



Metal ion-responsive photonic colloidal crystalline micro-beads with electrochemically tunable photonic diffraction colours



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ABSTRACT

This work reports a metal ion-responsive photonic colloidal crystalline (PCC) microspheric material and the convenient, reversible switching of its photonic diffraction properties by the redox reaction of copper in a simple electrochemical cell. The PCC micro-beads were fabricated from the orderly three-dimensional packing of core-shell nanoparticles with hydrogel coatings laden with anionic phosphate functionalities. Electrostatic binding of metal cations by the hydrogel coating lowered its internal osmotic pressure and caused shrinkage of the core-shell nanoparticles. This brought about a blue-shift of the photonic diffraction λ_{\max} of the micro-beads. The maximum shift, from 650 to 590 nm (colour change from magenta to green) was found to be produced by Cu^{2+} at a concentration of 1 mM. A simple electrochemical photonic device was constructed by sandwiching a suspension of the photonic micro-beads in 1 mM Cu^{2+} solution between two transparent ITO-glass electrodes. Photonic diffraction colour of the micro-beads was reversibly switched via the electrochemical reduction/oxidation of Cu^{2+} inside the device. The colour change can be observed by naked eyes under ambient light. This concept of rapid electrochemical regulation of photonic diffraction colour of PCC micro-beads may be useful in reflective displays applications.

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1. Introduction

The controlled reversible switching of patterned optoelectronic components between alternated luminescent/optical density/colorimetric states is the basis of modern information displays technologies [1]. Light emitting diode (LED) and liquid crystal display (LCD) are conspicuous examples of the use of optically active small molecules or polymer materials for display purposes [2,3]. Besides emissive displays, the manipulation of the orientation or migration of charged pigment particles to compose reflective

patterns constitutes another approach to display information [4]. There are numerous ways to achieve reflective displays and one of them that has aroused considerable interests in recent years is the use of photonic colloidal crystalline (PCC) materials. PCC materials assembled via the orderly packing of nano-sized particles into three-dimensional arrays are capable of selectively perturbing the propagation of electromagnetic waves [5,6]. If the distance separating the composing particles within a PCC material can be varied by an external influence, the material can produce specific photonic responses upon stimulation. Such a concept of stimulus-responsive photonic colloidal crystalline arrays (SRPCCAs) has spawned a wide variety of promising sensors for temperature [7,8], pH [9,10], magnetic and electric fields [11–13], small molecules and biomolecular analytes [14–17].

Ozin and co-workers developed the “Photonic Ink” (P-Ink) for full-colour displays applications in which the photonic diffraction properties of inverted opal gels derived from specific electroactive polymers are tunable over a wide range of the visible spectrum by adjusting the strength of an externally applied electric field

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[18–20]. A related photonic colour displays technology has also been reported by Han et al. where photonic properties of PCC materials formed from ZnS-silica core-shell nanoparticles, with a monolayer of anionic functional moieties on the surface, can be modified by externally applied electric field [21]. Lee et al. solved the problem of the angle dependence of electrically tunable PCC display pixels by incorporating $\text{Fe}_3\text{O}_4/\text{SiO}_2$ quasi-amorphous colloidal structures into the system [22]. At the moment, all the literature-reported electrically tunable PCC display pixels are in the form of PCC thin-films of noticeable sizes. While it facilitates spectroscopic measurements, PCC thin-films in the size range of millimetres may not be readily manufactured into micro-sized PCC display pixels due to the difficulties in minimizing the area of the thin-films and thus hindered the integration of which into delicate electronic devices. Having said that, it is still a considerable challenge to produce PCC thin-films massively and accurately into small pixels in which the modulation of photonic band-gap can be readily controlled individually or collectively with the application of electric fields. Furthermore, since most of the systems have to be operated in organic solvent-based electrolytes, the indium tin oxide (ITO) electrodes have to be sealed with epoxy. This increases the production costs and introduces toxicity.

Herein we demonstrate the fabrication of a novel type of microspherical SRPCCAs that are responsive to the presence of certain metal ions in the electrolyte solutions. A simple electrochemically induced redox system with a pair of ITO-glass electrodes was constructed to switch the photonic diffraction properties of the micro-beads while they are undergoing two different oxidation states of the metal ions. Photonic diffraction colour of the micro-beads was reversibly switched via the electrochemical reduction/oxidation of metal ions inside the device. The colour change can be observed by naked eyes under ambient light. This demonstrates the possibility of each photonic micro-bead being a well-defined colour pixel in which the concept may be applied in the industries of some colour-based electronic devices in future.

