (mainly H_2O), with poor quality compared to those prepared using organic solvents.[16] Achieving a controllable continuous percolation network between organic and inorganic materials with high repeatability and stability remains a difficulty. 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.[17]
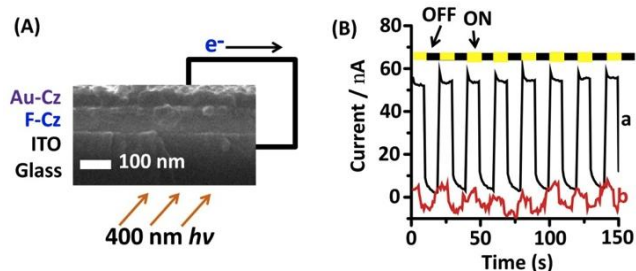

Fig. 4 (A) Cross-section SEM image of device. (B) Switching current of devices (4×4 mm) with structure (a) ITO/F-Cz/Au-Cz and (b) ITO/Au-Cz under 360 nm at 0 V.

Transparent Au-Cz film is highly conductive, so 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 cross-sectional morphology observed by the scanning electron microscopy (Fig. 4A) reveals incredibly flat interfaces of each layer which is necessary for the good interfacial interactions between organic layer and the electrodes. F-Cz film between ITO and Au-Cz electrodes displays repetitive and stable switching photovoltaic response upon irradiation by the 360 nm light. In contrast to the Au-Cz layer on an ITO without F-Cz film device gives only tiny noise signal (Fig. 4B), likely caused by the doping and dedoping processes of the trace anions at the positive and negative bias due to plenty of carbazole coupling reactions on the surface of gold nanoparticles. Although further research is needed to establish the exact performance of this device, this strategy, for the first time shows a general approach to fabricate entire device by the solution processing. In this strategy, the work function of an electrode could be tailored by an additional

electrochemical LbL assembly and electrochemical doping processes.[10b] Further, different organic/inorganic hybrids can enhance performance of the device made from one-pot solution-processing based on our previous study.[18]

In summary, we have developed an economical route to achieve an all-solution and vacuum-deposition free device under normal atmospheric pressure for both the photoactive layer and the electrode by using one type of electrochemical process. In this process, the gold nanoparticle distribution in multilayer film can be easily controlled in contrast to the previous reports for 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 cheaper copper nanoparticle or something else. This study is on the way.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, AFM and TEM images, UV-vis spectra, NMR spectra, etc. See DOI: 10.1039/c000000x/

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