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Pulsed laser deposition of graphite counter electrodes for dye-sensitized solar cells

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We report on pulsed laser deposition of graphite onto flexible plastic and conductive glass substrates for use as a counter electrode in dye-sensitized solar cells. The efficiency of as-prepared graphite electrodes was tested using CdS-sensitized solar cell architecture resulting in external quantum efficiency comparable to that of conventional platinum counter electrodes. This work highlights the possibility of using pulsed laser deposited graphite as a low-cost alternative to platinum, which could be fabricated both on flexible and rigid substrates. © 2010 American Institute of Physics. [doi:10.1063/1.3518481]

Dye-sensitized solar cells (DSSC) are promising candidates for the development of third-generation photovoltaic (PV) technologies that enable low-cost solution processing of active layer materials.¹ Remarkable power conversion efficiency of up to 11.1% has already been demonstrated for prototype DSSC cells paving the way for their commercialization.² On the other hand, an ongoing research on quantum dot-sensitized solar cells (QDSSC) is continuously improving the PV performance of these devices through the development of noncorrosive, solid hole-conductors^{3–5} and optimization of working electrode morphologies.⁶ To ensure a seamless transfer of DSSC and QDSSC technologies into mass production of PV modules, all the device components should be constructed from inexpensive, nontoxic, and widely available materials. At present, the working electrode architecture utilizing wide band gap metal oxides such as TiO₂, ZnO, and SnO₂ meets these requirements. Meanwhile, the common selection of counter electrode materials used in DSSC and QDSSC cells would benefit from low-cost alternatives.

Platinum is often chosen as a counter electrode material in DSSC due to its inertness, excellent conductive properties, and the ability to reduce iodine electrolyte with minimal overpotential.⁷ The incorporation of platinum coatings in mass production of solar cells, however, is hindered by its limited availability and high costs. Furthermore, several recent reports have indicated that DSSCs utilizing platinum counter electrode bear efficiency losses due to an increased in-series resistance,⁸ as well as oxidation and dissolution of platinum by the electrolyte and dye molecules.⁹ It should also be noted that solution-based sintering of platinum onto indium tin oxide (ITO)-covered glass requires heating of the platinum precursor to above 300 °C, which prevents the deposition of platinum electrodes onto plastic substrates for use in flexible DSSCs.

As a viable alternative to platinum, several groups have been investigating carbon-based thin films for the regeneration of holes.^{8,10–12} In addition to the wide availability of this element in nature and its low processing costs, carbon-based materials, such as graphite and nanotubes exhibit a number of promising PV characteristics, including good carrier mobility, resistance to corrosion, and the ability to reduce common electrolytes.¹³ A few recent reports have demonstrated that the performance of solar cells utilizing double-, or multi-walled carbon nanotube (CNT), or hard carbon spherules, is comparable to those based on platinum.^{8,10–12} Further improvement in the catalytic activity of graphite is also possible through the use of porous architectures that increase the electrolyte/electrode interfacial area.¹⁴

To date, preparation of carbon-based counter electrodes relies on the direct coating of the substrate with the CNT paste or a blend of colloidal suspension of carbon nanoparticles with TiO₂ or SnO₂,¹⁵ which makes it difficult to control the thickness and the quality of deposited films. As an alternative, in this work we explore the use of pulsed laser deposition (PLD) route to the preparation of graphite counter electrodes. PLD is a promising low-cost method for the preparation of thin films on a wide range of substrates. This method benefits from multiparameter tunability of film properties available via judicious tuning of experimental variables such as laser pulse width, wavelength, ablation time, substrate-target distance, laser fluence, and inert gas pressure.¹⁶ The present study demonstrates that a PLD layer of graphite deposited onto ITO-covered glass or flexible plastic substrates can be utilized in nanocrystal-sensitized solar cells leading to PV performance, which is comparable to that of platinum-based devices.

Thin films of graphite on ITO-covered glass and polyethylene terephthalate (PET) plastic substrates were fabricated according to the procedure, previously developed in our group.¹⁷ Briefly, PLD was carried out using Spectron SL456G (Rugby, Great Britain) Q-switched Nd:yttrium aluminum garnet laser (532 nm, 6 ns, 10 Hz) with 2.2 ± 0.12 J/cm² fluence, resulting in a deposition of ap-