2. Material and methods

2.1. Materials

All the chemicals were of analytical grade. Styrene (St), acrylic acid (AA), potassium persulfate (KPS), ethylene glycol methacrylate phosphate (EGMP), divinylbenzene (DVB) and *N*-isopropylacrylamide (NIPAM) were purchased from Aldrich. Styrene (St) and acrylic acid (AA) were distilled before use. Potassium persulfate (KPS) was recrystallized before use. Hydroxyethyl methacrylate (HEMA), hexadecene (HE), and *N,N'*-methylenebisacrylamide (NMBA) were obtained from Acros. Hypermer 2296 was obtained from Croda. They were all used as received. Double-distilled water was used in all the experiments.

2.2. Instrumentations

Electron microscopy (SEM and TEM) was carried out on a Philips XL30 ESEM-FEG environmental scanning electron microscope (SEM), and a FEI/Philips Tecna 12 Bio TWIN transmission electron microscope (TEM), respectively. Photographs of the PCC micro-beads were taken with an optical microscope (Olympus BX60) equipped with a CCD camera (AxioCam MRc 5). UV-Vis reflectance spectra of the micro-beads in the range 400–750 nm were measured using an optical microscope (Olympus BX60, 20 \times , NA=0.40) that was fitted to a SpectraPro 2300i spectrometer (Princeton Instrument) via an optical lens and a light guide. DC potential applied to the electrochemical cell was derived from an AC-DC power supply (Manson, SSP-7080).

2.3. Preparation of the monodispersed core-shell nano-sized particles and the microspherical photonic colloidal crystalline (PCC) micro-beads

Monodispersed core-shell nanoparticles were prepared by the seeded copolymerization of EGMP, NIPAM, and HEMA on nano-sized PS-co-PAA seeds using KPS as an initiator in a three-necked round flask with a reflux condenser and a mechanical stirrer. A typical synthesis of the core-shell nanoparticles was as follows: 5.3 g of St, 0.55 g of DVB, and 0.6 g of AA was dissolved in 100 ml of distilled water in a 250 mL round flask. When the mixture was refluxed at 100 °C for 3 min, polymerization was initiated by the addition of 5 mL of aqueous solution containing 62.7 mg of KPS. After the reaction for the preparation of the PS-co-PAA seeds has been running for 2 h under constant stirring, an aqueous mixture containing 1.0 g of EGMP, 1.0 g of NIPAM, 1.0 g of HEMA, 0.022 g of NMBA and 28 mg of KPS was then added. The polymerization reaction was allowed to continue for another 3 h at 100 °C. The resulting core-shell nanoparticles were collected by centrifugation at 15,500 rpm for 3 \times 20 min.

The procedure adopted for the fabrication of the PCC micro-beads was as follows: Firstly, 1 mL of aqueous suspension containing the monodispersed core-shell nanoparticles with a loading of 4.0 wt% was dropped into a test tube filled with 15 mL of hexadecene as an oil phase, and an amphiphilic block co-polymer and Hypermer 2296 (2.0 wt%) as a stabilizer. The resultant latex suspension in the test tube was then broken up into droplets by vigorous manual shaking, followed by pouring into a 15 cm diameter glass petri dish, which had been treated with octadecyltrichlorosilane to render its inner wall hydrophobic. The suspension in the glass petri dish was warmed to 50 °C for 72 h to allow the water within these droplets to slowly evaporate. During the evaporation, the core-shell nanoparticles self-assembled into microspherical orderly packed lattices. These resultant PCC micro-beads were collected and thoroughly washed with *n*-hexane to remove the hexadecene, and were used in the subsequent experiments.

