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Research Article

The Influence of Electrophoretic Deposition for Fabricating Dye-Sensitized Solar Cell

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Titanium dioxide (TiO_2) film was deposited on fluorine-doped tin oxide (FTO) glass substrate by electrophoretic deposition method (EPD). TiO_2 films were prepared with different I_2 dosages, electric field intensities and deposition time (D.T.), electrophotic deposition times. By different I_2 dosages, electric field intensities, deposition time, electrophotic deposition times fabricated TiO_2 films and compared photoelectric characteristics of TiO_2 films to find optimal parameters which were the highest photovoltaic conversion efficiency. And use electrochemical impedance spectroscopy (EIS) to measure the Nyquist plots under different conditions and analyze the impendence of dye-sensitized solar cells at the internal heterojunction. According to the experimental results, the I_2 dosage was 0.025 g which obtained the optimal characteristic parameters. Thickness of TiO_2 film was 10.6 μm, the open-circuit voltage (V_{oc}) was 0.77 V, the short-circuit current density (J_{sc}) was 7.20 mA/cm^2, the fill factor (F.F.) was 53.41%, and photovoltaic conversion efficiency (η) was 2.96%.

1. Introduction

Solar energy has been considered as a renewable energy of the next generation since fossil fuel was getting less and less. And dye-sensitized solar cell (DSSC), which was developed by O'Regan and Graetzel in 1991 [1], is highly potential in the solar energy. Titanium dioxide (TiO_2) had several advantages such as easily tunable bandgap and great absorption dye ability, so it has been a widely used material in many fields, such as photocatalysis, gas sensor, sunscreen, dye-sensitized solar cell, and other applications [2]. Titanium dioxide exists naturally in three nanocrystallines, namely, rutile (tetragonal, E_g = 3.05 eV), anatase (tetragonal, E_g = 3.23 eV), and brookite (orthorhombic, E_g = 3.26 eV).

There are several methods to manufacture titanium dioxide films, such as sputtering [3], hydrothermal method [4], doctor-blade [5], spin coating [6], chemical bath [7], electrophoretic deposition [8], and screen printing [9].

Electrophoretic deposition method has several advantages, such as high deposition rate, simple apparatus, and no binder required. And it also allows us to prepare any kind of conductive substrate shape. In addition, the electrophoretic deposition does not limit to the deposition temperature during processing of depositing TiO_2 film [10].

In this study, TiO_2 films were prepared by electrophoretic deposition method. Electrophoretic deposition was an attractive technique for the fabrication of films [11, 12]. Electrophoretic deposition was achieved via electrophoretic motion of charged particles in a suspension toward an electrode which depended on the particle charge and formation under the influence of an applied electric field [3].

Recently, for improving the photovoltaic conversion efficiency of dye-sensitized solar cell, the structure of TiO_2 has been developed in several forms such as nanosheet [8], nanowire [5], and nanopores [9].

2. Experimental Details

2.1. Material. Titanium dioxide (TiO_2) powder (P25) which was purchased from Degussa, Germany, contained 80% of anatase and 20% of rutile. The ruthenium-535 (N3) was purchased from UniRegion Bio-Tech, USA. The absolute ethanol was purchased from Katayama Chemical, Japan. The Acetylacetone (AcAc) was purchased from Acros Organics, Belgium. The lithium iodide (LiI) and 4-tert-butylpyridine (TBP) were purchased from Sigma-Aldrich, USA. The iodine (I_2) was purchased from Riedel-deHaen, USA. The 1-propyl-2,3-dimethylimidazolium iodide (DMPII) was purchased from Tokyo Chemical, Japan. And fluorine-doped tin oxide (FTO) glass substrate was purchased from C. P. Solar, Co., Ltd., Taiwan.

2.2. Preparation of TiO_2 Suspension and Electrophoretic Deposition. In this experiment, fluorine-doped tin oxide glass substrate was used as the cathode electrode, and platinum (Pt) was used as the anode electrode. The TiO_2 suspension consists of 0.25 g TiO_2 powder and 0.02 g I_2 in 25 mL of Acetylacetone. Before the cathode deposition, the TiO_2 suspension was placed in an ultrasonic vibrator to vibrate for 30 minutes. The distance between the cathode and the anode was fixed at 1 cm and 2 cm. After depositing the TiO_2 on FTO glass substrate, TiO_2 films were annealed at 450°C for 30 minutes. The purpose of annealing is to improve the connection between TiO_2 film and substrate. The postannealed electrodes were immediately immersed in an absolute ethanol solution of 3×10^{-4} M N3 dye for 24 h at room temperature.

