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SPRAY PYROLYSIS GROWTH ANDSYNTHESIS OF SILICA-DOPED NANO-HEMATITE Fe_2O_3

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Abstract

The spray-pyrolysis formation of photo-electrochemically active films is versatile and it allows additivesto be introduced in order to affect morphology and structure of deposits. Here, addition of tetramethoxysilane (TMS) in varying amounts to iron oxide precursor systems for spray pyrolysis is investigated and the dramatic effect on the photo-electrochemical water splitting current in aqueous 1 M NaOH is discussed.

Introduction

Hematite (α-Fe_2O_3) was found to be a good film component for photo- electrochemical electrodes for water splitting because it is abundant, cheap, and effective(1). Even more promising are modified hematitefilms, especially those obtained after doping with effective dopants such as silicon(2). The potential effectsof the dopants in photo-electrochemistry are complex and may be based on (i) altering the hematite bandgap, (ii) changing morphology, (iii) altering the crystal shape and orientation, (iv) blocking or enhancing recombination or catalysitc sites, and (v) affecting charge carrier mobility.

Atmospheric pressure chemical vapour deposition (APCVD) methods have been used previously for preparation of pure and Si-doped α-Fe_2O_3 (3) to investigate and improve the photo-electrochemical efficiency for splitting of water. It was found that some Si incorporated into Fe_2O_3 lattice as Si^{4+} and this led to some disordering in the iron oxide films (4). Meanwhile Saremi-Yarahmadi et al. (2) found also that the optical band gap of Si-doped Fe_2O_3 increases with increasing of TEOS (tetraethoxysilane) incorporation rate. It was observed that the incorporation of silicon into the hematite lattice reduced its particle size and increased the donor densities.

Reactive magnetron sputtering (4) was used to prepare un-doped hematite as well as Siand Ti-doped Fe_2O_3.From this study it was found that doping of hematite with siliconand titanium enhanced the photochemicalreaction of the film while decreasing the onset potential. Doping with titanium was found to be more effective than dopingwith silicon. Glasscock et al. (3) explained that dopants lead to passivity of the grain boundaries with improvements due to decreasing the recombination rate.

Tetraethoxysilane (TEOS) has been used to modify hematite with silicon, which affected beneficially the photochemical reaction of hematite in an aqueous electrolyte as Cesar et al. found [(5)]. They used atmospheric pressure vapour deposition (APCVD) to prepare the nanostructured silicon-doped hematite and pure hematite from $Fe(CO)_5$.Through this study, it was found that the substrate temperature has a considerable influence on the grain size and morphology. It was found also that the growth rate of films is slower at high temperatures. The feature size of the film was found to depend on the silicon content in iron oxide film. Silicon-hematite doping increases the electron density (10^{20} cm^{-3}), which can lead to formation of a space charge region inside the nano-structured hematite and this can help separating photo-generatedelectron-hole pairs. Cesar et al. also found that the recombination rate is much higher on the tin oxide-fluorine substrate in comparison to that in the bulk part of the hematite film.

Experimental

Chemical Reagents

Iron acetylacetonate $(C_5H_8O_2)_3Fe$ (99.9%), Ferrocene carboxlic acid and tetramethoxysilane (TMS,$Si(OCH_3)_4$), 99%) were obtained from Aldrich, while absolute methanol was from Fisher Scientific, and ferrocenecarboxlic acid 98% was from Alfa Aeser. These chemicals were bought commercially and usedwithout further purification. Water used in preparation of some solutions was filtered and doublede-ionized water (DDW, MilliQ water, from Elga system) with resistivity of ca. 18.2 M Ω cm.

Spray Pyrolysis Formation of Iron Oxide Films

Two different precursor solutions with different concentrations of either $Fe(acac)_3$ or ferrocenecarboxlic acid were used for spray pyrolysis. The solvent was DDW (doubledeionised water) mixed with either methanol or other organic solvents, as shown in Table 1. Different "apparent" dopant concentrations were obtained by adjusting the tetramethoxysilane (TMS) $Si(OCH_3)_4$) concentration.

Summary of doped and un-doped-iron precursor solutions used for spraypyrolysis at 500 °C.

