Room temperature fabrication of porous ZnO photoelectrodes for flexible dye-sensitized solar cells

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We fabricated ZnO photoelectrodes at room temperature by doctor-blading ZnO gel; the adequate interparticle connection and the effective ammonia activation process improved the flexible DSC's efficiency to 3.8% (under 100 mW cm^{-2}).

The dye-sensitized solar cell (DSC) is a promising cheap alternative to conventional solar cells.[1] Since Grätzel *et al.* reported the first efficient DSC in 1991, several kinds of DSCs have been developed.[2] Among them, flexible DSC is a new emerging research area showing potential application in mobile electronic products, building materials and so on. Many researchers are engaged in this promising area for its versatility and low cost. Up to now, two kinds of flexible substrates have been used, metal sheets and polymer substrates. Metal sheets have low resistance, and recently the efficiency of a corresponding flexible DSC reached 7.2%.[2a] Polymer substrates have advantages in transparency, low cost and anticorrosion properties. Typical polymer substrates cannot withstand high temperature treatments. Therefore, low temperature fabrication of porous photoelectrodes has been developed. Though low temperature fabrication usually proceeds at a temperature as low as 100–150 °C, room temperature fabrication is more attractive. It not only facilitates the manufacture of solar cells but also saves energy.

Surface activation and interconnection between nanoparticles are two key factors in the fabrication of high-quality porous photoelectrodes at low temperature. The methods reported for surface activation were microwave irradiation,[3] electron-beam annealing,[4] UV irradiation[5] and ozone treatment with UV irradiation.[6] Several other methods have been applied to improve the interconnection of nanoparticles, such as low temperature heating,[7] compression,[8] hydrothermal crystallization,[9] chemical-vapor deposition with UV irradiation,[10] electrochemical deposition[11] and electrophoretic deposition.[12] The highest efficiency is 4.1% (under 100 mW cm^{-2})[12] for low temperature fabricated flexible DSCs on polymer substrates, in which the TiO_2 photoelectrode is assembled with electrophoretic deposition followed by TiO_2 sol treatment. An alternative method is the layer transfer technique.[13] The TiO_2 layer on Au–glass is presintered at 450 °C to form particle interconnection, and then it is lifted off by dissolving the Au underlayer and compressed onto the indium tin oxide coated poly(ethylene terephthalate) (ITO–PET) substrate by high pressure. Though the prepared DSC has obtained an efficiency of 5.8% under 100 mW cm^{-2} illumination, this procedure may need simplification before practical applications.

As mentioned above, most of the reports on flexible DSCs are based on porous TiO_2 photoelectrodes. Though some promising routes for low-temperature sintering have been proposed, the efficiency of the flexible DSCs on polymer films is in general much lower than that of DSCs on FTO (F-doped tin oxide)–glass substrates sintered at high temperature. The main reason for the lower efficiency is usually given as the poor connection between TiO_2 particles.[14,15] ZnO is another wide band gap semiconductor which can be used in DSCs. It has excellent electrical characteristics, such as high electron mobility[16] and the fast diffusion of electrons in the ZnO nanostructure films.[17–19] We think these characteristics should facilitate the ZnO nanoparticles forming good electronic interconnections. The highest reported efficiencies of high-temperature prepared ZnO glass DSCs, which are fabricated by a compression method[20] or an electrochemical deposition method, are 4–5%.[21]

In this communication, a porous ZnO photoelectrode was fabricated at room temperature by doctor-blading ZnO gel. The corresponding flexible ZnO DSC yields a conversion efficiency of 3.8% (under 100 mW cm^{-2}). The ammonia activation and the $ZnAc_2$ assisted interparticle connection were appreciated. This work shows that ZnO is a promising material for room temperature fabrication.

ZnO sol was prepared typically by mixing 3.0 g ZnO powder (20 nm, Wako) and 4 mL HAc aqueous solution (0.1 M) together and then ball milling the mixture for 1 h. After it was aged at room temperature for 15 min, the ZnO sol was converted to ZnO gel. The prepared ZnO gel was coated on an ITO–PET film (sheet resistance, 13Ω/□, Tobi) or a FTO glass (TEC-8, LOF) by the doctor-blade technique. After drying at room temperature, the ZnO film was immersed in 0.3 M ammonia for 15 min. Then the activated film was rinsed with ethanol and dried in vacuum at room temperature. For comparison, the ZnO films without ammonia treatment or annealed at different temperatures were also prepared. The obtained ZnO photoelectrodes are transparent and their thickness is about 11 μm.