2.3. Fabrication of Dye-Sensitized Solar Cell. The Pt film was fabricated on FTO glass substrate by R.F. sputtering for 90 sec as the counterelectrode. The working electrode and counterelectrode were filled with the liquid electrolyte which consisted of 0.6 M DMPII, 0.5 M LiI, 0.05 M I_2, and 0.5 M TBP in 15 mL MPN. Finally, DSSC was sealed as the sandwich structure of DSSC device. The active area of the solar cell was 0.8 cm × 0.8 cm.

2.4. Measurement. Surface morphology of TiO_2 film was measured by scanning electron microscope (SEM). The short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (F.F.), and the photovoltaic conversion efficiency (η) of DSSC were measured by Keithley 2400 digital source meter under one sun illumination (AM 1.5 G, 100 mW/cm^2).

3. Results and Discussion

3.1. Electrophoretic Kinetics. According to the Hamaker equation [16, 17], the relation between the deposited weight (w) and the electric field intensity (E) is

$$\text{Mass} = \int_0^t AC\mu E\, dt, \tag{1}$$

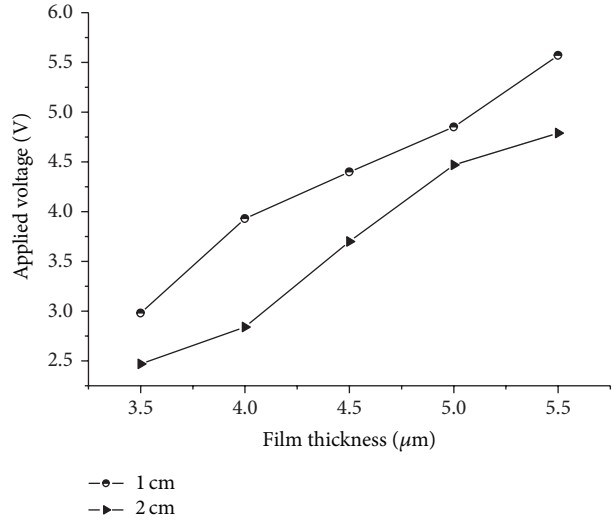

Figure 1: The TiO_2 films fabricated by different applied voltages and electrode distances.

where μ is the electrophoretic mobility, A is the surface area of the electrode, C is the concentration of the suspension, and t is the time.

The TiO_2 films were fabricated with different voltages. The larger applied voltage was applied, which could increase TiO_2 film thickness. The experimental results were as shown in Figure 1. The TiO_2 film thickness was a function of increasing applied voltage. Increasing the voltage could provide larger dragging force, so TiO_2 nanoparticles could obtain faster deposition rate. And we also increased the distance between two electrodes from 1 cm to 2 cm; the TiO_2 film thicknesses were thinner with increasing distance between two electrodes, which could lead the higher possibility for TiO_2 nanoparticles to collide each other that led to the deceleration and decreased deposition rate. In addition, the larger voltage generated faster deposition rate and formed the thicker TiO_2 film thickness, but it also led to the bigger crack on TiO_2 film, as shown in Figures 2(a)–2(f).

The numbers of crack seemed to depend on deposition electric field intensity. In the microstructure of TiO_2 film which deposited at 4.0 V/cm for 1 min, TiO_2 particles seemed to be separated, as shown in Figures 2(a) and 2(b), respectively. The microstructure of TiO_2 film which deposited at 4.50 V/cm for 1 min became more concentrated, as shown in Figures 2(c) and 2(d), respectively. And the TiO_2 film which was prepared at 5.0 V/cm has larger crack as shown in Figures 2(e) and 2(f), respectively. The main reason of crack was that the inorganic solvent rapidly was evaporated from the film surface during the drying process. The presence of nanopores on the film could be a great advantage of absorbing dye.