2.4. Measurement of reflectance spectra of the PCC micro-beads in pH buffers

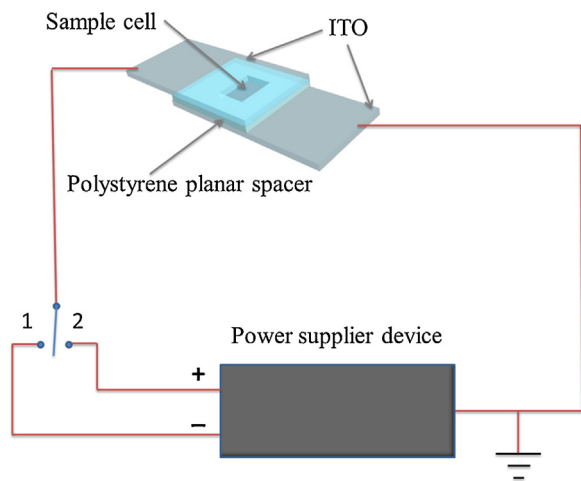
Suspensions of the PCC micro-beads in aqueous buffers of pre-determined pH were dropped onto the wells of depression microscope slides, which were then covered with cover slips and were immediately used for the measurement of reflectance spectra. All measurements were carried out at room temperature.

2.5. Measurement of photonic responses to various metal ions

Suspensions of the PCC micro-beads in aqueous solutions with the presence of various metal ions at concentrations of 10 μM , 100 μM , and 1 mM were dropped onto the wells of depression microscope slides, which were then covered with cover slips and were immediately used for the measurement of reflectance spectra. All measurements were carried out at room temperature.

2.6. Measurement of photonic responses to electrochemical redox reactions

A two-electrode electrochemical cell was constructed using a pair of planar ITO glass electrodes, of the size of glass slide for microscopy, sandwiching a 300 μm thick white-colour polystyrene planar spacer with a square hole of 1 \times 1 cm^2 cut out in the middle (Scheme 1). The square cavity created by the polystyrene planar spacer and the two ITO-glass electrodes was filled with PCC micro-beads dispersed in a 1 mM CuCl_2 solution and the electrochemical assembly was held in place by four paper binder clips. The device



Scheme 1. Design of the electrochemical cell.

was placed under the Olympus BX60 optical microscope equipped with a SpectraPro 2300i spectrometer. One of the ITO glass electrodes was grounded while the other electrode was connected to a DC power supply via a multiple-way switch. Electrochemical redox of the Cu(II) solution inside the device was effected by applying a negative DC potential to the ITO glass electrode for a brief period of <1 s. Polarity of the applied potential was reversible so as to control the presence of Cu(II) ions in the solution inside the device. After each brief application of DC potential to the ITO glass electrode, the circuit was opened and photonic responses of the PCC micro-beads were recorded.

Besides measuring reflective spectra of the micro-beads within the electrochemical cell, the L_{ab} values, according to the CIELAB colour space, of micro-beads under white light illumination from the optical microscope were also recorded. Differences in the diffraction colour of the micro-beads induced by the

electrochemical redox reaction were expressed as ΔE according to the CIE76 standard:

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$$

where $L_1 a_1 b_1$ and $L_2 a_2 b_2$ are the L_{ab} values of the micro-beads within the electrochemical cell in the absence and presence of Cu^{2+} in the electrolyte respectively.

3. Results and discussion

Typical TEM and SEM images of the nano-sized particles and their PCC micro-beads are shown in Fig. 1. The monodispersed core-shell nano-sized particles with diameter ca. 190 nm (Fig. 1A and B) were composed of PS-co-PAA cores and PEGMP-co-PHEMA-co-PNIPAM shells, which were fabricated by an emulsifier-free emulsion polymerization as reported in our previous works [10,23]. When these core-shell nano-sized particles were suspended in water and subjected to a water-in-oil emulsion, they underwent self-assembly and packed orderly into microspherical beads (Fig. 1C and D). The beads were rather polydispersed, with size ranging from 5 to 60 μm (Fig. 1C).

Fig. 2 summarizes the assembly procedures for the PCC micro-beads and their responses towards cations in the media. Infusion of cations into the phosphate-functionalized hydrogel shells of the nano-sized particles that composed the PCC micro-beads reduces the electrostatic repulsion among the anionic phosphate groups. The lowered internal osmotic pressure of the hydrogel caused shrinkage of the nano-sized particles, causing a reduction of their mean separation in the PCC lattice of the micro-beads. As a result, the photonic diffraction of the resultant PCC micro-beads shifted to shorter wavelengths [23–26].

