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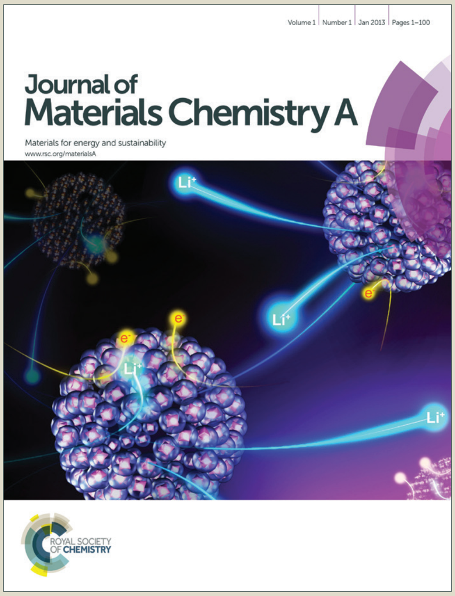

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CdSe quantum dots/molecular cobalt catalyst co-grafted open porous NiO film as a photocathode for visible light driven H_2 evolution from neutral water†

Peng Meng,[a] Mei Wang,*[a] Yong Yang,[a] Shuai Zhang[a] and Licheng Sun[ab]

An active noble-metal-free photocathode was fabricated by co-grafting water-soluble thioglycolic acid-stabilized CdSe quantum dots and a molecular cobaloxime catalyst (CoP) through chemical linkage on a p-type open porous NiO film. This photocathode was used as a working electrode in a three-electrode cell, which displayed a photocurrent density up to 110 μA cm^{-2} at an applied potential of 0 V vs. NHE in 0.1 M Na_2SO_4 solution at pH 6.8 upon visible light illumination. The comparative studies showed that the open porous NiO/CdSe electrode did display higher photocurrent density than that exhibited by an analogous planar NiO/CdSe electrode made by doctor-blading a NiO paste. Long-time photoelectrolysis experiments revealed that about 83% of photocurrent density remained after 3.5 h illumination at −0.2 V vs. NHE. The open porous NiO/CdSe/CoP photocathode showed considerably better current density and photocatalytic stability compared to the so-far reported dye- or QDs-sensitized NiO cathodes with a cobaloxime catalyst chemically attached or physically adsorbed on the electrode surface under similar conditions.

[a] *State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian 116024, China. E-mail:symbueno@dlut.edu.cn*
[b]*Department of Chemistry, KTH Royal Institute of Technology, Stockholm 10044, Sweden.*

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Introduction

Envisaging the serious problems of energy shortage and CO_2 over-discharge, development and utilization of sustainable and clean energy sources to reduce our reliance on fossil fuels and to cut the CO_2 emission is an important, urgent, and challenging task facing the human society.[1,2] One of the ideal and perpetual solutions to the global energy problem is conversion of solar energy to conveniently usable and storable energy in the form of H−H bond by solar-driven water splitting. To this holy aim, generally three technological approaches have been pursued, namely mixed colloidal and/or molecular photocatalyst homogeneous systems, photovoltaic (PV)/electrolyzers, and integrated photoelectrochemical (PEC) cells.[3,4] Among these three approaches, the integrated PEC cell is a more promising way for large-scale H_2 production in an aqueous solution from the perspective of efficiency, cost, and safety of the solar-to-hydrogen conversion process. A PEC cell can be constructed with compatible photoactive anodic and cathodic electrodes, to form a dual-illuminated tandem PEC cell, or by integration of a light absorber-sensitized electrode, either a photoanode or a photocathode, with a photo-inactive electrode, to build a single-illuminated PEC cell.[5,6] Therefore, development of photoanodes and photocathodes is a crucial prerequisite to the establishment of robust, energy-efficient and cost-effective PEC cells for overall water splitting to H_2 and O_2.

Since 2008, nickel oxide with good stability and transparency has been used as a wide band gap p-type semiconductor for the fabrication of p-type dye-sensitized solar cells,[7–12] while the NiO-based photocathodes used for the hydrogen evolution reaction (HER) have received attention only in recent years.[13–20] In the pioneer work, it was found that the organic dye-sensitized NiO photocathodes with or without HER catalyst displayed low photocurrent and poor stability in the HER.[13,14] Chemically bonding both a ruthenium polypyridylchromophore and a cobaloxime catalyst to the NiO film, either with a cascade or a parallel linkage, provided more stable NiO-based photocathode, which displayed the photocurrents of about 13−20 μA cm^{-2} at an applied potential of −0.2 V vs. NHE (the potentials mentioned hereafter are versus NHE if not specially denoted) for the HER.[15,16] The reason for the low activities of these sensitized NiO photocathodes may stem from several factors: (i) the small hole diffusion coefficient in NiO,[21,22] (ii) the competition of the hole injection from a sensitizer to the valence band of NiO with the fast recombination between the reduced dye and the holes generated in NiO, and (iii) poor sensitizer loading dominantly due to the low specific surface area of NiO. Some recent studies showed that compared to dye-sensitized NiO photocathodes, the quantum dot (QD)-sensitized NiO cathodes exhibited much larger hole diffusion coefficient.[23,24] Semiconductor QDs with good photostability and broad absorption spectral range in the solar spectrum are more promising light harvesting alternatives to molecular chromophores for fabricating highly efficient and durable photocatalytic systems. Although in recent years many hybrid systems comprising semiconductor QDs and non-noble metal molecular catalysts have been reported to be active and stable for photochemical H_2 production in the presence of sacrificial electron donors,[25–29] there are very limited examples for the p-type semiconductor-based photocathode integrated with a non-noble metal molecular catalyst.[19,30] During the progress of this work, three reports on the semiconductor QDs-sensitized p-type NiO photocathodes for the HER came out in the literatures.[18–20] One presents a CdSe QD-sensitized NiO photocathode without HER catalyst, which displays a photocurrent lower than 20 μA cm^{-2} at the applied potential of 0 to −0.5 V vs. Ag/AgCl.[18] The other report describes a CdS-sensitized NiO photocathode.[19] When a cobaloxime catalyst was physically absorbed onto the surface of CdS-sensitized NiO, the initial photocurrent of this electrode increased from 17.5 to 25 μA cm^{-2} at an applied potential of about 0 V with an apparent photocurrent decay from the very beginning of illumination, possibly due to escaping of the molecular cobalt catalyst from the surface of