3.2. J-V Characterization of DSSC. There were few factors that could influence TiO_2 films in the preparing process, such as (a) the limitation of distance between two electrodes [16], (b) the decreasing of the suspension concentration [18],

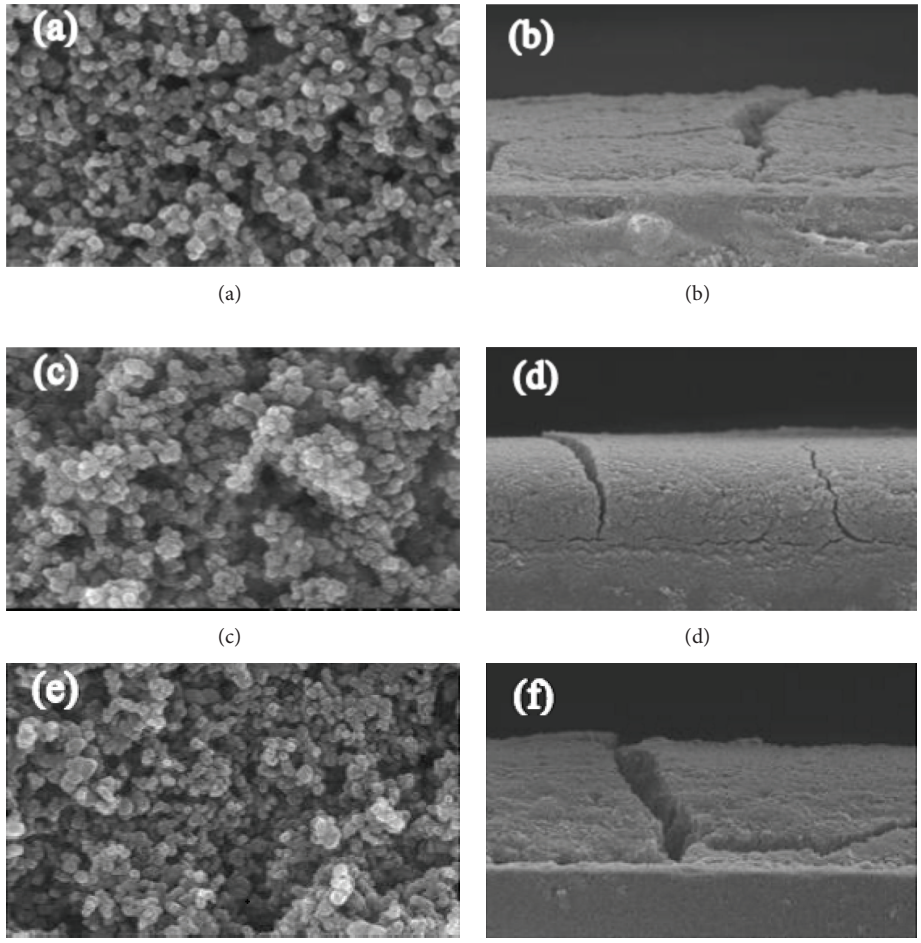

FIGURE 2: The SEM images of (a) TiO_2 film and (b) cross-section deposited at 4.0 V/m. (c) TiO_2 film and (d) cross-section deposited at 4.50 V/cm, (e) TiO_2 film, and (f) cross-section deposited at 5.0 V/m.

(c) the increasing of deposition resistance [19], and (d) the mobility of TiO_2 nanoparticles in the electrophoretic solution [20]. In this experiment, the TiO_2 films were fabricated by different deposition time, as shown in Figure 3. We found optimal properties of DSSC in deposition time at 60 s. Moreover, the more I_2 dosages at the same deposition time could lead TiO_2 nanoparticle (TNP) to carry more electric charges on the TiO_2 nanoparticle surface. So the mobility of TiO_2 nanoparticle could increase by increasing electric charge at TiO_2 nanoparticle surface [19]; the deposition rate and the thickness of TiO_2 film were increased by increasing I_2 dosages. The experimental results were shown as listed in Table 1.