Fig. 3 shows the photonic responses of the PCC micro-beads, due to the swelling and shrinking of the hydrogel coating on the core-shell nanoparticles within those beads, towards different metal ions. The shift in the reflectance peak ($\Delta\lambda_{\text{max}}$) was determined by the difference between the photonic diffraction wavelength

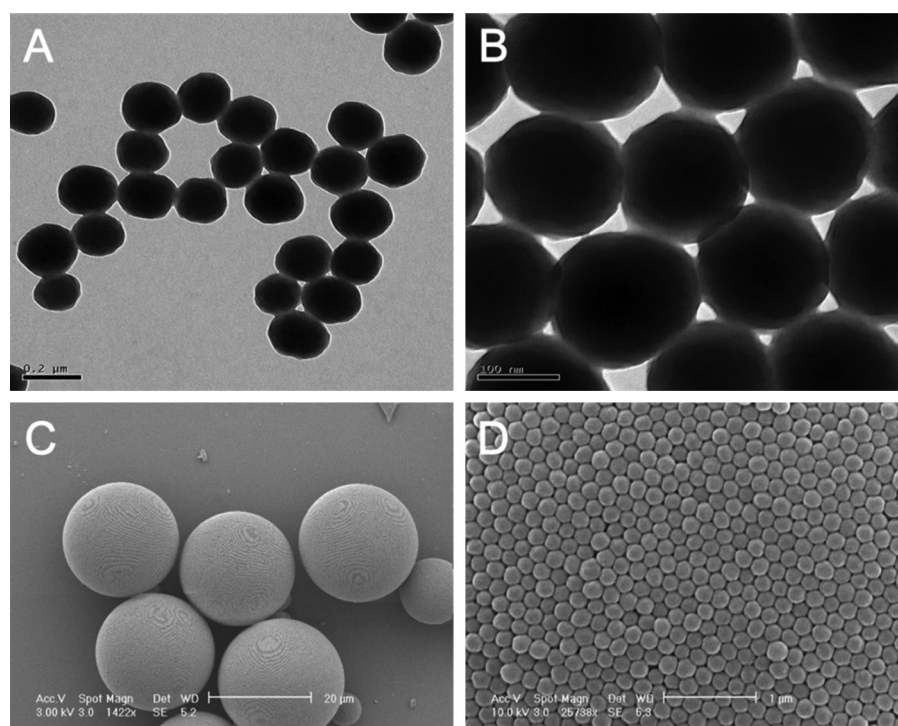


Fig. 1. PCC micro-beads assemblies: (A) and (B) TEM images of the monodispersed core-shell nano-sized particles with diameter of ca. 191 nm; (C) SEM image of assembled PCC micro-beads, and (D) surface morphology of the micro-beads.

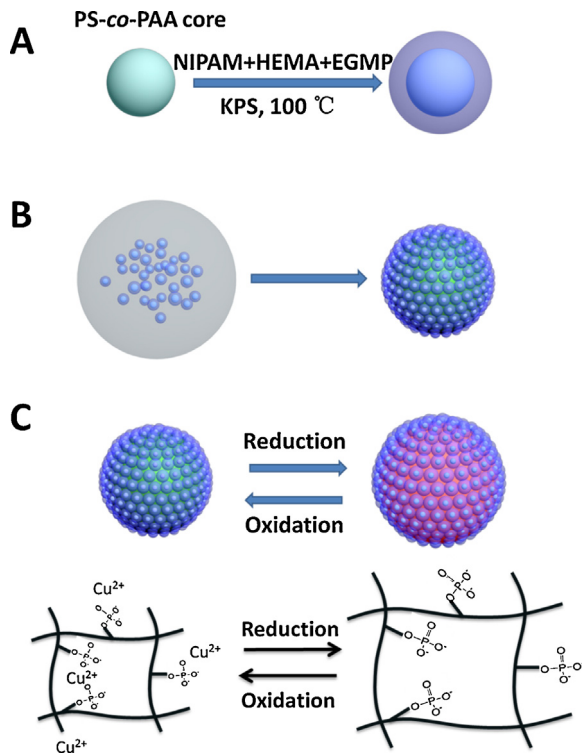


Fig. 2. Schematic illustration of the PCC micro-beads: (A) the preparation of core-shell nanoparticles; (B) the assembly of core-shell nanoparticles into PCC micro-beads; (C) metal ion-responsive swelling and shrinking of the PCC micro-beads, and its hydrogel coating of the core-shell nanoparticles.

