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ORIGINAL CONTRIBUTION

Effect of particle diameter on the electro-optical property of reflective electrochromic display based on monodisperse viologen-modified polymeric microspheres

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Abstract A reflective electrochromic display (R-ECD) based on viologen-modified polymeric microspheres was prepared and the influence of particle size on the electro-optical characteristics was investigated. The diameters of the viologen-modified polymeric microspheres were altered changing the solvency of the medium during the dispersion polymerization. The chloro-functionalized polymeric microspheres were produced through seeded polymerization, and then the viologen moieties reacted with the methyl chloride functional groups. It was found that the coloration efficiency and the response time of the R-ECD were significantly affected by sizes of microspheres. In addition, the R-ECD had good cyclic stability because the viologen moieties were stably grafted on the surface of the microspheres.

Keywords Reflective electrochromic display (R-ECD) · Microsphere diameter · Coloration efficiency · Response time · Cyclic stability

Introduction

Viologen, the common name given to *N*,*N*′-disubstituted-4,4′-bipyridinium dications by Michaelis in 1933 [1, 2], has been extensively studied as a herbicide [3], electron mediator [4], and catalyst [5]. The compound is typically derived from diquaternizing a 4,4′-bipyridine and changes color depending on the redox state by electron-transfer interactions between component molecules [6–10]. This chromogenic property suggests that viologen is potentially useful for the fabrication of electronic devices such as electrochromic or photochromic displays [11–15]. However, tens of seconds are needed to recognize the color changes in the case of a conventional electrochromic display (ECD) [16]. In addition, there is poor cyclic stability in such an ECD resulting from the various side effects of viologen such as the aging process [17], dimerization [18], and comproportionation [19]. Because of the drawbacks of the viologen, the conventional type of ECD is insufficient for electronic display application.

It is well known that reflective-type displays have a much higher resolution and readability than transmissive-type displays in direct sunlight. Furthermore, a simpler fabrication process is possible because backlighting is unnecessary. In our previous studies [20–22], we proposed a novel reflective ECD (R-ECD) utilizing polymeric microspheres with viologen pendants. The R-ECD had an original white background without using any additional reflection mainly because of the micron size range of the polymer particles and the bleached state of viologen pendants. However, the coloration time of 4 s was deficient for display, which resulted from a small amount of viologen and nonconductive polymer substrate in the R-ECD device. Therefore, the chain length of the viologen was controlled to ensure fast electron-transfer interactions of the viologen from electrolyte, achieving 0.92 s at the longest chain length in our previous work [22]. The aim of the present paper is to investigate the relationship between the diameters of particles and the electro-optical properties of the R-ECD.

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In the present research, the influence of particle size on the electro-optical characteristics of the R-ECD was investigated. The diameters of the polystyrene (PS) particles were controlled by the medium solvency in the dispersion polymerization. The chloro-functionalized polymer particles produced by seeded polymerization were refluxed with 1-heptyl-4-(4-pyridyl)-pyridinium bromide; finally, the polymeric microspheres containing viologen pendants were obtained. The preparation process of the viologen-modified polymeric microspheres was monitored through a scanning electron microscope. The respective response times of the R-ECD cells using different-sized particles were measured, and the relationship between the particle diameter and the electro-optical properties is discussed. In addition, the cyclic stability of the R-ECD cells was also measured.

Experimental

Materials

Inhibitors in styrene (St, Junsei), 1,6-hexandiol dimethacrylate (HDDM, Sartomer), chloropropene (CP, 98%, Aldrich) were removed by passing through a removing column (Aldrich). 1-Chlorododecane (CD, TCI) and 1-heptyl-4-(4-pyridyl)-pyridinium bromide (Aldrich) were reagent grade. Poly(vinyl pyrrolidone) (PVP, M_w= 40,000 g/mol, Aldrich), aerosol-OT (AOT, Wako), poly (vinyl alcohol) (PVA, M_w=88,000–92,000 g/mol, 87–89% hydrolyzed, Kuraray), and sodium lauryl sulfate (SLS, Yakuri) were used without further purification. 2,2′-*Azobis* (isobutyronitrile) (AIBN, Junsei) and benzoyl peroxide (BPO, Aldrich) were recrystallized from methanol before use. Distilled deionized water (DDI), ethanol (99.9%, J. T. Baker), methoxy ethanol (Yakuri), and toluene (Taejung) were used as solvents.