Figure 4 showed *J-V* curves of DSSCs, which were prepared with different weights dosages of iodine (I_2). The optimal I_2 dosage was 0.025 g and the thickness was 10.6 μm. In comparison with TiO_2 films which have been prepared with different I_2 dosages, both the short-circuit current density and TiO_2 film thickness were proportional. The thicker thickness of TiO_2 film could increase the amount of

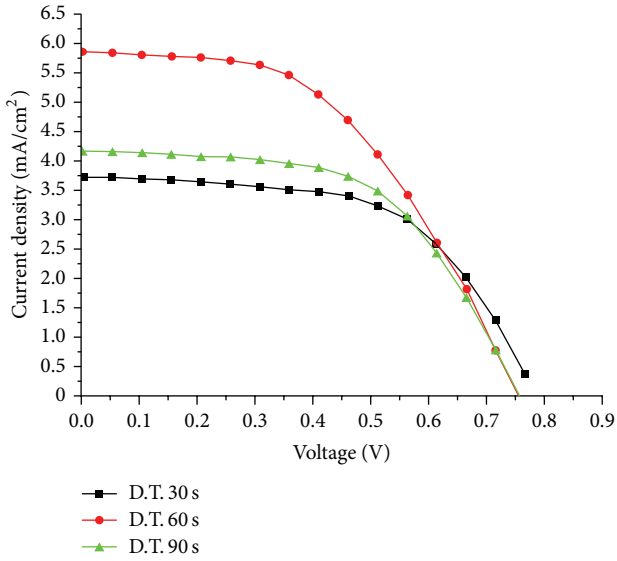

FIGURE 3: The TiO_2 films fabricated by different deposition time.

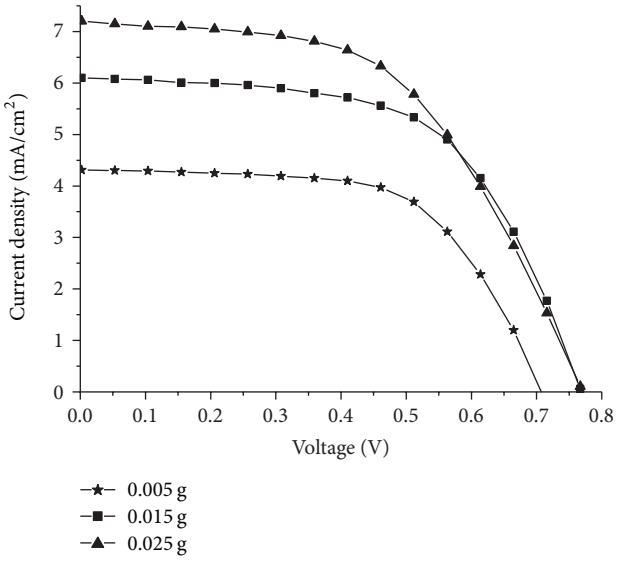

Figure 4: The TiO_2 films fabricated by different I_2 dosages.

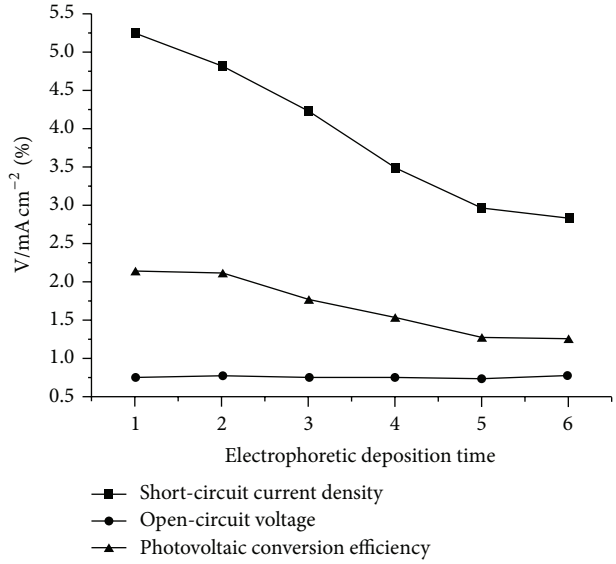

Figure 5: The effect of electrophoretic deposition times on properties of DSSC.

Table 1: The thicknesses and deposition rates with different I_2 dosages.