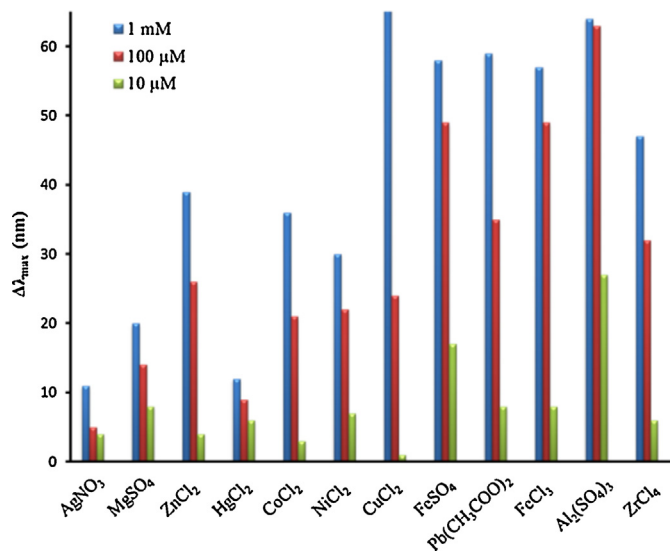


Fig. 3. Photonic responses, in terms of $\Delta\lambda_{\max}$, of the photonic micro-beads to various metal ions at 10 μ M, 100 μ M, and 1 mM in aqueous solution.

of the micro-beads in the absence and presence of metal ions in aqueous solutions. Towards all the selected metal ions, photonic responses of the micro-beads increase with ion concentration. Cu^{2+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, Pb^{2+} and Al^{3+} have induced relatively greater responses ($\Delta\lambda_{\max} > 55$ nm) than the other metal ions tested. Amongst those five species, Cu^{2+} and Al^{3+} have shown the most pronounced shifts in diffraction wavelength at lower metal ion concentration. In fact, $\Delta\lambda_{\max}$ induced by Al^{3+} at 100 μ M and 1 mM was more or less the same, indicating that equilibrium of the ionic-induced shrinking of the hydrogel coating on the core-shell nanoparticles that assemble

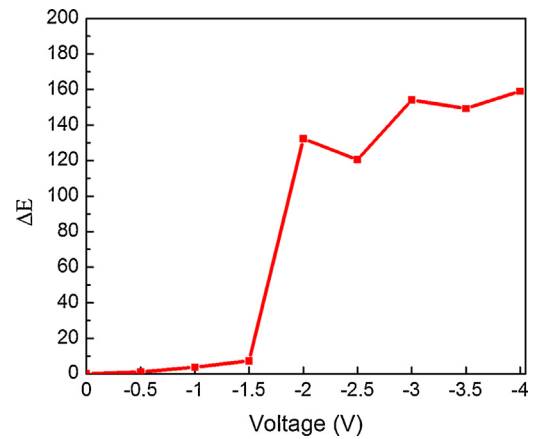


Fig. 4. Effect of voltage applied to the electrochemical cell on diffraction colour (in term of ΔE according to the CIE76 standard) of the photonic micro-beads in 1 mM CuCl_2 solution.

the micro-beads was reached at $1 \text{ mM} \geq [\text{Al}^{3+}] \geq 100 \text{ mM}$. For the other metal ions, including Cu^{2+} , there were significant differences in $\Delta\lambda_{\max}$ between 100 μ M and 1 mM. This was probably due to the lower charge density of these metal ions compared to Al^{3+} . Nevertheless, the greatest $\Delta\lambda_{\max}$ (ca. 70 nm) was achieved with 1 mM of Cu^{2+} . Also, the standard reduction potential of Cu^{2+} ($E^\circ = +520$ mV) is much higher than that of Al^{3+} ($E^\circ = -1660$ mV). Thus, 1 mM Cu^{2+} was chosen to be the working electrolyte for the construction of the electrochemical cell (Scheme 1).

The simple electrochemical cell consisted of a 300 μ m thick chamber created by a polystyrene spacer, with a square hole cut out in the middle, sandwiched by two transparent ITO-glass electrodes for the regulation of metal ions in the enclosed electrolyte solution. Initially, micro-beads were suspended in an aqueous solution of metal ions. One of the ITO-glass electrodes was grounded, while a negative potential was applied to the other ITO-glass electrode for a brief period of < 1 s. Metal ions in the solution were reduced at that cathode and the solution inside the electrochemical cell became deprived of metal ions. This constituted the “reduction” conditions of the device. Then a positive potential was applied briefly to the ITO-glass electrode. Reduced Copper(0) deposited on the electrode were oxidized and migrated back into the solution, and, hence, into the micro-beads. This constituted the “oxidation” conditions of the device. In this way, the electrochemical cell regulated the introduction and withdrawal of Copper(II) ions into and from the photonic micro-beads.