NiO to the solution.[14] Just before the submission of this paper, we found a report on the CdSe QDs/NiO photocathode, which displayed a stable photocurrent density up to 60 μA cm^{-2} at an applied potential of −0.1 V in a neutral medium under visible-light irradiation.[20]

In this communication, we report an efficient and stable photocathode comprising a cobaloxime catalyst, CdSe QDs, and the open porous p-type NiO film for H_2 evolution from neutral aqueous solution (Fig. 1). The molecular cobalt catalyst, $[CoCl(dmgH)_2(pyridyl\text{-}4\text{-}hydrophosphonate)]^-$ (CoP, dmgH = dimethyloxime), was covalently tethered through a phosphonate anchoring group to the surface of the NiO film which was sensitized by CdSe QDs. The purpose is to speed up the electron transfer from the conduction band (CB) of CdSe QDs to the catalyst and therefore to reduce the possibility of recombination between the reduced QDs and the holes generated in NiO. Such a cobaloxime catalyst and its analogues have previously been chemically linked to ruthenium polypyridyl-sensitized TiO_2 particles,[31–33] CdSe/ZnS core-shell QDs,[34] and to photo-inactive cathodes.[35,36] To our knowledge, there is only two examples of the photocathode that has a cobaloxime catalyst chemically attached to a sensitized NiO film and displayed a photocurrent density lower than 20 μA cm^{-2}.[15,16] In the present work, we co-grafted a cobaloxime catalyst and a light absorber through chemical bonds to the electrode surface. The water-soluble thioglycolic acid (TGA)-stabilized CdSe QDs was used as light harvester, in which the TGA functions not only as a capping ligand to protect QDs from aggregation but its carboxylate also acts as an anchoring group of CdSe QDs onto the surface of NiO. The open porous NiO was used to increase the real surface area of NiO,[37] which would allow to increase the loading amounts of sensitizer and catalyst, and therefore to enhance the light harvesting and H_2-evolution efficiencies. The porous NiO/CdSe/CoP photocathode displayed a photocurrent density of about 110 μA cm^{-2} at an applied potential of 0 V in neutral water under illumination of visible light (λ > 400 nm). The long-time illumination experiment at a controlled applied potential showed that the stability of the CdSe QD-sensitized NiO photocathode with a covalently attached cobaloxime catalyst is considerably improved as compared to the same photocathode but with a physically adsorbed cobaloxime catalyst.

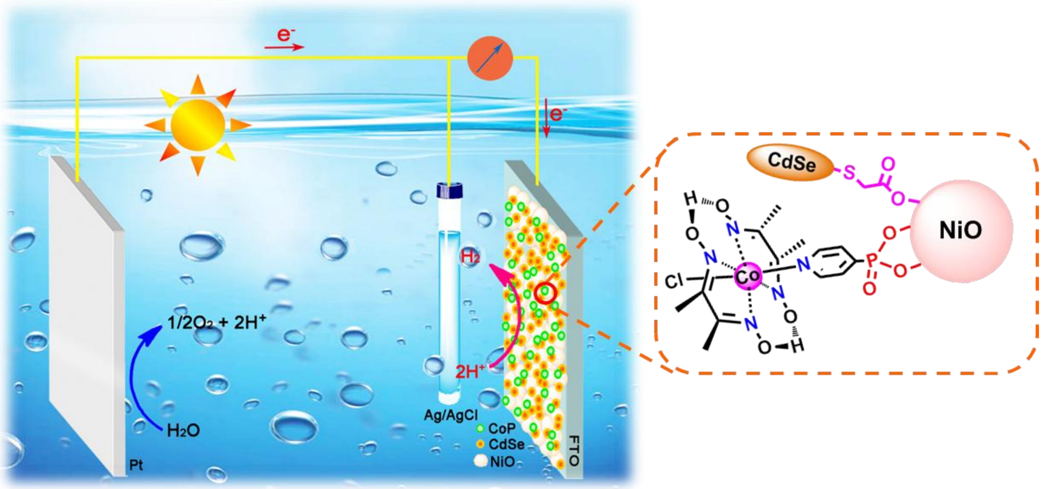


Fig. 1 Schematic diagram of a photoelectrochemical cell, consisting of a photocathode with a cobaloxime catalyst anchored to the CdSe QD-sensitized NiO film on a FTO glass substrate and with a Pt wire as counter electrode for water splitting.

Results and discussion

First of all, a thermodynamic analysis of the redox properties of p-type NiO, CdSe QDs, and cobaloxime catalyst was made. The estimated valence band and conduction band energy levels of CdSe QDs are 1.30 and −0.97 V, respectively.[38] The valence band of CdSe QDs is much more positive than that of NiO (the reported values are in the range of 0.5 to 0.7 V)[15,39] and the conduction band of QDs is more negative than the reduction potentials of the Co^{III}/Co^{II} ($E_p = -0.15$ V) and Co^{II}/Co^{I}($E_{onset} = -0.6$ V) processes of the cobaloxime complex,[32] indicating that both the hole injection from CdSe QDs to NiO and the electron transfer from CdSe to the cobalt catalyst are thermodynamically favorable. An energy illustration for the proposed working principle of the simultaneously CdSe-sensitized and cobaloxime-grafted p-type NiO photocathode is shown in Fig. 2. Upon illumination, CdSe QDs absorb light and the electron in its valence band is excited to the conduction band. The photogenerated holes in the QDs inject to the valence band of p-type NiO and finally move to the counter electrode and the photogenerated electrons of the CdSe QDs transfer to the nearby anchored cobaloxime complex, which catalyzes water reduction to H_2 at the cathode when it is reduced to the Co^I species.

