Graphene based photoanode for DSSCs with high performances

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1. Electron transport in the photoanode

The schematic diagrams of the electron transport in the photoanode are shown in the Fig. 5 of the manuscript, and the energy level of TiO_2 in the work layer is ignored. Graphene is a semi-metal with the zero-energy band structure, while TiO_2 is a semi-conductor. Therefore, the resistance of TiO_2 is much higher than that of the 3DGNs. Moreover, the continuous construction of the 3DGNs provides a 3D fast transport network in the work layer for the electrons transport, which has been proved by our previous reports [1, 2]. The photo-induced electron transport in the work layer is dependent on graphene rather than TiO_2. Therefore, the energy band of TiO_2 is neglected (between the dye and graphene), which is the general treatment way in previous reports [3, 4].

2. Controlling the surface functional groups of the RGO

Briefly, the graphene oxide (GO) samples can be prepared by the modified Hummer's method and Zhang reported approach to control the original functional group (including types and ratio) of the GO, and the obtained GO products are labeled as GO (h) and GO (x), respectively [5, 6]. The major surface functional groups of the GO (h) and GO (x) are carboxyl and hydroxyl, respectively [5, 7]. Then, two ways are used to reduce the GO samples, achieving the RGO samples with various reduction degrees and functional group types. As for the first method reported by Xu et al., the alcohol is used as the reduction agency to react with the GO (h) and GO (x) [8]. Briefly, a certain amount GO sample was dispersed in 50 mL of ethylene glycol and a 60min sonication treatment is performed. Then, the suspension was heated to 160^0C

for 5 h under vigorous stirring. After a following centrifuge process, the sample was washed by deionized water for three times. Lastly, the obtained paste was dried at 60^0C in a vacuum oven (named RGO (h, e) and RGO (x, e)). By reducing by the ethylene glycol, the epoxy groups are almost removed, while partial hydroxyl and carboxyl groups are remained. In the second method, hydrazine is employed to reduce the GO samples. Briefly, 2 mL hydrazine was added into the 30 mL GO solution (2 mg/mL) dropwise at 98^0C for a certain time (2-6 h, the obtained products named RGO (h, h) and RGO (x, h)). By using the hydrazine as the reduce agency, all functional groups are removed synchronously. Moreover, order to precisely adjust the ratio of the carboxyl and hydroxyl groups, partial hydroxyl groups can be converted into carboxyl groups by using the NaOH and chloroacetic acid [9]. Briefly, an aqueous suspension of GO was bath sonicated for 1 h to obtain a solution. NaOH and chloroacetic acid were added into the suspension and the mixture was bath-sonicated for a certain time to convert the hydroxyl groups into carboxyl group partially.

In this study, the sample with the requirement of $C_{element}$: $C_{hydroxyl}$: C_{epoxy}: $C_{carboxyl}$ =63: 16: 3:18 ($C_{element}$: $C_{function}$ = 1.7: 1) is prepared as following: 25 ml the as prepared GO (x) (the concentration is $\sim$2 mgml^{-1}) was treated by the NaOH (1.2 g) and chloroacetic acid (1 g) for 1h to achieve the part convert of hydroxyl to carboxyl, and then the obtained sample was reduced by using the ethylene glycol for 3 h.

3. Particles average size of the RGO-TiO$_2$ in the scattering layer

The average size of the RGO-TiO$_2$ can be controlled by adjusting the reaction conditions during the hydrothermal reaction. With an increasing reaction time and temperature, the average size enlarges, and the specific relationship between these parameters are listed in the Table S1.

Table S1 Average sizes of the resulting RGO-TiO$_2$ with the various reaction

parameters.

Average sizes(nm)	Reaction time(h)	Reaction temperature(^{0}C)
550	12	150
700	12	180
950	12	220
1100	18	150
1300	24	150
2000	24	180

4. XPS curves of the RGO with a controllable surface functional groups
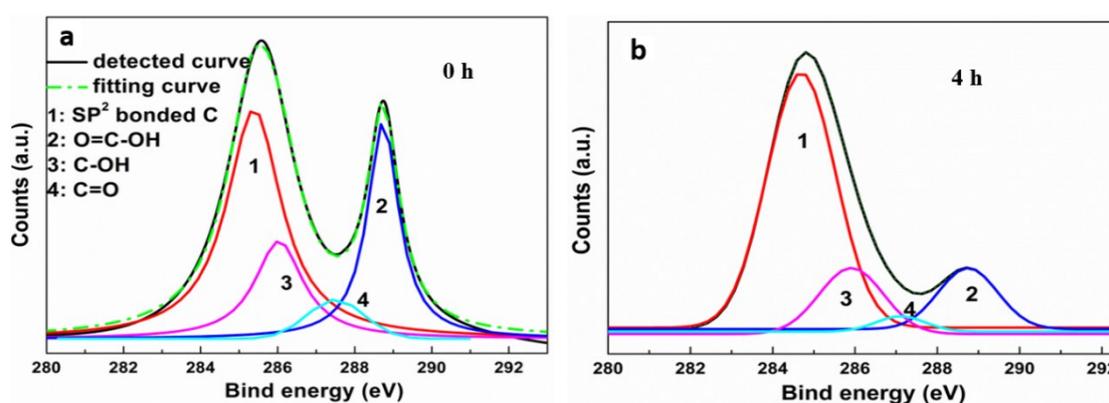

Fig. S1 XPS patterns of the adopted RGO with and without reduction.

After optimizing the reduction degree of the RGO in the transport layer, work layer and scattering layer, the J_{SC}, V_{OC}, FF and η are 24.6 mAcm^{-2}, 707, 0.64 and 11.13%.

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