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Enhancement of electrochemical luminescence (ECL) from nanopores of TiO_2

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Introduction: Gratzel et al. have reported that dye sensitized solar cells equipped with nano-porous TiO_2 layers exhibit more than 10% photo-energy efficiencies[1]. The enhancement has been explained by the large charge separation areas fabricated with nano-porous TiO_2 and electrolytes filling the pores[1]. Our objective is to realize visible emissions from cells equipped with nano-porous TiO_2 layers and electrolytes filling the nano-pores.

Experimental: We used ECLs from ($Ru(bpy)_3^{2+}$), because this has been intensively studied [2-10]. We used the simplest cell: glass/Fdoped SnO_2 /porous TiO_2/($Ru(bpy)_3(PF_6)_2$ in acetonitrile /F doped SnO_2/Glass(Figure 1).

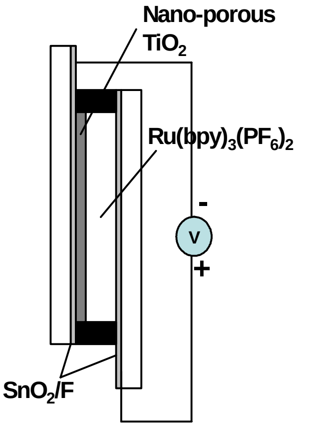

Figure 1 Cell configuration

Results and Discussion: Three electrodes consisting of nano-porous TiO_2 layer, dense TiO_2 layer, and SnO_2/F layer without TiO_2 layer were employed. When voltage was applied, three cells showed almost the same current-voltage behaviors, leading to the conclusion that current does not changed even when porous TiO_2 layers with large surface areas were employed. Figure 2 shows the relationship between applied voltage and ECL. Drastic increases in ECL were observed for cells equipped with nano-porous TiO_2 layers. ECL from the cell with dense TiO_2 layers did not change, compared with that without TiO_2 layers, suggesting that the intense ECL is not associated with TiO_2 itself, but the nano-porous structures. $Ru(bpy)_3(PF_6)_2$ has a photo-luminescence at 596.5 nm in acetoritrile when this was excited with 350nm light. ECL from the cell with TiO_2 layers had the maximun wavelength at 620.4 nm. The ECL was red-shifted by 23.9 nm. The half value width of ECL from the cell having porous TiO_2 layers was 104 nm, larger than that of 65 nm of PL. This suggests that species for ECL might be somehow restricted mortionally.

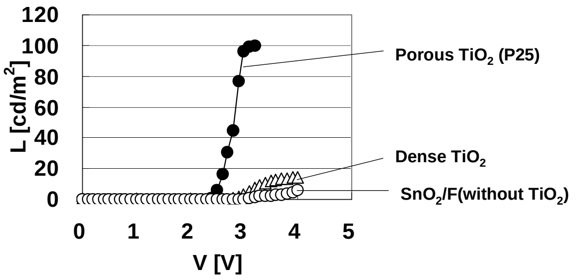

Figure 2 The relationship between luminescence and voltage applied
TiO_2：P25 ; $Ru(bpy)_3(PF_6)_2$ 0.15M in MeCN; 1cm² cell, t:11 µm

The intense ECL was obserbed only when minus voltage was applied to TiO_2 layers.

Table 1 summarized ECL from various metal oxides. ECL from TiO_2 with higer surface areas tended to emit stronger light. ECL increased with an increase in the thickness of TiO_2 films and had 260cd/m² at 30 µm thickness when 3 V was applied. Enhanced ECL was observed for cells bearing nanoporous ZnO layers, but not observed in case of nanopolous SnO_2 layers.

ECL mechanism has been reported as follows[2-10]. On a cathode, Ru(II) was reduced to form Ru(I). On a anode, Ru(II) was oxidized to form Ru(III). They diffuse each other in acetonitrile from anode and cathode. Ru(I) collides with Ru(III) to form excited Ru(II)*. ECL is observed when the excited Ru(II)* goes down to the ground state Ru(II).

Table 1 ECL from cells bearing various porous metal oxides

		m^2/g(5)	$L[cd/m^2]$(6)	$J[mA/cm^2]$(7)	lm/W(8)	t(µm)(9)	Ru(M)(10)	V(V)(11)
TiO_2	F6 (1)	97.0	47.6	12.6	0.4	7	0.06	3.0
	F5(1)	69.0	69.5	13.3	0.5	7	0.06	3.0
	P25(2)	49.0	69.8	12.9	0.6	7	0.06	3.0
	G1(1)	6.0	7.4	17.6	0.0	7	0.06	3.0
	G2(1)	3.0	4.9	16.0	0.0	7	0.06	3.0
	P25(2)	97.0	260.0	35.0	0.6	30	0.16	3.3
ZnO	(3)	35.0	82.7	25.4	0.3	7	0.08	3.0
SnO_2	(4)	23.0	1.2	16.1	0.0	7	0.08	3.0
non	-	-	0.3	11.5	0.0	-	0.06	3.0

1) Showa Denko K.K. 2)Nippon Aerosil Co., Ltd.
3) Nanoteck ZnO (C.I. Kasei Corporation) 4) Nanoteck SnO_2 (C.I.Kasei Corporation)
5) Surface area 6) Luminescence 7)Current density at a diffinite voltage(3.0 or 3.3 V)
8) Efficiency (lumen/W) 9) Metal oxide thickness 10) Ru concentration in MeCN
11) Voltage applied

How is ECL from cells bearing porous TiO_2 enhanced? One possible explanation was that electron injection from porous electrodes increased with an increase in the surface areas. This was denied by the fact that currents for cells bearing porous TiO_2 was almost the same as those without porous TiO_2 layers. The other explanation is that chances for collision between Ru(I) and Ru(III) increased. The collision chance decreases at least the following mechanims. One is that Ru(I) or Ru(III) reaches the opposite electrode and makes electron exchanges on the opposite electrodes. The other possibility is that Ru(I) or Ru(III) is deactivated by some reasons during diffusions in acetonitrile. Ru(I) is expected to be less stable than Ru(III). If the former is the major reason, ECL enhancement should occur whether plus or minos voltage was applied to the TiO_2 electrode. However, the ECL enhancement occurred only when minous was applied to the TiO_2 electrode. The latter mechanism explains well all the phenomena observed. On the porous TiO_2 cathode, Ru(II) is reduced to form Ru(I). The less stable Ru(I) was stabilized within the nano-pores in cathode TiO_2 layers. $Ru(I)^+$ may be bonded to TiO^- on the nanopore walls with ionic interactions. The Ru(III) species diffuse from anodes to cathode TiO_2 nano-pores and collisions occur within the nanopores. This would increase the collision opprtunities between Ru(I) and Ru(III). The fact that ECL increased with an increase in the porous TiO_2 thickness also support this mechanism.

Conclusion: We found that electrochemical luminescences enhanced drastically by use of cathodes with nano-porous TiO_2 layers. It is likely that the enhancement is associated with increases in collision opprtunity between Ru(I) and Ru(III) in the nano-pores of TiO_2 layers.

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