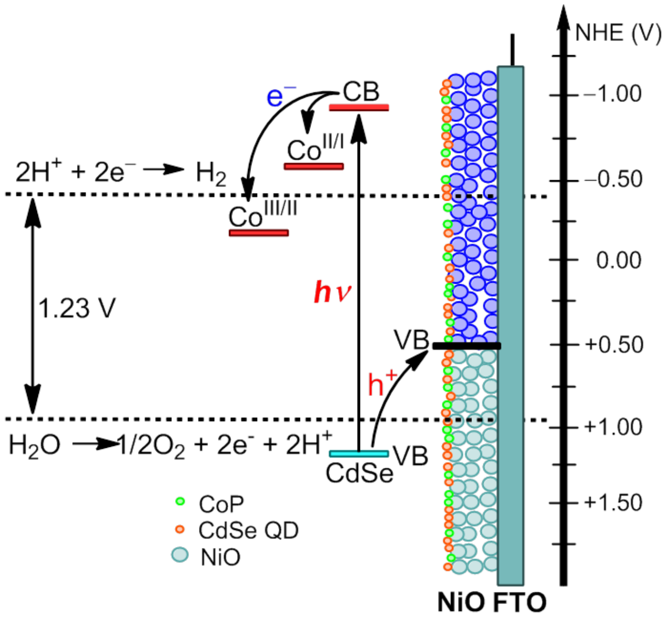


Fig. 2 An energy illustration for the electron transfer and hole injection at the simultaneously CdSe-sensitized and cobaloxime-grafted p-type NiO photocathode.

The cobaloxime complex, $(Et_3NH)[CoCl(dmgH)_2(pyridyl\text{-}4\text{-}hydrophosphonate)]$, was prepared according to the literature procedure.[31] To increase the specific surface area of NiO film, an open porous p-type NiO film on a FTO glass was fabricated using a recently reported green solvothermal synthesis method.[37] In this study, CdSe QDs were formed and grafted on the surface of the NiO cathode by two methods. One of the methods was to generate CdSe QDs on the porous NiO film by repeating the successive ionic layer adsorption and reaction

(SILAR) procedure.[18,23] The other method is the one-pot adsorption and reaction (OPAR) by immersing the NiO film in an aqueous solution containing $Cd(AcO)_2$, Na_2SeSO_3, and TGA in a molar ratio of 1:16:0.22 at ~5 ℃ for 2 d.[40] In addition, we also tried to adsorb CdSe QDs on the NiO surface by drop-casting or spin-coating the pre-synthesized colloidal CdSe QDs solution onto the NiO film, but the resulting photocathodes displayed low photocurrents and poor stability. Therefore, only the CdSe QD-sensitized NiO photocathodes that were fabricated by the SILAR and OPAR methods were used for the further detailed studies.

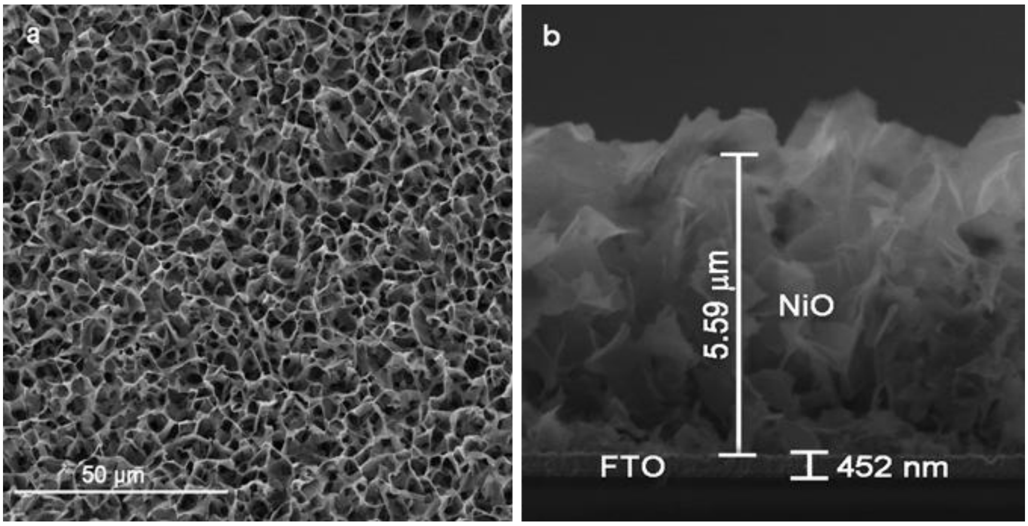


Fig.3 (a) Top-view and (b) side-view SEM images of the prepared open porous NiO film on an FTO glass.