To determine the minimum potential needed to produce a noticeable shift in the photonic diffraction colour of the micro-beads, the difference in colour of the micro-beads suspended in an aqueous 1 mM CuCl_2 solution within the device, in terms of ΔE in accordance with the CIE76 standard, at various applied reduction potential was investigated. Fig. 4 shows the ΔE vs. applied potential (V). A drastic change in ΔE (ca. 130) was observed at an applied potential of ≤ -3 V. Therefore, ± 3 V was adopted for the switching of diffraction colour of our photonic micro-beads for the rest of our studies. Control experiments have been carried out using deionized water and 1 mM NaCl solution to replace the CuCl_2 electrolyte. No switching of diffraction colour of the photonic micro-beads was observed whatsoever.

Fig. 5 shows the reflectance spectra of the photonic micro-beads within the electrochemical cell under acidic/alkaline, and “oxidation”/“reduction” conditions. Photonic properties of the micro-beads were unaffected by the media pH over the range of $4 < \text{pH} < 9$, and colour changes were only resulted from the redox reaction of Cu ions. The reflectance spectrum of the micro-beads under “reduction” condition resembled that in deionized water,

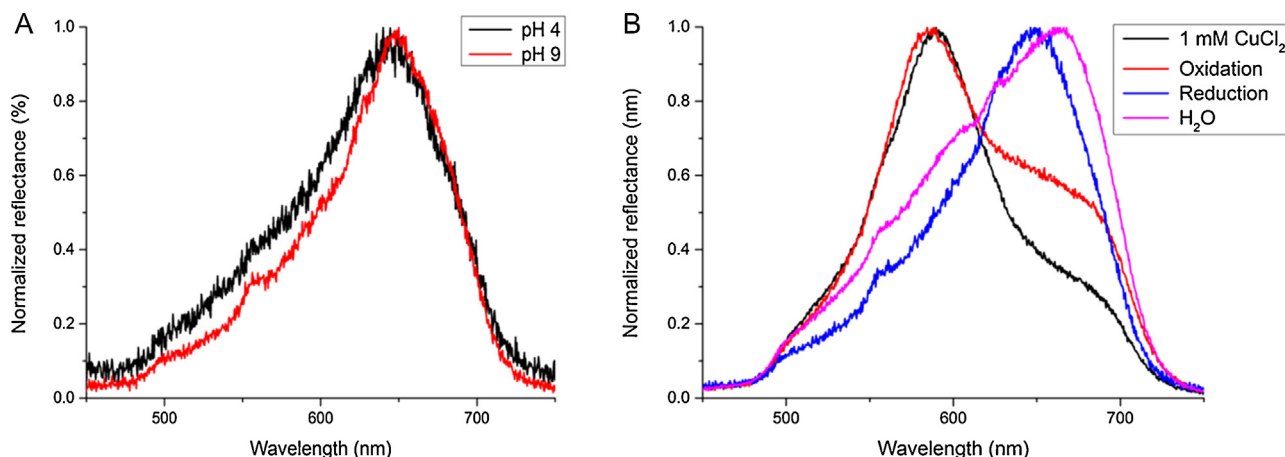


Fig. 5. Normalized reflectance spectra of the photonic micro-beads within the electrochemical cell: (A) under acidic and alkaline conditions; (B) under “reduction” and “oxidation” conditions of the electrochemical cell, reflectance spectra of the micro-beads suspended in 1 mM CuCl_2 solution and deionized water were included for comparison.