Sample	Chemical composition	Precursor solution	Si content
1F0Si	Fe_2O_3	0.5 M ferrocenecarboxlic acid/ 3:1 methanol : butanol	0 %
3F0Si	Fe_2O_3	0.05 M ferrocenecarboxlic acid/ 1:3 methanol : butanol	0 %
5SiF	Si-Fe_2O_3	50 mL 0.05 M ferrocenecarboxlic acid + 15 µL TMS conc. soln. was sprayed on FTO, tech 15 for 13 mins. Annealed at 500° C for 2 hrs.	4 %
2SiF	Si-Fe_2O_3	25 mL 0.169 M ferrocenecarboxlic acid + 2 µL TMS conc. soln. then 18 mL 0.05 M $Fe(acac)_3$ was sprayed on top. Annealed at 500° C for 2 hrs.	4 %
2F0Si	Fe_2O_3	0.5 M $Fe(acac)_3$ / 1:1 Methanol:DDW	0 %
3SiF	Si-Fe_2O_3	0.05 M $Fe(acac)_3$ + 300µL TMS conc. soln. was sprayed on FTO, tech 15 for 12 mins. Annealed at 500° C for 2 hrs.	40 %
4SiF	Si-Fe_2O_3	50 mL 0.05 M $Fe(acac)_3$ + 15 µL TMS conc. soln. was sprayed on FTO, tech 15 for 12 mins. Annealed at 500° C for 2 hrs.	4 %
6SiF	Si-Fe_2O_3	50 mL 0.05 M $Fe(acac)_3$ + 1.875 µL TMS conc. soln. was sprayed on FTO, tech 15 for 13.4 mins. Annealed at 500° C for 2 hrs.	0.5 %

7SiF	Si-Fe_2O_3	50 mL 0.05 M Fe(acac)$_3$ + 3.75 µL TMS conc. soln. was sprayed on FTO, tech 15 for 12.5 mins. Annealed at 500^o C for 2 hrs.	1 %
8SiF	Si-Fe_2O_3	50 mL 0.05 M Fe(acac)$_3$ + 7.5 µL TMS conc. soln. was sprayed on FTO, tech 15 for 12.50 mins. Annealed at 500^o C for 2 hrs.	2 %

Results and Discussion

Effects of Doping Fe_2O_3 with Si on Morphology

Figure 1 shows the SEM front pictures of un-doped and Si-doped Fe_2O_3, as a comparison between un-doped Fe_2O_3 prepared by using Ferrocenecarboxlic acid precursor solution (A), and that of 4% Si-doped Fe_2O_3 prepared from the sameprecursor after adding 4% atomic weight of (TMS) into the Ferrocenecarboxlic acid precursor solution (C). From this comparison it was found that the insertion of Si^{4+}, asit was estimated elsewhere [1, 5], affects the particle size and shape.

