Fast and Low Voltage-driven Solid-state Electrochromics Using 3-D Conductive FTO Nanobeads Electrodes

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Experimental

Preparation of FTO nano-beads

In a typical preparation process of FTO hollow nanobeads, 24 mg of $SnCl_2 \cdot 2H_2O$, 4.5 mg of NH_4F and 450μl water were mixed and magnetically stirred for 2 hours. Then, 275μl 200nm PS suspension was added in the mixture, followed by stirring for 24 hours. 50μl of the resulting suspension was spread on 1.0 inch ×1.0 inch commercial FTO substrate with scotch tape to define the area. The samples were dried at room temperature overnight, following by 2 hours at 170℃, 3 hours at 340 ℃ and 2 hours at 450 ℃ with heating rate 1 ℃/min. This process yields approximately 15-20μm 3-D FTO hollow nanobeads film. The samples were then treated at 300 ℃ in argon for 30 min to improve the electrical conductivity with temperature rising rate = 1 ℃ /min.

Preparation of PMMA-P(VAc-MA)+$LiClO_4$-based sol-gel electrolytes

0.13g of polymethyl methacrylate (PMMA) and 0.28g copolymer of polyvinylacetate (VAc) methyl acrylate (MA) was dissolved in 1ml propylene carbonate. Then 0.1g $LiClO_4$ was added in the polymer solution and stirred overnight.

Viologen coating on FTO nanobeads electrodes

A FTO nano-beads electrode was soaked in 0.04M 1,1′-diethyl-4,4′-bipyridinium diiodide in ethanol/acetonitrile(v=1:1) solution. Then, the electrode is dried for 30mins at 80℃.

Electrochromic Characterization

A square wave voltage was supplied by a function generator (Agilent 33220A) to powder the EC devices. The voltage can be switched on from 0V to a given value between ±5V within 50 ns. The periods of the alternating square wave voltage can be set for different values as needed such as 8 s, 4 s, 2s, 1s, 0.5s and 0.3s used in our tests.

Plots of reflection vs. time of the EC devices was measured by the strip-chart function on UV-Vis (Ocean Optic USB2000). Optic probe was placed on sample holder and attached on surface of the devices.

Temperature dependent measurement was conducted by placing the EC devices in a car cooler (Wagon Tech) that can adjust the temperature between 3-70℃. A thermocouple was taped onto the surface of the devices to precisely record the actual sample temperature.

Table S1 Response Time vs Temperature defined at different change of percentage

Temp/K	T_{co}/ms 75% Co	T_{de}/ms 75% De	T_{co}/ms 85% Co	T_{de}/ms 85% De	T_{co}/ms 95% Co	T_{de}/ms 95% De
279.55	532	1040	803	1533	1230	2327
287.55	422	604	689	937	931	1216
296.65	272	400	373	609	540	861
307.65	216	429	332	385	422	854
317.75	137	266	240	385	359	528
327.55	117	167	194	221	275	353

T_{co}: response time of coloring process

T_{de}: response time of decloring process

Co: coloring

De: decloring

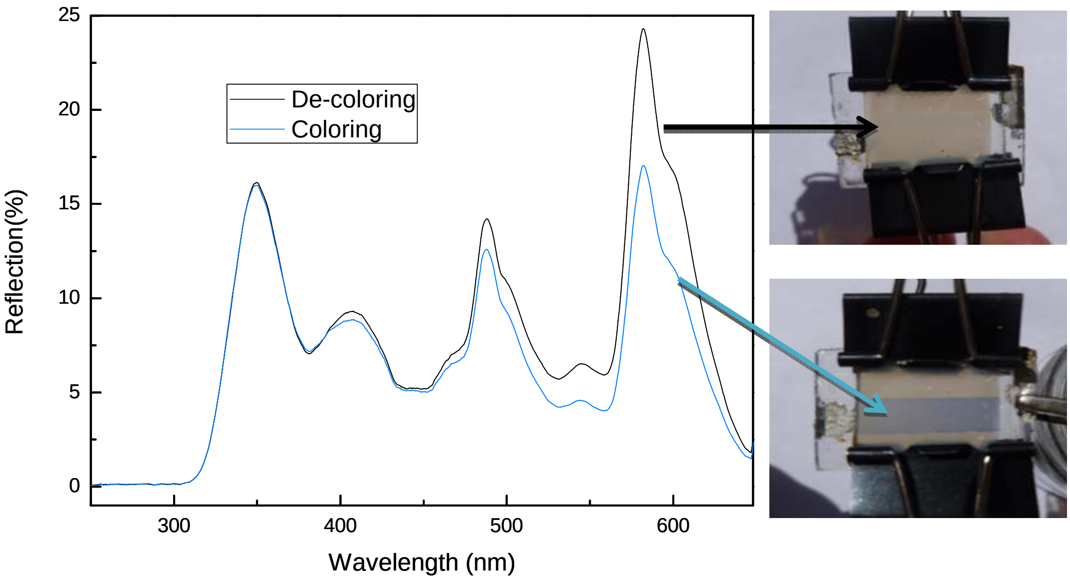

Figure. S1 Full reflection spectra of the device at coloring (blue curve) and de-coloring (black curve) states. Note that the spectra are the sum of all components in the device including electrolytes, FTO glass, FTO nanobeads as well as viologen, instead of viologen along, while many reported spectra change of viologen are taken in solution phase.[references 8 and 17]

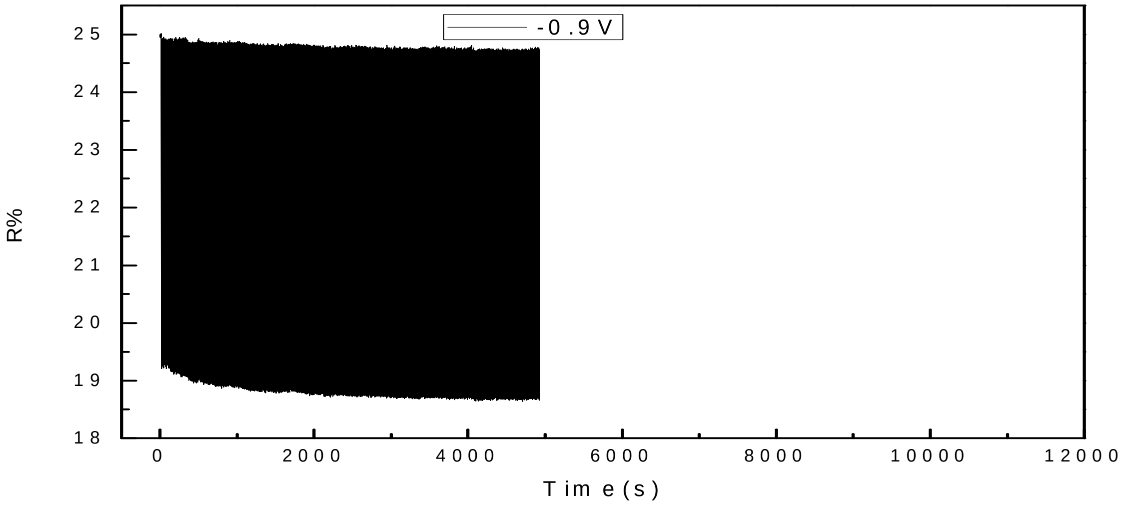

Figure. S2 Full graph of the reversibility test at ±0.9V.