The morphology of the prepared NiO film was characterized by scanning electron microscopy (SEM). As shown in Fig. 3, the surface of FTO glass substrate is covered with a layer of uniform films with a thickness of approximately 5.6 µm. The film is composed of nanoflakes interconnected with each other to form an open porous network structure. Such an open porous nanostructure allows easy access of electrolyte to the entire nanoflakes that could increase the loading amounts of sensitizer and catalyst. The CdSe QD-sensitized NiO films prepared by the SILAR and OPAR procedures were characterized by SEM and transmission electron microscopy (TEM). Figs. 4a and 4d show that after sensitized by CdSe QDs the NiO film remains its porous nanostructure and the TEM images (Fig. 4) clearly show that CdSe QDs have been grafted on the nanoflake surface of the porous NiO film by both methods. Fig. 4b and the inset in Fig. 4a show that the distribution of CdSe QDs on the NiO film made by SILAR procedure is not uniform, as reported in the literatures,[18,23] and some apparent aggregated big clusters of CdSe QDs exist on the surface of the NiO nanoflakes. In contrast, for the CdSe-sensitized NiO film that was prepared by the OPAR method, CdSe QDs are uniformly dispersed on the NiO nanoflake surface as shown in Fig. 4e and the inset in Fig. 4d. The EDX (Figs. S1 and S2) and the inductively coupled plasma optical emission spectroscopic (ICP-OES) analysis give similar results for the loading amounts of Cd^{2+}, which were estimated to be 0.30 (Cd/Se = 0.99–1.19 mol/mol) and 0.12 mg cm^{-2} (Cd/Se = 0.74–0.87 mol/mol) on the sensitized NiO film made by the OPAR and SILAR methods, respectively. As presented in Fig. S3, the wavelength thresholds of the CdSe QD-sensitized porous NiO film made by the OPAR and SILAR methods are 610 and 716 nm, corresponding to the band gaps of 2.03 and 1.73 eV, respectively. The mean diameters (D) of QDs were estimated to be 5.1 and 16.2 nm for the sample prepared by the OPAR and SILAR procedures on the basis of the equations reported by Peng and coworkers.[41] The apparent red shift of the absorption band edge and the large average particle size of the CdSe QDs on the NiO film deposited by the SILAR method is consistent with its TEM images in Fig. 4b and the inset of Fig. 4a.

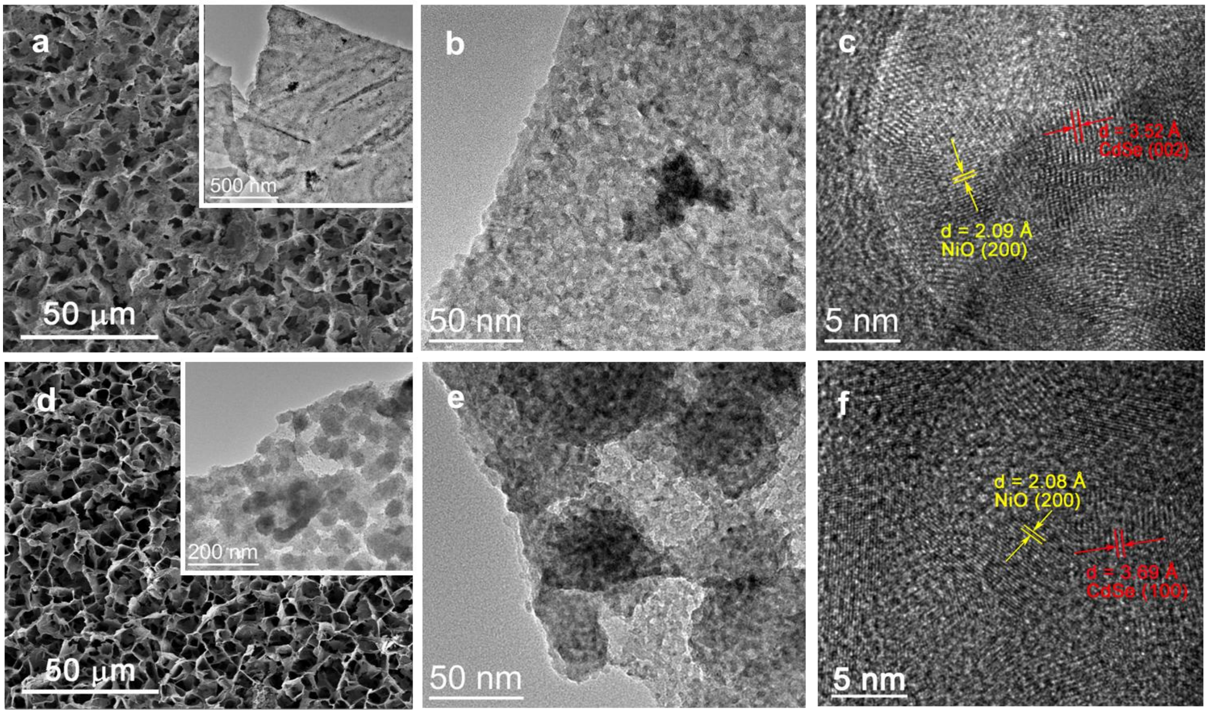


Fig. 4 (a and d) Top-view SEM images of the CdSe QD-sensitized porous NiO films (insets: high magnification SEM images of a piece of nanoflakes); (b and e) TEM images of a piece of nanoflakes; (c and f) High resolution TEM of the CdSe-sensitized NiO film; the samples for (a)–(c) were made by the SILAR procedure and those for (d)–(f) were fabricated by the OPAR method.

The CdSe QD-sensitized NiO electrode was immersed in a methanol solution of the cobaloxime catalyst (1.0 mM) for 3 h under nitrogen atmosphere in the dark, followed by washing with methanol and water, respectively, for several times and drying in vacuum at room temperature. The as-prepared photocathode, NiO/CdSe/CoP, was stored under nitrogen in the dark and ready for further photoelectrochemical testing. To determine the loading amount of cobalt complex, the material on a FTO glass plate was completely dissolved in aqua regia, which was analyzed by ICP-OES. The average values obtained from three independently prepared samples show that the loading amount of CoP is about 3.08 nmol cm^{-2}, corresponding to the Co/Cd atomic ratios of about 3.08:2.67 for the NiO-CdSe-CoP cathode made by the OPAR method and 3.08:1.07 for the electrode fabricated by the SILAR procedure.