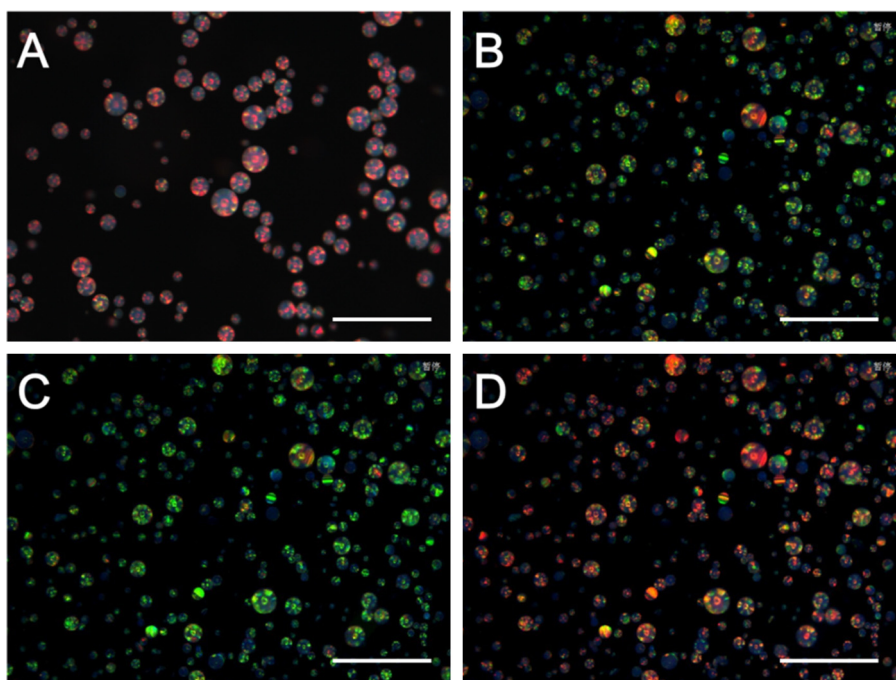


Fig. 6. Microscope images of the photonic micro-beads: (A) photonic micro-beads in deionized water; (B) photonic micro-beads in a 1 mM CuCl_2 solution, while (C) and (D) show the corresponding colour change of the micro-beads under “oxidation” and “reduction” conditions of the device respectively. The scales bars are 250 μm .

while that under “oxidation” condition resembled the spectrum obtained when they were suspended in CuCl_2 solution. These demonstrate that a brief application of potential to the ITO-glass electrodes can control the movement of Cu^{2+} ions into and out of the micro-beads, and, in turn, shifts the photonic diffraction colour of the micro-beads (Fig. 6).

To demonstrate the repetitive switchability of photonic micro-beads, a video showing a rapid succession of alternating reduction and oxidation events can be found in the [Supporting Information](#). The polarity of the ITO-glass electrodes was switched every 3–4 s and the whole process was viewed and recorded by an optical microscope. The photonic micro-beads were initially green in colour when they were immersed in 1 mM CuCl_2 in the electrochemical device (Fig. 6B). Upon the application of a reduction potential (–3 V) to the ITO electrode, they turned from green to magenta (Fig. 6D). When potential of the electrode was switched back to +3 V, the original green colour was restored (Fig. 6C). The

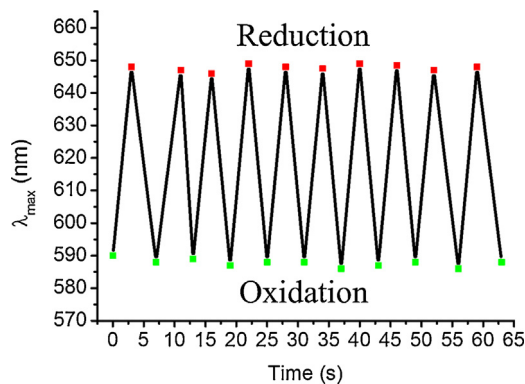


Fig. 7. Reversible switching of photonic diffraction λ_{max} of the micro-beads as the electrochemical cell cycled between “reduction” and “oxidation” conditions.

redox events have been rapidly repeated for 10 times without any lost in the fidelity of the photonic responses (Fig. 7).

4. Conclusions

We have demonstrated that with the introduction of phosphate groups into the hydrogel coating of core-shell nanoparticles, the assembled PCC micro-beads exhibit drastic photonic responses towards metal ions, in particular, Cu^{2+} . Rapid, controllable and reversible switching of the photonic diffraction properties of such a SRPCCA can be brought about in a simple electrochemical cell. The colour change can be observed by naked eyes. In future, by integrating SRPCC micro-beads into photonic devices as pixels, each pixel can be controlled individually. Furthermore, such photonic beads have unique optical property of viewing angle independence. This concept of electrochemically regulating the photonic diffraction properties of SRPCC micro-beads should warrant further exploration as a mean to achieve colourful electronic-paper-like reflective displays and information storage devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2015.09.116>.

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