I_2 dosage (g)	Deposition rate (μm/sec)	Thickness (μm)
0.025	0.177	10.6
0.015	0.150	9.0
0.005	0.125	7.5

dye absorption which could generate more photoelectrons. Zhang et al. [21, 22] reported that the thicker thickness of TiO_2 film could increase dye desorption and the current density value was dependent on the light absorption which is strongly related to the amount of dye molecules being adsorbed. And, the TiO_2 nanoparticles deposited on the conductive substrate were due to an electrostatic attraction force between nanoparticles and FTO glass surface. Nanoparticles were formed by the electrostatic force with the cathode surface, because TiO_2 nanoparticles were accumulated with H^+ ions [23, 24].

Table 2 showed the comparison of DSSCs parameters with other references [3, 13–15]; we found that the suspension amount could affect the thickness of TiO_2 film; larger suspension amount had longer distance effect, so the TiO_2 film thickness could be thinner.

The increasing TiO_2 film thickness could increase dye loading of DSSC to generate more photoexcited electrons under the sun irradiation 100 mW/cm^2, so the current density was increased by 18% (from 6.09 mA to 7.02 mA) [13].

The photovoltaic conversion efficiency could influence not only the thickness of TiO_2 layer but also the structure of TiO_2 layer. In this study, the structure of photoelectrode was nanopores which were stacked by TiO_2 nanoparticles. In the other hand, there were many studies about the structure of TiO_2 layer in the photoelectrode which was TiO_2 nanotube (TNT). Since the structure of TiO_2 nanotube had greater specific surface area than nanoparticles, and effectively enhance the absorption amount of dye and the photoelectric conversion efficiency can be further enhanced [25, 26]. The nanotube structure fabricated by anodizing method is best arrayed, simple, and easy for fabrication and has low equipment cost. Through parameters, the fabricated nanoporous structure can be adjusted to achieve neatly arrayed nanoporous structure with pores in appropriate size. The photovoltaic conversion efficiency (2.96%) of DSSC thickness 10.6 μm was higher than the DSSC (2.60%) thickness 10.0 μm in [3]. The electrical field intensity during the deposited TiO_2 films caused nonuniform film, so it has lower absorption amount of dye and the photovoltaic conversion efficiency.

For the same structure of photoelectrode [14, 15], the thickness of TiO_2 film could be observed as an important relationship between short current density and photovoltaic conversion efficiency. If the thickness was 6.0 μm, the TNT-TNP mixed structure of photoelectrode had performance higher than TNT or TNP, because the TNT-TNP mixed structure had enlarged specific surface area at the same active area with better current density and photovoltaic conversion efficiency of DSSC.

From Figure 5, the J_{sc} and η were decreased with increasing electrophoretic deposition times. But, the V_{oc} was not significantly change with increasing electrophoretic deposition times. The results explained that effect of electrophoretic deposition times on photovoltaic properties was dramatic, which resulted from suspension concentration which was changed, compared with initial suspension concentration, which led to nonuniform TiO_2 charge quantity in TiO_2 suspension in repeated process of electrophoretic deposition.

3.3. Analysis of the Electrochemical Impedance Spectroscopy. Electrochemical impedance spectroscopy (EIS) is an electrochemical measurement method which inputs sinusoidal

Table 2: The comparison of DSSCs parameters with other references [3, 13–15].

Sample structure	Thickness (μm)	V_{oc} (V)	J_{sc} (mA/cm^2)	F.F. (%)	η (%)	Reference
TNP	6.6	0.80	5.17	55.5	2.30	
TNP	7.5	0.71	4.31	62.0	1.89	
TNP	7.9	0.72	3.30	62.1	1.49	
TNP	9.0	0.77	6.09	58.9	2.76	In this study
TNP	10.6	0.77	7.20	53.4	2.96	
TNP	12.9	0.74	4.44	46.8	1.55	
TNP	15.9	0.75	6.31	53.4	2.54	
TNP	10.0	0.69	5.70	66.00	2.60	[3]
TNT	22.0	0.70	13.90	47.7	5.43	[13]
TNT-TNP	6.0	0.75	11.50	53.3	4.89	[13]
TNT-TNP	15.5	0.75	19.50	49.6	7.40	[13]
TNP	1.5	0.30	0.49	50.0	0.07	[14]
TNP	4.2	2.20	0.74	53.0	0.87	[14]
TNP	6.0	0.75	7.95	74.0	4.37	[15]

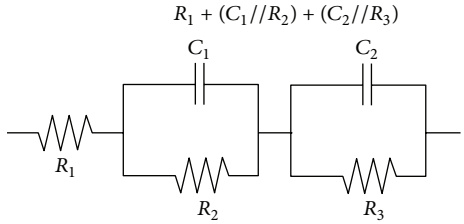

Figure 6: The equivalent circuit model of DSSC.