The porous ZnO photoelectrodes were sensitized by immersing them in 0.3 mM N719 dye (*cis*-bis(isothiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylato)Ru(II) bis-TBA) in anhydrous ethanol solution for 2.5 h. The dye loading was determined by desorbing the dye from the sensitized film of a known area in a measured volume of NaOH aqueous solution and measuring its absorption

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spectrum. In order to prevent short circuit of the flexible cells, SiO_2 gel electrolyte was used in this study. The electrolyte consisted of 0.6 M methylhexylimidazolium iodide, 0.05 M iodine, 0.2 M LiI, 0.5 M *tert*-butylpyridine and 6 wt% SiO_2 powder (14 nm, Degussa) in 3-methoxypropionitrile–acetonitrile (v/v = 50%/50%). The counter electrode of the glass DSCs was FTO glass coated with a layer of sputtered Pt. The flexible counter electrode was fabricated similarly to the literature:[8] 3 mL 10 mM H_2PtCl_6 in 2-propanol and 3 g Sb doped SnO_2 nanoparticles were mixed, dried and then pyrolyzed at 380 °C for 25 min. The resulting powder was ballmilled together with 12 mL ethanol for 8 h. The obtained paste was doctor-bladed on the ITO–PET substrates and dried at room temperature. Finally, the powder layer with substrate was compressed at 90 MPa.

The photocurrent–photovoltage measurements were recorded with a potentiostat (Princeton Applied Research, Model 263A). A solar light simulator (Oriel, 91192) was used as a white light source to give an AM1.5 illumination on the surface of the solar cells. The intensity of incident light was measured with a radiant power/energy meter (Oriel, 70260) before each experiment.

Fig. 1 shows *I–V* curves of glass DSCs employing ZnO photoelectrodes with and without ammonia treatments. The device that employs ZnO photoelectrode without ammonia treatment performs poorly, and the conversion efficiency is only 0.74%. With ammonia treatment we find a remarkably enhanced photocurrent of J_{SC} = 11 mA cm^{-2}. This enhancement by a factor of 5, an open circuit potential of V_{OC} = 575 mV, and a fill factor of *FF* = 71% lead to an efficiency of 4.5%. This implies that ammonia treatment is an effective room temperature surface activation method for ZnO photoelectrodes.

In order to estimate the interconnection among the nanoparticles, we investigated device performance subject to different annealing temperatures. The ZnO layers after ammonia treatment were further annealed at different temperatures for 30 min. If the interconnection of nanoparticles is not enough, the efficiency of the devices will increase remarkably after high temperature annealing. Fig. 2 shows the efficiency of DSCs as a function of annealing temperature. From the curve we can see, below 300 °C, that increasing the annealing temperature has little effect on the final efficiency. Further increase of the annealing temperature quickly decreases the efficiency of the device because of the ZnO particle growth. This result indicates that the room temperature prepared ZnO photoelectrode has adequate interparticle connectivity.

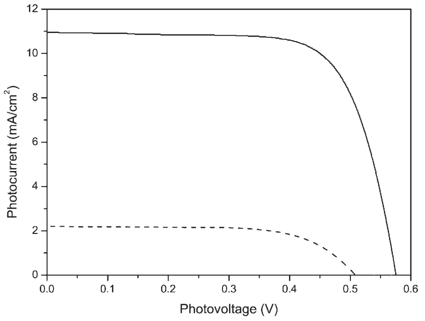


Fig. 1 Photocurrent–photovoltage relation of DSCs employing room temperature fabricated ZnO layers on the FTO glass with (solid line) and without (dashed line) ammonia activation (under 100 mW cm^{-2}).

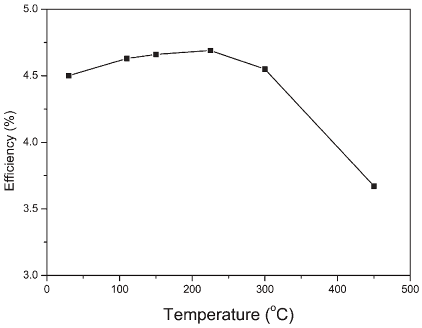
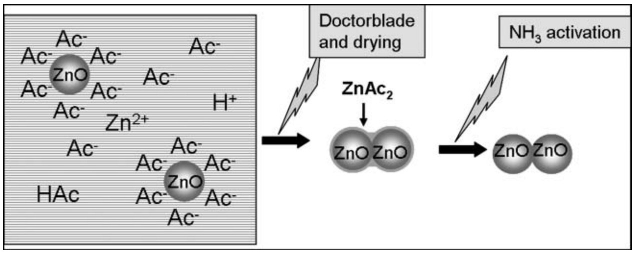


Fig. 2 The efficiency of ZnO glass DSCs annealed at different temperatures for 30 min (under 100 mW cm^{-2}).