Polystyrene particles by dispersion polymerization

PS seed particles were prepared using dispersion polymerization [23, 24]. PVP, AOT, and the solvent mixture were weighed into a 250-ml four-necked glass flask equipped with a reflux condenser, nitrogen inlet apparatus, and a mechanical stirrer. After vigorous stirring for 30 min, the mixture of St and AIBN was poured into the reactor. The homogeneous solution was polymerized at 70 °C for 24 h under a nitrogen atmosphere. The stirring speed was set at 40 rpm throughout the polymerization. The obtained products were purified three times with ethanol by centrifugation at 2,800 rpm for 10 min to remove the surface anchored PVP molecules. The particles were dried under a vacuum oven before use. A standard recipe of dispersion polymerization is summarized in Table 1.

Preparation of viologen-modified polymeric microspheres

Seeded polymerization [20, 25] was carried out in a four-necked glass reactor equipped with a mechanical stirrer, a reflux condenser, and a nitrogen gas inlet apparatus. The PS seed particles (0.2 g) dispersed in the SE solution (40 g 0.25 wt.% of SLS in ethanol aqueous solution; EtOH/DDI= 1:5, g/g) were swollen with fine CD emulsions. After confirming the complete disappearance of the emulsions, a mixture of the second monomers (St/HDDM/CP=6.5 g/0.5 g/3.0 g) and BPO (0.1 g) emulsified by an ultrasound homogenizer in the SE solution (20.0 g) were poured into the flask. The swelling continued for another 6 h at 30 °C, then the swollen particles were stabilized with 5 wt.% of a PVA aqueous solution (50.0 g). The polymerization was carried out at 80 °C for 10 h. The chloro-functionalized particles were repeatedly washed with water, decanted, and dried under ambient temperature.

A one-necked glass flask equipped with a reflux condenser was employed for the refluxing process. The chloro-functionalized particles (0.2 g) were dispersed in toluene (50 ml), and 1-heptyl-4-(4-pyridyl)-pyridinium bromide (0.4 g) was added. The solution was gently refluxed for 4 h. For a good yield of the S_N2 reaction [9] between the nitrogen and alkyl chloride groups, the solution was magnetically stirred throughout the refluxing. After cooling, polymeric microspheres containing viologen pendants were collected and repeatedly washed with ether and warm ethanol.

Fabrication of R-ECD cells

The R-ECD cells consisted of two species of indium tin oxide (ITO) coated glass (30 Ω, Samsung Corning), on which the ITO layers faced each other. The cell gap was supported by a 75-μm-thick polyethylene telephtalate film spacer. The operation area in the cells was about 2×2 cm.

Table 1 Standard recipe for the preparation of polystyrene particles[a]

Ingredients	Quantity (g)			
Styrene	12.50			
AIBN[b]	0.125			
PVP[c]	1.79			
AOT[d]	0.2			
Ethanol	85.0	80.75	76.5	76.5
DDI water	–	4.25	8.5	–
Methoxy ethanol	–	–	–	8.5

[a] 70 °C; 24 h; 40 rpm; 10 wt.% of monomer concentration based on total weight

[b] Initiator: 1 wt.% of 2,2′-*azobis*(isobutyronitrile) based on total monomer content

[c] Stabilizer: poly(vinyl pyrrolidone), M_w=40,000

[d] Costabilizer; di-2 ethylhexyl ester of sodium sulfosuccinic acid

The viologen-modified polymeric microspheres were mixed with an electrolyte supplied by Cheil Industries, at a weight ratio of 1:1. The mixture was rubbed onto an ITO glass and sandwiched using another piece of ITO glass, and then all edges of the cell were sealed with an insulating epoxy resin. The device fabrication process was performed in a dry box filled with an argon gas. The cross-sectional view of the R-ECD cell is shown in Scheme 1.