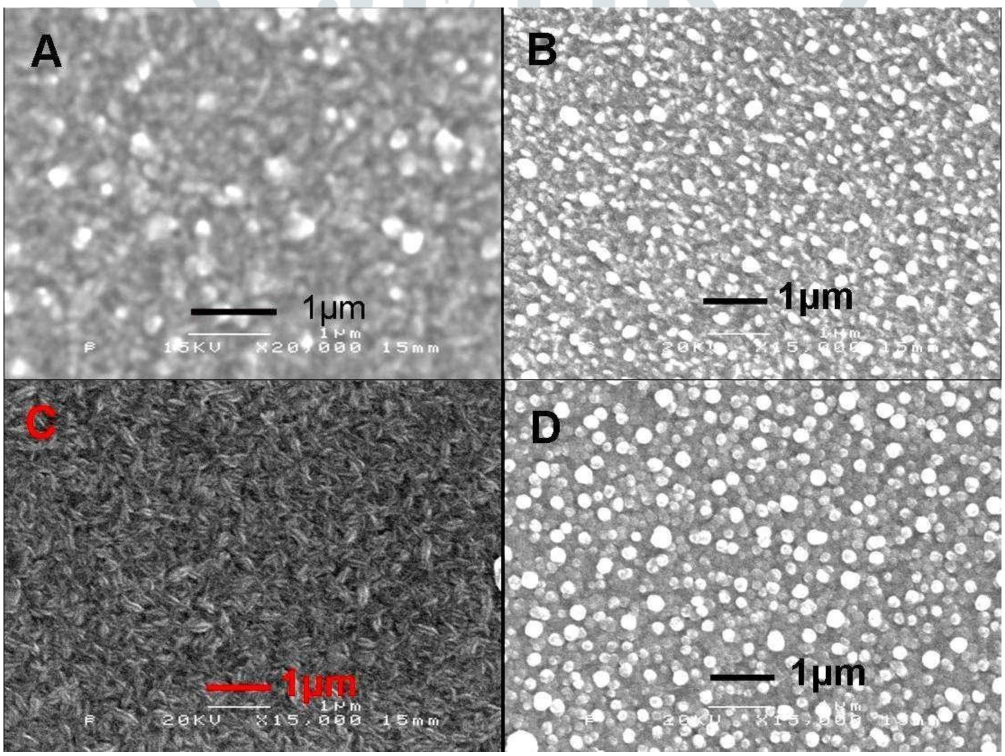

Figure 1. SEM images of; A: 0% Si-Fe_2O_3 (1F0Si), B: 4% Si-Fe_2O_3 (4SiF1) C: 4% Si- Fe_2O_3 (5SiF4), and D: 40% Si-Fe_2O_3 (3SiF3).

Particles in image A are almost circular and bigger while in image C, they are coffee bean shaped and much smaller. Images B and D are for 4% and 40% Si-Fe_2O_3 doped using Fe(acac)$_3$ precursor solution containing the above ratios of atomic weight

contents. Although, the samples in image A and those in images B and D were prepared from different precursor solutions (from ferrocenecarboxlic and Fe(acac)$_3$) precursor solutions), it can be noticed that they are similar in the shape, which is almost circular with a particle size slightly smaller in B and D than in A. However, in a comparison between image B (4% Si-Fe_2O_3) and that of D (40% Si-

Fe_2O_3), it canbe noticed that there is no a big difference in either shape or in the particles size.

Incident Photon to Current Efficiency (IPCE) Studies

It was found that silicon doping strongly increases the efficiency of Fe_2O_3 electrodes possibly because it acts as an electron donor due to substitution of Fe^{3+} by Si^{4+} in the Fe_2O_3 lattice. This is believed to improve electrical conductivity, the charge transfer, and consequently decrease the recombination rate of the photo-generated pairs. The trend in photo-activity is confirmed in IPCE measurements (see Figure 2).

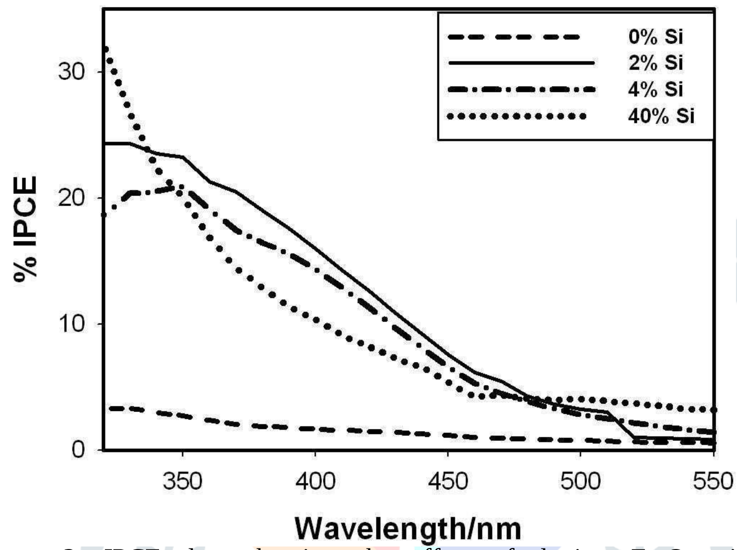

Figure 2. IPCE data showing the effect of doping Fe_2O_3 with different concentrations of Si using the spray pyrolysis method (0%= 2F0Si, 2%=8SiF, 4%=4SiF, 40%=3SiF). Data obtained in 1 M NaOH, at applied potential 0.7 V vs. Ag/AgCl and by illuminating by 75W Xenon lamp

An increase in the doping level from 0% to 2% causes a significant increase in photo-electrochemical activity.Any further increase is not detrimental but also not beneficial. It is likely that even lower levels of silicon doping may suffice. Excess silicon may simply be present as trace silicate impurity. The smaller grain size causedby silicon doping increases the surface area and porosity of the photo-anode and consequently this may increase the light harvesting effect.

Conclusions

It has been shown that spray pyrolysis offers a simple methodology for the formation of highly active hematitephoto-absorber layers. In particular, when used in conjunction with silicon doping high efficiencies (IPCE upto 20%) can be achieved. The choice of hematite precursor appears to be not very important and tetramethoxysilane offers good doping effects.

In future, film efficiency can be improved further by (i) systematically changing the film thickness, (ii) furtherdecreasing the doping level, and (iii) developing layer structures with morphology/structural gradients from the substrate to the hematite solution interface to aid charge separation and to restrict recombination.

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