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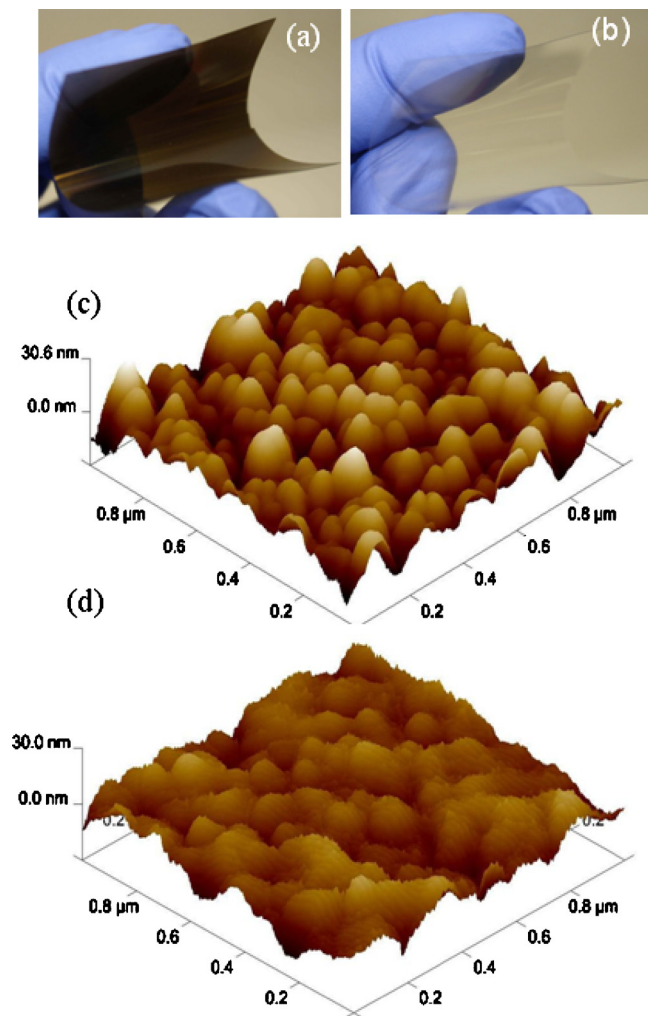


FIG. 1. (Color online) (a) An optical image of the PLD graphite film on PET. (b) PET only. (c) AFM topographic image of the graphite film on ITO/glass. (d) AFM of the graphite film on PET.

proximately 500 nm graphite layer in 20 min. An apparent change in the substrate color from clear to black associated with the film deposition is illustrated in Figs. 1(a) and 1(b). The developed film is strongly adherent to the substrate, and structurally uniform with no visible damage to either plastic or ITO substrates due to the laser-induced plumes. The absence of any visible peeling of the film due to bending or twisting of plastics implies its sufficient flexibility [see Fig. 1(a)].

The surfaces of graphite films on ITO-covered glass and PET substrates were investigated using atomic force microscope (AFM) (Veeco NanoMan, Plainview, New York) [Figs. 1(c) and 1(d)]. Analysis of AFM topographic images has shown that the overall quality of the deposited graphite layer is dependent on the substrate material. For instance, a typical root-mean-square (rms) roughness value of the graphite film on plastic was 6.5 nm, which exceeds the rms roughness of a bare plastic substrate (2.6 nm). On the other hand, rms roughness of graphite film on ITO/glass is 4.5 nm, which is almost similar to that of bare ITO/glass (4.7 nm). Interestingly, the ITO-supported films consisted of grains that were thicker at their bases and taper toward the summit, which was not the case for the plastic substrates.

The performance of graphite counter electrodes was tested using a CdS-sensitized prototype solar cell, con-

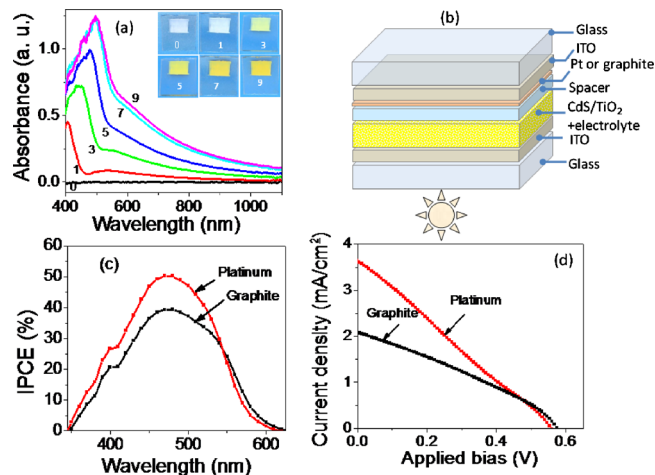


FIG. 2. (Color online) (a) Development of absorption spectra of CdS-sensitized TiO₂ at different coating cycles; the inset shows the progressive darkening of the CdS/TiO₂ film upon the increasing number of coating cycles. (b) A schematic diagram of the device layer. (c) IPCE spectra of the two solar cells using platinum and graphite counter electrodes. (d) *J-V* characteristics of CdS-sensitized solar cells using platinum and graphite as counter electrodes.