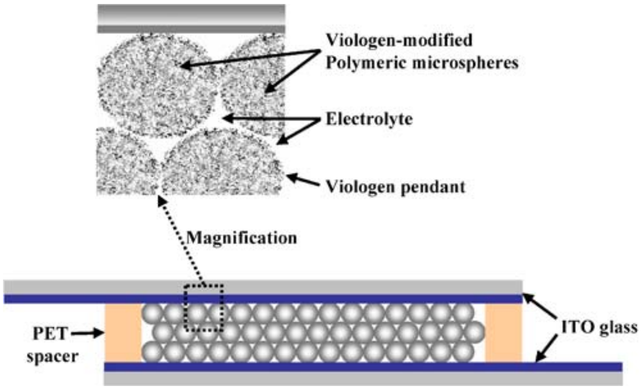
Characterizations

The swelling stages and packed particles in the R-ECD cells were monitored by an optical microscope (OM, Nikon Microphot Fax), and the polymeric microspheres were observed with a scanning electron microscope (JSM-6300, JEOL) and Fourier transform infrared (FT-IR; Mahgna IR-550, Nicolet). The determination of the effective chloro groups on the particles was carried out based on the nucleophilic attack of the deprotonated glycine on the chloro groups [25]. The dispersed particles in DDI water were reacted with 0.3 M glycine and 0.175 M NaOH. The reaction was carried out at 35 °C for 5 h. To evaluate and exclude the possible hydrolysis of chloro groups, a blank without glycine/NaOH was run. After the reaction, the reactant was centrifuged, and the supernatant was reacted again with a 0.05 M $AgNO_3$ aqueous solution. The release of chloride ions was determined as a function of $AgNO_3$ concentration. Reflectance transients of the R-ECD were recorded using a white light-emitting diode array spectrophotometer in combination with a digital multimeter (Keihley 2000) as shown in Scheme 2.

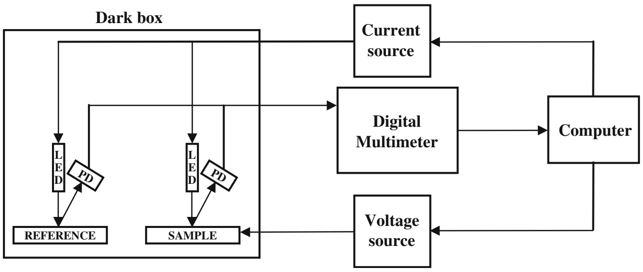
Results and discussion

Diameter alternation of seed particles

The sizes of PS seed particles were adjusted to control the size of the viologen-modified polymeric microspheres.



Scheme 1 Cross-sectional view of the manufactured R-ECD device (The space cell gap=75 μm)



Scheme 2 Schematic diagram of the experimental setup used to measure the response time of the R-ECD devices

Many parameters in the dispersion polymerization could affect the properties of the polymer particle. The solvency of the reaction medium was controlled without changing the other properties, such that the particle diameter could be varied [26, 27]. In this work, the medium composition was controlled using ethanol (ET99), a mixture of ethanol/DDI water (95/5: ET95, 90/10: ET90, w/w), and ethanol/methoxy ethanol (90/10 w/w, EM10) following the reaction recipe shown in Table 1. The particle size decreased by increasing the DDI water content because the medium solvency against the polymer chain was diminished during polymerization. A larger size was obtained by mixing 10 wt.% of methoxy ethanol with ethanol as shown in Table 2. In addition, a high monodispersity and the smooth surface of the PS particles were confirmed in Fig. 1. By using the particles as seed particles, seeded polymerization and the refluxing process were carried out to produce the viologen-modified polymeric microspheres.

