Enhanced dye illumination in dye−sensitized solar cells employing TiO_2/GeO_2 photoanodes

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Supporting theory

Fresnel theory has been employed to reveal the potential mechanism of transimission enhancement in GeO_2 incorporated TiO_2 photoanodes.

$$n = \sqrt{n_0 n_s} \qquad \text{(S1)}$$

where n_0 is the refractive index in upper layer, n is the refractive index in the middle layer, and n_s is the infractive index in the lower layer.

It is a prerequisite to match the refractive indexes well of mediums well in fabricating an antireflective film for transmission enhancement. The refractive index (n_0) of incident light in air is 1, therefore, n should match well with square root of n_s. It is known that the refractive index of GeO_2 (n) is around 1.99, whereas that is 2.55 for anatase TiO_2 (n_s), suggesting that the square root of n_s is approximately 1.60. However, the further decrease of n_s benefiting from the nanoporous structure of TiO_2 results in a complete matching of $\sqrt{n_0 n_s}$ with n.

Actually, the optical dispersion of TiO_2 obeys [S1]:

$$n_s^2 = 5.913 + \frac{0.2441}{\lambda^2 - 0.803} \qquad \text{(S2)}$$

where λ is wavelength of incident light.

The optical dispersion of GeO_2 obeys [S2]:

$$n^2 = 1.286 + \frac{1.0704\lambda^2}{\lambda^2 - 0.01} + \frac{1.102\lambda^2}{\lambda^2 - 100} \qquad \text{(S3)}$$

From Fresnel law, we can obtain the following relationship:

$$t_{12} = \frac{2n_1}{n_1 + n},\ t23 = \frac{2n}{n_2 + n},\ r21 = \frac{n_1 - n}{n_1 + n},\ r23 = \frac{n_2 - n}{n_2 + n} \qquad \text{(S4)}$$

t_{12} is amplitude reflectivity from air to GeO_2, t_{23} is the amplitude reflectivity from GeO_2 to TiO_2, r_{21} is the amplitude reflectivity from GeO_2 to air, and r_{23} is the amplitude reflectivity from GeO_2 to TiO_2. The transmission enhancement of the GeO_2 incorporated TiO_2 photoanode after repeated reflection and transmission can be calculated according to:

$$T = \frac{(t_{12}t_{23})^2}{1 - 2r_{21}r_{23}\cos\varphi + (r_{12}r_{23})^2} \qquad \text{(S5)}$$

T represents transmission, $\varphi = \frac{4\pi}{\lambda} d\cos\theta$ is phase difference, d is the thickness of GeO_2, θ is the angle of incident light. In our experiment, the DSSCs are illuminated perpendicularly by the simulated solar, therefore, θ is 0°. After simulation by a programe, we find that the theoretical fitting and the experimental curve match well in the photoanode from TiO_2/0.5 wt% GeO_2 nanocrystallines.

Supporting program

```
clear all

close all
```

```
lamada=linspace(0.29,1.05,1000);
n1=1*linspace(1,1,1000);
n=1*(1.286+1.0704*lamada.^2./(lamada.^2-0.01)+1.102*lamada.^2./(lamada.^2-100)).^0.5;
n2=0.5*(5.913+0.2441./(lamada.^2-0.0803)).^0.5; %, 0.5
d=1e-6; %
fy=4*pi./(lamada*1e-6).*n*d;
t12=2*n1./(n1+n);
t23=2*n./(n+n2);
r21=(n1-n)./(n1+n);
r23=(n2-n)./(n2+n);
%R=((n1-n).^2.*(cos(fy/2)).^2+(n1.*n./n2-
n2).^2.*(sin(fy/2)).^2)./((n1+n).^2.*(cos(fy/2)).^2+(n1.*n./n2-n2).^2.*(sin(fy/2)).^2);
T=(t12.*t23).^2./(1-2*r21.*r23.*cos(fy)+(r21.*r23).^2);
plot(lamada,n)
figure
plot(lamada,n2)
%figure
%plot(lamada,n)
T1=T*100;
lamada1=lamada*1000;
figure
plot(lamada1,T1)
```

Supporting references

[S1] J. R. Devore, Refractive indices of rutile and sphalerite. J. Opt. Soc. Am. 41 (1951) 416.

[S2] G. Ghosh, Dispersion-equation coefficients for the refractive index and birefringence of calcite and quartz. Opt. Commun. 163 (1999) 95.