The photoelectrochemical measurement was carried out in a standard three-electrode cell, using bare porous NiO, NiO/CdSe, or NiO/CdSe/CoP as working electrode, a Pt wire as counter electrode, and Ag/AgCl as reference electrode in a 0.1 M Na_2SO_4 aqueous solution at pH 6.8. A 300W xenon lamp equipped with a $\lambda > 400$ nm cutoff filter was used to illuminate the NiO-based sample electrode. The bare NiO is visible light inert and therefore it has a negligible contribution to the photocurrent of the electrode. As shown in Fig. 5, the photocurrent was generated upon the light on-off cycles of illumination on the NiO/CdSe photocathodes in the PEC cell at an applied potential of 0 V. The instant response of the photocurrent to the chopped illumination indicates the efficient separation of the electron-hole pairs in the system induced by visible light. The NiO/CdSe photocathodes prepared by the SILAR and OPAR procedures displayed similar photocurrent densities (68–73 μA cm^{-2}) at an applied potential of 0 V, though the amount of CdSe QDs grafted on the NiO film by the SILAR procedure is only about 2/5 of that anchored by the OPAR method. The possible reason might be that the CdSe QDs were dominantly grafted on the top layer of the NiO film which was prepared by the SILAR procedure, while the CdSe QDs were homogenously distributed on the entire porous NiO film which was made by the OPAR method. The light absorption efficiency of the CdSe QDs grafted in the inner layer of the porous NiO film would be impaired.

To make a comparison, the NiO film electrode that was prepared by doctor-blading a NiO paste on the surface of FTO glass plate was used to fabricate the CdSe QD-sensitized NiO electrode by the OPAR method, which displayed a photocatalytic current density of 43 μA cm^{-2} at an applied potential of 0 V upon illumination under identical conditions (Fig. S4). The geometric photocurrent density of the CdSe QD-sensitized open porous NiO electrode at the applied potentials of 0 V is enhanced by a factor of about 1.7 as compared to that displayed by the corresponding CdSe QD-sensitized planar NiO electrode, most possibly due to the increase of the real surface area of the open porous NiO film. The CdSe QD-sensitized NiO electrodes so far reported displayed the photocurrent densities of 20–60 μA cm^{-2} at −0.1 to −0.5 V applied potentials.[18,20]

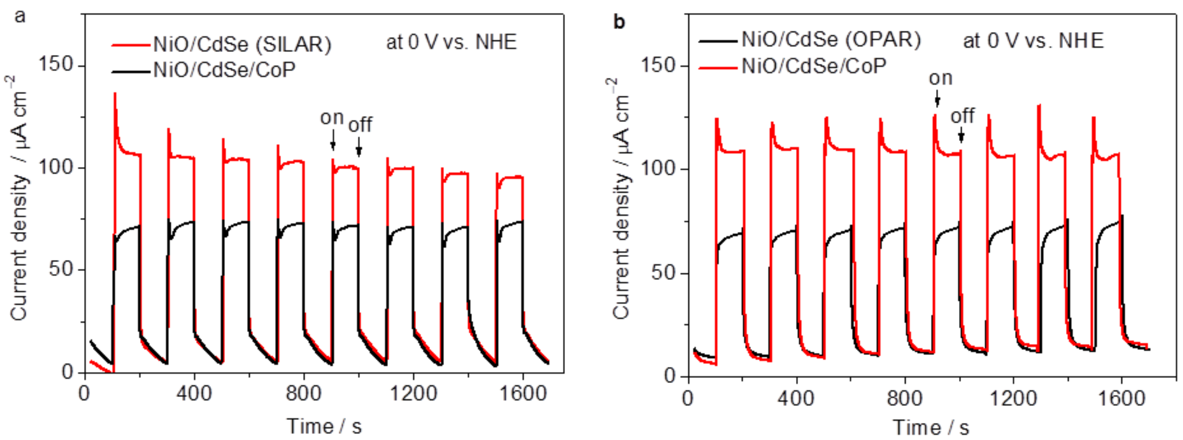


Fig. 5 Transient current responses of the photocathodes made by the SILAR (a) and OPAR procedure (b) to on-off cycles of illumination on photocathodes at 0 V versus NHE in a three-electrode PEC cell of 0.1 M Na_2SO_4 solution at pH 6.8.

Upon illumination, the photocurrent densities of CdSe QD-sensitized porous NiO cathodes grafted by CoP catalyst reached 104–110 μA cm^{-2} at 0 V, which is about 3–8 fold of those observed for the dye-sensitized NiO cathodes with a cobaloxime catalyst chemically attached or physically adsorbed on the electrode surface under the similar conditions.[14–16] Furthermore, we also made a reference electrode in which a cobaloxime catalyst without phosphonate anchoring group was physically adsorbed on the CdSe QD-sensitized porous NiO film, denoted as NiO/CdSe/Co. This photocathode displayed an initial photocurrent density of about 100 μA cm^{-2} at 0 V upon illumination (Fig. 6a), which is comparable to that obtained from the NiO/CdSe/CoP electrode containing covalently bonded cobaloxime catalyst; but the photocurrent density of NiO/CdSe/Co electrode quickly decreased to about 65 μA cm^{-2} in a period of about 800 s, suggesting a nearly complete desorption of the cobaloxime catalyst from the NiO/CdSe electrode. Similarly, a very recently reported photocathode with the same cobaloxime catalyst physically absorbed on the surface of the CdS QD-sensitized NiO film exhibited an initial photocurrent density of 25 μA cm^{-2} at an applied potential of 0 V upon illumination, with a rapid decay in photocurrent.[19] The chemical attachment of a HER catalyst to the sensitized NiO electrode would expedite the electron transfer from CdSe QDs to the neighboring anchored cobalt catalyst and therefore suppress the recombination of the holes generated in NiO with the reduced CdSe QDs, leading to a more stable photocurrent compared to the NiO/CdSe electrode with physically adsorbed cobalt catalysts.