Viologen-modified polymeric microspheres

St, HDDM, and CP were chosen as the second monomers, and the total amount of this mixture was fixed at 50-fold based on the weight of seed particles. The composition ratio of St/HDDM/CP was fixed at 65:5:30 by weight percent following our previous work [20]. A 1:5 ratio of ethanol/water solution containing 0.25 wt.% SLS was used as a medium in the seeded polymerization for the efficient swelling of excessive monomer emulsions into the PS seed particles. The second monomer emulsions remained in the medium at lower ethanol amounts; at higher amount of ethanol, the emulsions were dissolved into the medium resulting in poor conversion. Under these conditions, no emulsions remained in the medium, and spherical polymeric microspheres with smooth surfaces were observed as shown in Fig. 2a–d. It was also confirmed in Table 2 that the various-sized chloro-functionalized polymeric microspheres that sustained their original monodispersity were obtained according to the diameter of seed particles.

The structural difference between the PS seed particles and the chloro-functionalized polymeric microspheres was examined by using FT-IR measurements. After seeded

Table 2 Characteristics of the PS seed and chloro-functionalized and viologen-modified polymeric microspheres

Symbol[a]	PS seed particles		Chloro-functionalized microspheres			Viologen-modified microspheres	
	D_n (μm)	PSD[b]	D_n (μm)	PSD	[Cl][c] (%)	D_n (μm)	PSD
ET90	1.14	1.01	3.3	1.01	45.0	3.3	1.01
ET95	1.50	1.01	4.6	1.01	43.3	4.6	1.01
ET99	2.02	1.01	6.0	1.01	40.0	6.0	1.01
EM10	2.44	1.01	7.9	1.01	31.7	7.9	1.01

[a] ETα: α indicates the purity of the ethanol medium; EMα: α is the wt.% of methoxy ethanol in the ethanol medium.

[b] Particle size distribution: D_w/D_n

[c] Effective chloro-functional groups (methyl chloride groups on the surface)/(weights of chloropropene used in the second monomer)×100 (%)

polymerization, the CH_2–Cl spectrum by the CP and sharp characteristic carbonyl peaks by the HDDM newly appeared at 1,263 and 1,720 cm^{-1}, respectively (Fig. 3b). The methyl chloride functional groups for the reaction with 1-heptyl-4-(4-pyridyl)-pyridinium bromide were confirmed utilizing a conductometric titration method. As shown in Table 2, the percentages of the effective functional groups against the CP weight used in the second monomer gradually increased as the diameter decreased because of the specific surface area of the particles. The results indicated that larger contents of the viologen moiety, which mainly affects the electro-optical property of the R-ECD, can be incorporated on the surface of the microspheres. Many nodules emerged on the surface without affecting the size and monodispersity of particles as confirmed in Fig. 2e–h. From the results, it could be determined that the tertiary amine in the 1-heptyl-4-(4-pyridyl)-pyridinium bromide reacted with the methyl chloride group on the surface.

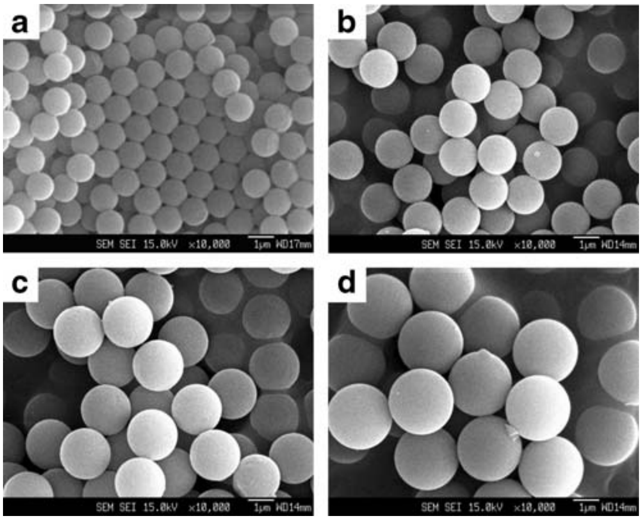


Fig. 1 SEM photographs of the PS seed particles by dispersion polymerization: ET90 (**a**), ET95 (**b**), ET99 (**c**), EM10 (**d**) as a reaction medium