We suggest the mechanism of this room temperature fabrication process in Scheme 1. The nanoparticles have high surface area and it is easier for them to aggregate together. The aggregated ZnO nanoparticles, therefore, are difficult to uniformly disperse in water. When adding ZnO powder into dilute acetic acid solution, the surface of the ZnO nanoparticles can be etched by the acid.[22] This etching process can help to separate the aggregated ZnO powders and thus uniform ZnO colloid is obtained. The etching process also forms $ZnAc_2$ which dissolves in the solution as electrolyte (Scheme 1a). The electrolyte can assist the interconnection of ZnO nanoparticles when the doctor-bladed layer is drying. Firstly, the Ac^- can screen the surface charge of the ZnO nanoparticles.[23] Therefore, the nanoparticles can easily approach each other and good interparticle connection can be formed. Another factor is its binder effect. Binder is usually needed in preparing thick layers to avoid cracking. Normally some polymers are used as binders, but removing these polymers is difficult in the low temperature process. In this case $ZnAc_2$ acts as binder to connect the ZnO particles together as well as to attach the film to the substrate (Scheme 1b). Therefore, the obtained ZnO layer is crack-free and mechanically stable. In the as-prepared ZnO layers, there is also $ZnAc_2$ coated on the surface of the ZnO nanoparticles, which prevents the dye adsorption and decreases the effective adsorption area. The density of dye adsorption is 1.25 × 10^{-8} mol cm^{-2} which only covers about 10% of the surface of the porous ZnO layer. The efficiency of DSCs using this photoelectrode is only 0.74% (Fig. 1). Therefore, surface activation is necessary. The traditional surface activation method is a high



Scheme 1 (a) In the prepared ZnO sol, Ac^- ion screens the surface charge of the ZnO nanoparticles and there is Zn^{2+} which comes from etching ZnO by HAc. (b) After drying the prepared ZnO layer, the $ZnAc_2$ acts as binder to connect the ZnO particles together in the prepared ZnO layer and it coats the surface of ZnO nanoparticles too. (c) During ammonia treatment, $ZnAc_2$ was removed and the ZnO surface was changed to hydroxyl terminated.

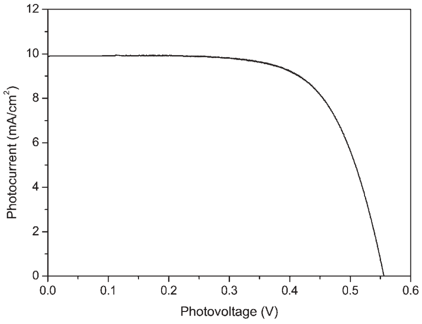


Fig. 3 The photocurrent–photovoltage relation of room temperature fabricated ZnO flexible DSCs under 100 mW cm^{-2} AM1.5 illumination.

temperature anneal. Herein we developed a room temperature surface activation method of ammonia treatment. Ammonia treatment can remove the $ZnAc_2$ coated on the surface of the ZnO nanoparticles by forming dissolvable $Zn(NH_3)_4^{2-}$ ions. Therefore, the effective adsorption area of the porous ZnO layer was increased (Scheme 1c). After ammonia treatment dye adsorption reached 1.16×10^{-7} mol cm^{-2}, which is close to the dye adsorption density of high temperature activation ZnO layers (1.19×10^{-7} mol cm^{-2}). From Fig. 1 we find that ammonia treatment also can increase the open circuit voltage. The open circuit voltage (V_{OC}) of the device employing ammonia treated ZnO photoelectrodes is 575 mV, and V_{OC} of the device with as-prepared ZnO photoelectrodes is only 505 mV. Ammonia can adsorb on a ZnO surface by coordination interaction.[24] Some amines adsorbed on the TiO_2 surface can reduce recombination and then increase the open circuit voltage.[25] The present study shows that a trace amount of ammonia adsorbed on the ZnO surface has a similar effect.

Flexible DSCs with ZnO photoelectrodes on the ITO–PET substrates were fabricated at room temperature. Fig. 3 shows the I–V curve of the device under 100 mW cm^{-2}. The photovoltaic characteristics are J_{SC} = 9.9 mA cm^{-2}, V_{OC} = 556 mV, FF = 68% and final efficiency of 3.8%. The photocurrent and efficiency are less than those of the ZnO glass DSCs (11.0 mA cm^{-2} and 4.5%). This can be explained by the difference in transmittance of the substrates to sunlight. The transmittance of ITO–PET is lower than that of the FTO–glass substrate at wavelength less than 540 nm, especially at wavelength less than 380 nm.

In summary, at room temperature, we fabricated an efficient porous ZnO photoelectrode with high surface activity and good interparticle connectivity. The room temperature fabricated ZnO glass DSC has an efficiency of 4.5% (under 100 mW cm^{-2}), which comes up to the reported high temperature fabricated ones. The flexible DSCs employing this kind of ZnO photoelectrode on ITO–PET have obtained an efficiency of 3.8% (under 100 mW cm^{-2}), which can compete with the low temperature fabricated flexible TiO_2 DSCs. The room temperature fabrication method not only satisfies the requirement of polymer substrates, but also saves energy and facilitates the manufacture. The present results show that the prepared ZnO layer is a promising photoelectrode material for flexible DSCs. If dye aggregation on the ZnO surface could be avoided and polymer substrates with higher transmittance in the near UV range could be found, the performance of the ZnO flexible DSC will be further improved.

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