structed according to a previously reported methodology.^{18,19} First, the working electrode was prepared by screen printing Degussa P25 TiO₂ paste onto ITO-covered glass followed by sintering the TiO₂ film at 450 °C for 1/2 h to improve carrier mobility.²⁰ The deposition of CdS on TiO₂ was carried out *in situ* through nine cycles of successive ionic layer adsorption and reaction (SILAR),¹⁸ and was monitored by recording progressive absorption spectra of the composite CdS/TiO₂ film after each deposition cycle [Fig. 2(a)]. An apparent increase in the optical density near the band gap of CdS ($\lambda \approx 450$ nm) confirms the growth of CdS nanoparticles, while the onset of the absorption at higher wavelengths ($\lambda > 550$ nm) attests the formation of type II CdS/TiO₂ heterostructures.²¹ The increase in the absorption below the band gap of CdS is attributed to the excitation of intermediate states that exist at the junction of both materials.²² It should also be noted that a greater rate of the absorption change during early stages of the SILAR process is generally expected due to a larger TiO₂ surface area available for CdS growth, which is later reduced due to pore filling effect.

PV characteristics of CdS/TiO₂ films were measured using a polysulfide redox couple (S^{2-}/S_x^{2-}) prepared by mixing 0.5M Na₂S, 1.5M sulfur, and 0.2M KCl in methanol and water (7:3).¹⁹ Iodine-based electrolyte (I^-/I_3^-), which is commonly used for the DSSC, was not employed in this work due to the strong corrosive action of this material toward most inorganic semiconductors. For comparative tests, platinum counter electrodes were also prepared by spreading few drops of 5 mM chloroplatinic acid in 2-propanol on the ITO/glass and heating the electrode to 400 °C for 1 h.

The performance of graphite films was investigated in a two-electrode electrochemical cell comprising a CdS/TiO₂ working electrode, redox electrolyte, Parafilm™ spacer (thickness 125 μm), and the graphite/ITO electrodes, as shown in Fig. 2(b). For comparison, a similar cell was assembled using a platinum-coated ITO slide as a counter electrode. The incident photon to charge-carrier efficiency (IPCE) was measured with the monochromatic excitation from xenon arc lamp using a setup from PV Measurements,

TABLE I. Parameters measured in I - V curve using platinum and graphite counter electrode.

Counter electrode	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill factor (%)	η (%)
Platinum	3.69	0.559	25.62	0.51
Graphite	2.13	0.575	31.16	0.37

Inc (Boulder, Colorado). The measurements were carried out shortly after the cell assembly to avoid solvent evaporation and possible deterioration of the CdS sensitizer. Figure 2(c) compares characteristic IPCE spectra of the two cells comprising PLD graphite and platinum-coated counter electrodes. For both cell types, photocurrent spectra cover most of the visible range, which is consistent with the absorption profile of CdS NCs, and reach their highest values near 475 nm. The maxima of IPCE recorded at this wavelength were 40% and 50% for graphite and platinum-based counter electrodes, respectively.

Current-voltage characteristics were measured under air mass 1.5 G (100 mW/cm²) solar simulator using I - V data acquisition system from PV Measurements, Inc. by illuminating the 0.88-cm²-device on the working electrode side. J - V characteristics of typical CdS-sensitized solar cells utilizing platinum and graphite counter electrodes are compared in Fig. 2(d). The power conversion efficiency (PCE) of a best-performing platinum-electrode cell was 0.51% (see Table I), which is in good agreement with the measurements reported for CdS/TiO₂ devices by other groups,²³ while a champion graphite-electrode cell showed a PCE value of 0.37%, reflecting a somewhat reduced short circuit current density (J_{sc}) compared to that of platinum. The observed difference between J_{sc} values for the two cells is not surprising since the morphology of the graphite film was not optimized for highest current density. It is expected that a careful adjustment of PLD parameters for the deposition of graphite films will increase the value of J_{sc} for graphite-electrode cells. Overall, the measured PV characteristics of graphite electrodes (IPCE and PCE) were found to be nearly comparable to those of platinum, which, based on the relative costs of graphite and platinum materials implies that the cost of solar energy conversion in graphite-based solar cells can potentially become lower than that of platinum-based devices.

In conclusion, we have demonstrated a simple method for growing graphite films onto conductive transparent substrates for use as low-cost counter electrodes in dye- and nanocrystal-sensitized solar cells. The performance param-

eters of fabricated graphite electrodes were measured using a prototype CdS-sensitized solar cell and found to be similar to those of conventional platinum electrodes, indicating that the PLD development of graphite films on ITO may potentially enable lower costs of the solar energy production in DSSC and QDSSC devices.

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