Electro-optical properties

The R-ECD devices were simply fabricated by mixing the viologen-modified polymeric microspheres and electrolyte between two pieces of ITO glass as shown in Scheme 1. In

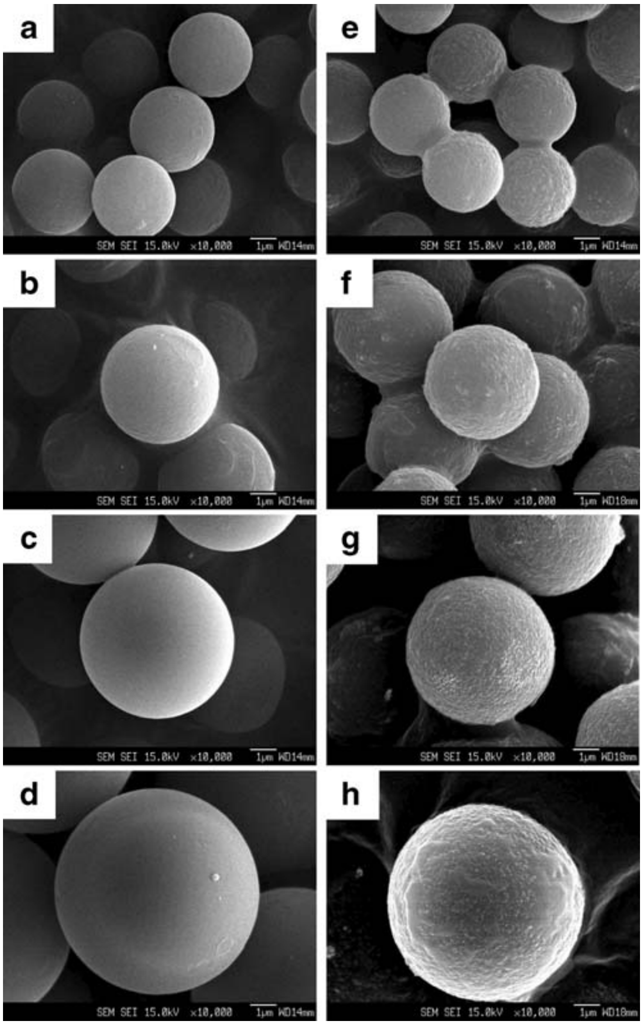


Fig. 2 SEM photographs of the chloro-functionalized (**a**–**d**) and the viologen-modified polymeric microspheres (**e**–**h**). **a**, **e** ET90, **b**, **f** ET95, **c**, **g** ET99, **d**, **e** EM10

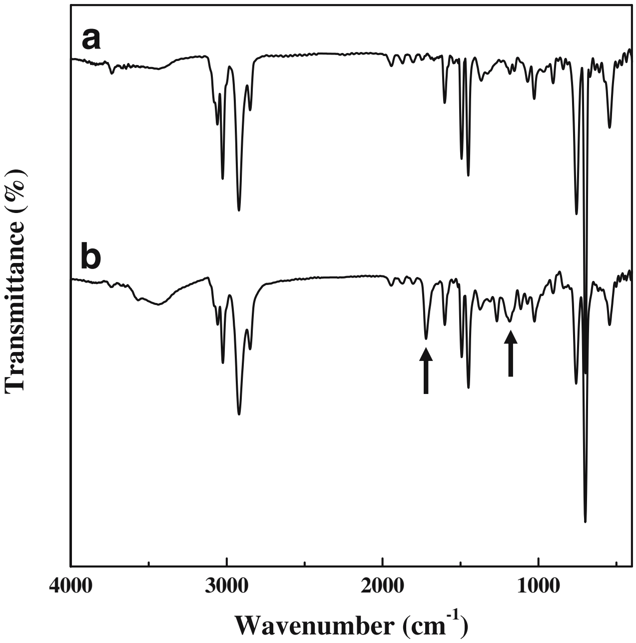


Fig. 3 FT-IR spectra of the PS seed particles (*a*), and the chloro-functionalized microspheres (*b*)