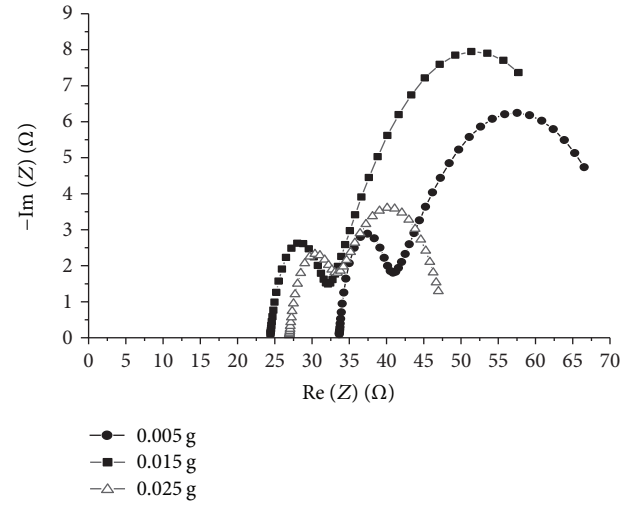

Figure 7: The Nyquist plots of DSSCs prepared with different I_2 dosages.

wave alternating current and the equivalent circuit model. The equivalent circuit model can describe the junction impedance, and the EIS measurement system can compute the value of junction impedance by Ohm's law. In the electrochemical system, the dye-sensitized solar cell consists of the anode electrode, the cathode electrode, and the electrolyte. Figure 6 showed the equivalent circuit model in the study. Table 3 described the physical meaning of each symbol in equivalent circuit model. Figure 7 showed the Nyquist plots of DSSCs which were prepared with different I_2 dosages. The Nyquist plots were formed by real part impedance (Re(Z)/Ohm) and imaginary impedance ($-$Im(Z)/Ohm). And Table 4 showed the resistance and capacitance values which were measured by EIS. The experimental results showed increasing R_3 value with increasing I_2 dosage. The larger R_3 value led to the fact that the electrons were more difficult to transmit at TiO_2/dye and electrolyte interface. However, the amount of absorbed dye increased with increasing the TiO_2 thickness [26]. And the photovoltaic conversion efficiency had been improved.

Table 3: The physical meaning of resistances and capacitances symbols.

Symbol	Physical meaning
R_1	Serial resistance of FTO glass/wire.
$C_1//R_2$	Impedance at Pt/electrolyte interface.
$C_2//R_3$	Impedance at TiO_2/dye/electrolyte interface.

4. Conclusions

Nanocrystalline TiO_2 films were deposited on FTO substrates by the electrophoretic deposition method. The film thickness and crevices numbers of TiO_2 film were increased with the deposition electric field intensity. And the thickness of TiO_2 film increased with increasing deposition time and I_2 dosage. By controlling the I_2 dosages which could increase the surface electric charge of TiO_2 particles, so the photovoltaic efficiency of DSSC was improved. The amount of absorbed dye was found to increase TiO_2 thickness so as to improve the photovoltaic conversion efficiency of DSSC. However, the thicker TiO_2 films could obtain the larger impedance at TiO_2 layer. The experimental results showed that the TiO_2 film deposited for 60 sec which had the optimal TiO_2

Table 4: The resistances and capacitances values of TiO_2 films prepared at 60 sec with different I_2 dosages.

I_2 dosage (g)	R_1 (Ω)	C_1 (mF)	R_2 (Ω)	C_2 (mF)	R_3 (Ω)
0.005	33	16.00	35	0.018	6
0.015	24	25.00	41	0.062	7
0.025	27	1.67	8	0.530	17

film thickness of 10.6 μm, the open-circuit voltage (V_{oc}) was 0.77 V, short-circuit current density (J_{sc}) was 7.20 mA/cm^2, fill factor (F.F.) was 53.41%, and photovoltaic conversion efficiency (η) was 2.96%.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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