The photoelectrochemical measurement was also carried out in a 0.1 M phosphate buffer solution (PBS) at pH 6.8 under otherwise identical conditions. A high initial photocurrent density over 200 μA cm^{-2} was attained for the porous NiO/CdSe/CoP electrode in PBS at an applied potential of −0.2 V (Fig. S5a), which was quickly decreased to about 95 μA cm^{-2} in a period of about 1000 s, while under the same conditions but in 0.1 M Na_2SO_4 solution the NiO/CdSe/CoP electrode displayed a stable photocurrent density around 110 μA cm^{-2} (Fig. S5b). The decay of the photocurrent in PBS is possibly due to the fact that the phosphonate linkage between the cobaloxime catalyst and NiO film is partially substituted by the phosphate of buffer, resulting in the escape of the cobalt catalyst from the electrode surface to the solution.

The results obtained from these comparative experiments indicate that the high photocurrent density of the present NiO electrode stems from the broad visible light absorption of CdSe QDs, the open porous nanostructure of NiO, and the direct chemical linkage of the molecular cobalt catalyst to the electrode surface. For a convenient comparison, Table 1 summarizes the photoelectrocatalytic data of our porous NiO/CdSe/CoP and

NiO/CdSe/Co electrodes together with all reported photocathodes based on non-noble molecular catalysts and/or p-type semiconductor, which shows that porous NiO/CdSe/CoP electrode is the most active photocathode amount these electrodes.

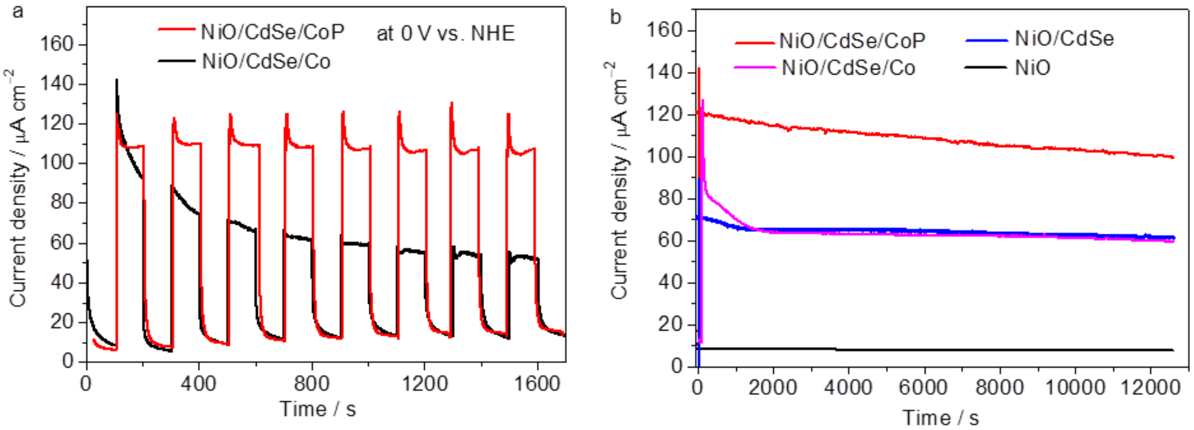


Fig. 6 (a) Transient current responses to on-off cycles of illumination on photocathodes, NiO/CdSe, NiO/CdSe/CoP, and NiO/CdSe/Co, at 0 V versus NHE in a three-electrode PEC cell of 0.1 M Na_2SO_4 solution at pH 6.8. (b) Curves of photocurrent density versus time for the prepared porous NiO-based photocathodes over 3.5 h illumination at an applied potential of −0.2 V.

Table 1 Comparison of different photocathodes in a three-electrode PEC cell for the HER