addition, the device had an innate white background (Fig. 4a) because of the micron-sized particles, which reflect light, and the bleached state of zero potential viologen pendants. The viologen moieties were converted from the dication state to the radical cation state resulting in a dark color when 2.7 V was applied to the device as shown in Fig. 4b. The OM images of the inner R-ECD prepared by the viologen-modified polymeric microspheres were shown in

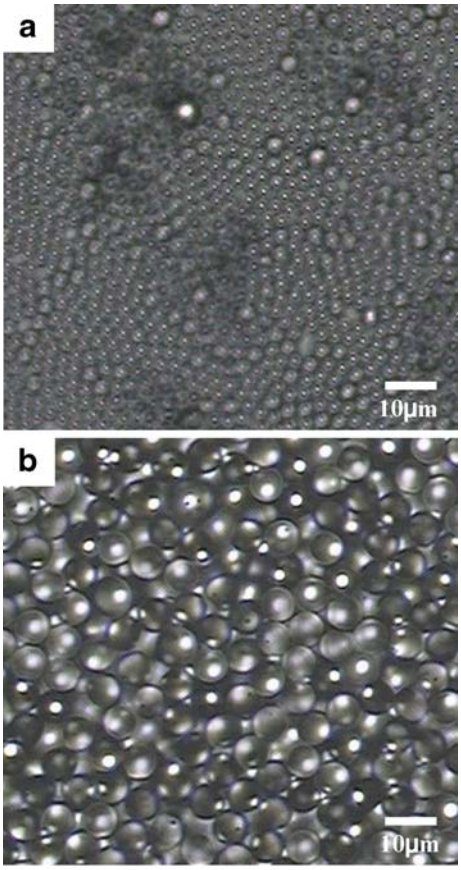


Fig. 5 OM images of the inner R-ECD devices using ET90 (**a**) and EM10 (**b**) as seed particles

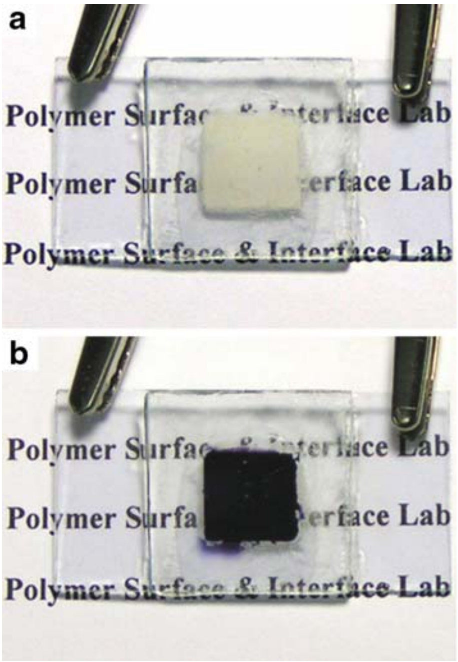


Fig. 4 Photo images of the R-ECD devices without an applied potential (**a**), and with an applied potential of 2.7 V (**b**)

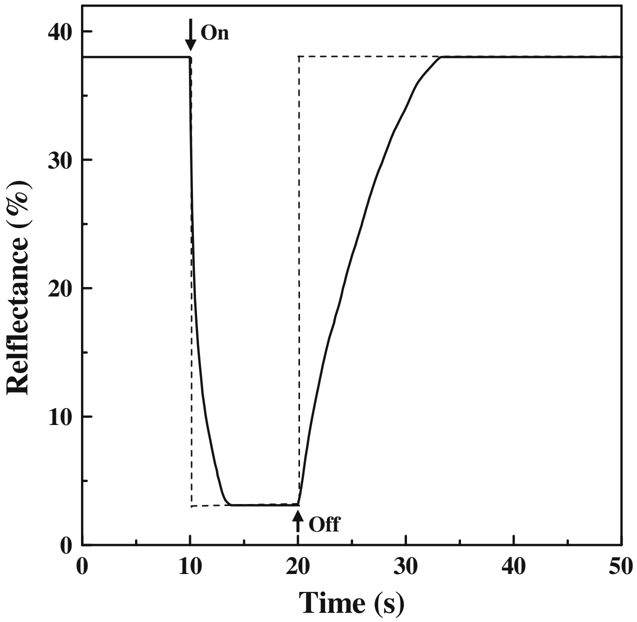


Fig. 6 The reflectance transients of the R-ECD using ET90 as a function of time (2.7 V for 10 s)

Table 3 The electro-optical properties of the R-ECD cells

Symbol	R_{i}[a] (%)	R_{f}[b] (%)	ΔR[c] (%)	t_{c}[d] (s)	t_{d}[e] (s)
ET90	38.0	3.1	34.9	0.97	6.7
ET95	38.0	8.5	29.5	1.3	4.6
ET99	38.0	11.1	26.9	2.2	5.3
EM10	39.0	16.1	22.9	3.9	5.6

[a] Initial reflectance value

[b] Final reflectance value

[c] Reflectance changes between initial and final reflectance value

[d] Coloration time [28]

[e] Decoloration time [28]

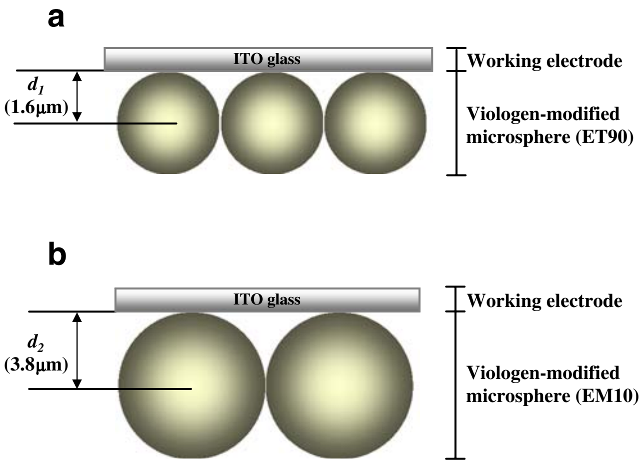


Fig. 7 A schematic representation of the inside of the R-ECD device using different particle sizes: ET90 (**a**) and EM10 (**b**)

Fig. 5, using ET90 (Fig. 5a) and EM10 (Fig. 5b) as seed particles. The viologen-modified polymeric microspheres were densely filled in the R-ECD because of high monodispersity and multilayered because of a thick cell gap (75 μm).

In Fig. 6, the solid line depict the reflectance changes (Δ*R*) of the R-ECD using ET90 seed particles as a function of time, and the dotted line guided the applied potential (2.7 V) to the device (On) for 10 s then removed (Off). The response time, coloration (t_{c}) and decoloration time (t_{d}), are defined as the time needed to reach two thirds of the final change in the reflectance [28]. The electro-optical characteristics of the R-ECD using different sized viologen-modified microspheres are summarized in Table 3. Upon decreasing the diameter of the viologen-modified microspheres, there was a substantial increase (up to 35%) in the Δ*R* of the R-ECD. This occurred because the viologen content on the surface of the viologen-modified polymeric microspheres varied according to the particle size. As mentioned in Table 2, the concentration of the methyl chloride functional groups, which directly affect the content of the viologen pendants, was influenced by the particle diameters. Closer packing of the particles was confirmed when smaller microspheres were used in the R-ECD device (Fig. 5). To conclude, a higher coloration efficiency of the R-ECD was obtained because of the smaller viologen-modified polymeric microsphere, which affect the larger viologen pendants.