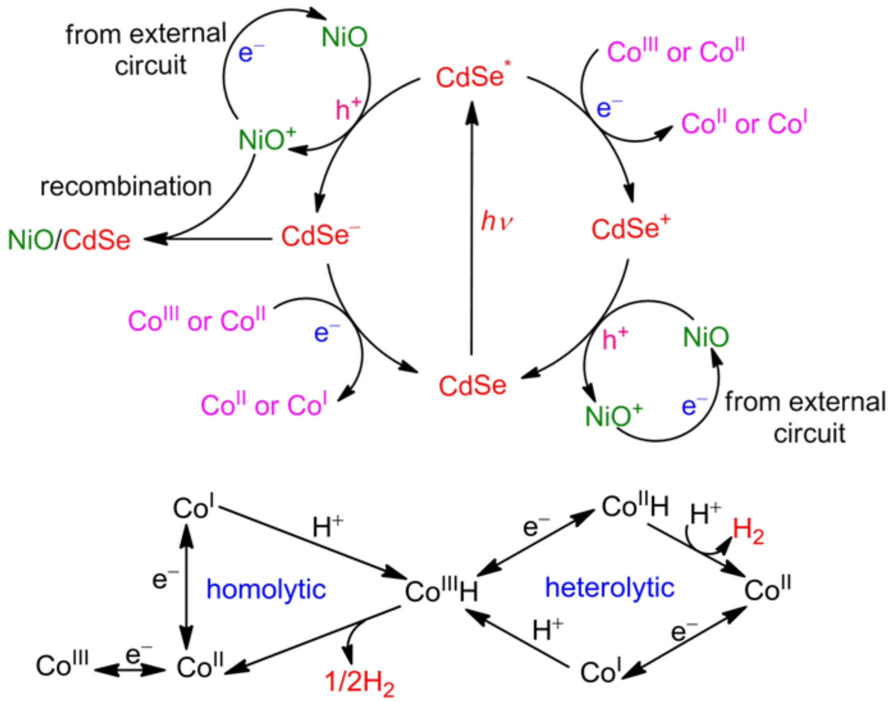
Photocathode	Conditions	Photocurrent density at an applied potential (V vs. NHE)	Stability and Faradaic efficiency	Ref.
FTO|porous NiO-CdSe-CoP	pH 6.8, 0.1 M Na_2SO_4, $\lambda > 400$ nm	102 μA cm^{-2} at 0 V 106 μA cm^{-2} at −0.1 V 118 μA cm^{-2} at −0.2 V	A 17% decay in current was observed over 3.5 h illumination at −0.2 V	Present work
FTO|porous NiO-CdSe-Co	pH 6.8, 0.1 M Na_2SO_4, $\lambda > 400$ nm	100 μA cm^{-2} at 0 V	Photocurrent decayed quickly	Present work
FTO|NiO-CdSe	pH 6.8, 0.1 M $LiClO_4$, 0.01 M PBS, $\lambda > 420$ nm	< 20 μA cm^{-2} at 0 to −0.5 V		[18]
FTO|NiO-CdSe (CdSe: 0.3 mg cm^{-2})	pH 6.8, 0.1 M Na_2SO_4, $\lambda > 400$ nm	60 μA cm^{-2} at −0.1 V	Photocurrent is stable over 45 h illumination at −0.1 V	[20]
FTO|NiO-CdS	0.05 M Na_2SO_4	17.5 μA cm^{-2} at 0 V		[19]
FTO|NiO-CdS-Cobaloxime	0.05 M Na_2SO_4	25 μA cm^{-2} at 0 V	Photocurrent decayed quickly	[19]
FTO|NiO-Al_xO_y-OOCRuP-Cobaloxime	pH 7 PBS, $\lambda > 420$ nm	~19 μA cm^{-2} at 0 V	Photocurrent is stable over 2.5 h illumination at −0.1 V	[15]
FTO|NiO-Organic dye-Cobaloxime	pH 7 PBS, $\lambda > 400$ nm	20–35 μA cm^{-2} at 0 to −0.2 V	Photocurrent gradually decayed	[14]
FTO|NiO-Ru2P-Cobaloxime	pH 7 PBS, $\lambda > 400$ nm	13 μA cm^{-2} at −0.2 V		[16]
FTO|NiO-Organic dye	pH 7, 0.1 M Na_2SO_4, $\lambda > 420$ nm	Over 4 h illumination: 3.9 μA cm^{-2} at 0 V		[13a]
FTO|PS-b-P2VP-templated NiO-Organic dye[a]	pH 4.5, 0.1 M acetate buffer, $\lambda > 400$ nm	~10 μA cm^{-2} at +0.2 V		[13b]
FTO|PS-b-P2VP-templated NiO-Organic dye[a]	pH 4.5, 0.1 M acetate buffer, $\lambda > 400$ nm, 10 mM $[Co(NH_3)_5Cl]Cl_2$	~200 μA cm^{-2} at +0.2 V	Photocurrent is stable	[13b]
Au|InP-$[Fe_2S_2(CO)_6]$	pH 7, 0.1 M $NaBF_4$, 3 M NaCl, 395 nm LED	200 nA cm^{-2} at −0.1 V 263 nA cm^{-2} at −0.2 V 375 nA cm^{-2} at −0.3 V	Photocurrent is stable over 1 h illumination at −0.2 V	[30]

[a] PS-b-P2VP = polystyrene-block-poly-(2-vinylpyridine)

A controlled potential photoelectrolysis experiment of 0.1 M Na_2SO_4 solution at pH 6.8 was carried out at an applied potential of −0.2 V under illumination to explore the stability and efficiency of the porous NiO/CdSe/CoP photoelectrode for the HER. To have a steady baseline and minimize the impact of background, the spectra were recorded after the application of −0.2 V to the system for 1 h in the dark. The photocurrent of 120 μA cm^{-2} at an applied potential of −0.2 V slowly decayed by about 17% during 3.5 h illumination (Fig. 6b). The gas evolved during the experiment was confirmed by gas chromatography. The amount of H_2 generated is 3.4 μmol over 2-h illumination and in the meantime the cumulated charges passed through the external circuit is 0.81 C, indicative of a Faradaic efficiency of 81% (Fig.

S6). Under identical conditions, the corresponding NiO/CdSe/Co electrode displayed comparable initial photocurrent density to the NiO/CdSe/CoP electrode, but the photocurrent density dropped in 1400 s illumination to the level (~66 μA cm^{-2}) of the NiO/CdSe electrode that has no cobalt catalyst. The CdSe QD-sensitized porous NiO photoelectrode with a cobaloxime catalyst chemically linked to the surface of the NiO film is significantly more stable than the dye- or QD-sensitied NiO electrode with a physically adsorbed cobaloxime catalyst.[14,19]

The possible mechanism of the NiO/CdSe/CoP cathode is proposed in Scheme 1 according to the related mechanistic studies of the CdSe QD-sensitized p-type NiO photocathodes used in solar cells[21,22] and the cobaloxime catalyst used in the homogeneous H_2-generation systems.[42,43] Upon illumination, CdSe QDs harvest visible light and the absorbed photons trigger the excitation of electron from the valence band of CdSe QDs to the conduction band. The photogenerated hole in the valence band of CdSe is injected to the valence band of NiO. The hole at NiO combines then with an electron that is delivered by electrode, or transfers to the counter electrode through the external circuit. According to the literatures, the hole injection from the excited CdSe QDs to the attached NiO occurs on the picosecond timescale,[44] while the direct electron transfer from the excited QDs to the cobalt(III) complex takes place on the nanosecond timescale.[45] Therefore it is mostly possible that the dominant pathway is the hole injection from the excited $CdSe^*$ QDs to NiO followed by the electron transfer from the reduced species, $CdSe^-$ QDs, to the CoP catalyst to form Co^{II} and then Co^{I} intermediates. In the subsequent dark reaction, the important Co^{III}-hydride intermediate might be formed by the protonation of the Co^{I} species. The further reactions of Co^{III}–H to form molecular hydrogen may undergo by subsequent reduction and further protonation, leading to heterolytic cleavage of the Co^{II}–H bond (a heterolytic route), and/or by a bimolecular reaction of two Co^{III} hydrides with homolytic cleavage of the Co^{III}–H bond (a homolytic route).