It was also found that the response time of the R-ECD improved to less than a second as the particle diameter decreased. Generally, the switching speed of electrochromic

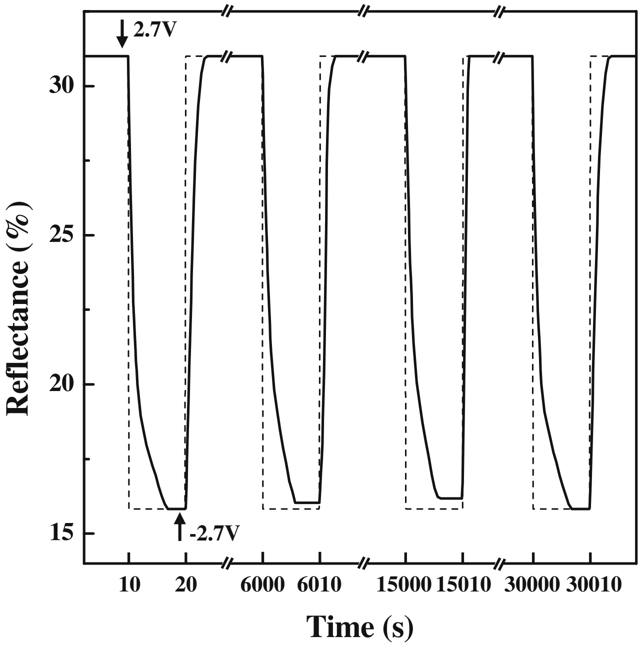


Fig. 8 The reflectance transients of the R-ECD using ET90 as a function of time (30 s for one cyclic test, 1,000 cycles, the potential ranges 2.7 to −2.7 V)

materials is dependent on several factors such as the ionic conductivity of the electrolyte, the accessibility of the ions to the electroactive sites (ion diffusion), the magnitude of the applied potential, the film thickness, and the morphology of the thin film [28]. As mentioned earlier, it was reasonable to think that the content of the viologen pendants affected the coloration efficiency of the device, not the response time. Hence, it is supposed that the distance (*d*) between the working electrode and viologen decreased, which resulted in a fast electron transfer to the viologen pendants when microspheres of smaller size were used as shown in Fig. 7 ($d_1 < d_2$). A rapid response time could be obtained in this R-ECD, although the actual relationship between viologen contents and the response time has not been determined. A more detailed exploration of the operation mechanism of the R-ECD is underway.

The electrochromic stability is usually associated with the electrochemical stability because the degradation of the active redox couple results in the loss of electrochromic contrast and the performance of the electrochromic materials [29]. A thousand cyclic tests of the R-ECD prepared by the smallest viologen-modified microspheres (ET90) were carried out in the potential range of 2.7 to −2.7 V to investigate the stability of the viologen pendants. During the measurements, the ΔR of the R-ECD gradually decreased as shown in Fig. 8 (the solid line) mainly as a result of the evaporation of the electrolyte in the device. After replenishing the electrolyte, the original magnitude of ΔR was obtained, and no sign indicating adverse side reactions were observed. In addition, the same stability results were confirmed when viologen-modified polymeric microspheres of different sizes were utilized. This led to the general conclusion that the R-ECD has good cyclic stability because the viologen moiety was stably grafted on the microsphere surface.

Conclusion

The influence of the microsphere diameters on the electro-optical properties of the R-ECD was investigated. The sizes of PS seed particles were controlled utilizing the medium solvency during the dispersion polymerization, and the viologen-modified polymeric microspheres of different sizes were prepared using the same condition in the seeded polymerization. Through conductometric titration analysis, it was confirmed that the methyl chloride functional groups were largely incorporated when the smallest-sized seed particle was used owing to the large specific surface area. Simultaneously, high contents of the viologen pendants were introduced on the surface of the microspheres and resulted in a higher coloration efficiency of the R-ECD. In addition, a rapid response time of less than 1 s was obtained because the distance between the electrode and the viologen pendants became smaller. The results of the cyclic stability tests implied that the R-ECD had a good stability because of chemically grafted viologen moieties on the surfaces of the microspheres.

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