Scheme 1 Proposed mechanisms for (top) the photoinduced hole injection and electron transfer upon illumination and (bottom) the dark reaction of H_2 generation catalyzed by the cobalt complex.

Conclusions

In summary, an efficient noble-metal-free photocathode was fabricated by chemically co-grafted CdSe QDs and a cobaloxime catalyst to the surface of the open porous NiO film on a FTO glass substrate. Upon illumination of visible light on the NiO/CdSe/CoP cathode, a photocurrent density around 110 μA cm^{-2} was generated at an applied potential of 0 V in a neutral aqueous solution. The activity of this photocathode is more than three times higher than those reported to date for the dye- or QDs-sensitized NiO cathodes with a cobaloxime catalyst chemically attached or physically adsorbed on the electrode surface under similar conditions. This photocathode functioned in a neutral media for a long time and maintained about 83% photocurrent (100 μA cm^{-2}) after 3.5 h illumination at an applied potential of −0.2 V, giving a Faradaic efficiency of about 81% for H_2 evolution. The enhanced activity and improved stability of the photocathode compared to the so far-reported NiO-based photocathodes is ascribed to the good photophysical property of CdSe QDs, the open porous nanostructure of NiO, and the stable chemical linkage of the molecular cobalt catalyst to the electrode surface. The continuous work is focused on stably grafting other p-type semiconductors of high carrier mobility and more efficient and robust HER catalysts to a cathode to further enhance the device performance.

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References

1 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. USA*, 2006, **103**, 15729–15735.

2 N. Armaroli and V. Balzani, *Angew. Chem. Int. Ed.*, 2007, **46**, 52–66.

3 T. J. Jacobsson, V. Fjällström, M. Edoff and T. Edvinsson, *Energy Environ. Sci.*, 2014, **7**, 2056–2070.

4 J. R. McKone, N. S. Lewis and H. B. Gray, *Chem. Mater.*, 2014, **26**, 407−414.

5 M. G. Walter, E. L. Warren, J. R. Mckone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**, 6446–6473.

6 Z. Huang, C. Xiang, H.-J. Lewerenz and N. S. Lewis, *Energy Environ. Sci.*, 2014, **7**, 1207–1211.

7 S. Mori, S. fukuda, S. Sumikura, Y. Takeda, Y. Tamaki, E. Suzuki and T. Abe, *J. Phys. Chem. C*, 2008, **112**, 16134−16139.

8 Y. Mizoguchi and S. Fujihara, *Electrochem. Solid- State Lett*., 2008, **11**, K78−K80.

9 J. He, H. Lindström, A. Hagfeldt and S. E. Lindquist, *J. Phys. Chem. B*, 1999, **103**, 8940−8943.

10 S. Uehara, S. Sumikura, E. Suzuki and S. Mori, *Energy. Environ. Sci*., 2010, **3**, 641−644.

11 A. Nattestad, A. J. Mozer, M. K. R. Fischer, Y. B. Cheng, A. Mishra, P. Bäuerle and U. Bach, *Nat. Mater.*, 2010, **9**, 31−35.

12 L. Li, E. A. Gibson. P. Qin, G. Boshloo, M. Gorlov, A. Hagfeldt and L. Sun, *Adv. Mater.*, 2010, **22**, 1759−1762.

13 (*a*) L. Tong, A. Iwase, A. Nattestad, U. Bach, M. Weidelener, G. Götz, A. Mishra, P. Bäuerle, R. Amal, G. G. Wallace and A. J. Mozer, *Energy Environ. Sci.*, 2012, **5**, 9472−9475; (*b*) J. Massin, M. Bräutigam, N. Kaeffer, N. Queyriaux, M. J. Field, F. H. Schacher, J. Popp, M. Chavarot-Kerlidou, B. Dietzek and V. Artero, *Interface Focus*, 2015, **5**, 20140083.

14 (*a*) L. Li, L. Duan, F. Wen, C. Li, M. Wang, A. Hagfeldt and L. Sun, *Chem. Commun*., 2012, **48**, 988−990; (*b*) F. Li, K. Fan, B. Xu, E. Gabrielsson, Q. Daniel, L. Li and L. Sun, *J. Am. Chem. Soc.*, 2015, **137**, 9153−9159.

15 Z. Ji, M. He, Z. Huang, U. Ozkam and Y. Wu, *J. Am. Chem. Soc.*, 2013, **135**, 11696−11699.

16 K. Fan, F. Li, L. Wang, Q. Daniel, E. Gabrielsson and L. Sun, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25234–25240.

17 Z. Yu, F. Li and L. Sun, *Energy Environ. Sci.*, 2015, **8**, 760−775.

18 M. A. Par, S. Y. Lee, J. H. Kim, S. H. Kang, H. Kim, C. J. Choi and K. S. Ahu, *Phys. Status. Solidi. A*, 2014, **211**, 1868−1872.

19 Y. Na, B. Hu, Q.-L. Yang, J. Liu, L. Zhou, R.-Q. Fan and Y.-L. Yang, *Chin. Chem. Lett.*, 2015, **26**, 141−144.

20 B. Liu, X.-B. Li, Y.-J. Gao, Z.-J. Li, Q.-Y. Meng, C.-H. Tung and L.-Z. Wu, *Energy Environ. Sci.*, 2015, **8**, 1443−1449.

21 K. Zheng, K. Žídek, M. Abdellah, W. Zhang, P. Chábera, N. Lenngren, A. Yartsev and T. Pullerits, *J. Phys. Chem. C*, 2014, **118**, 18462−18471.

22 F. Safari-Alamti, J. R. Jennings, M. A. Hossain, L. Y. L. Yung and Q. Wang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4767−4774.

23 S. H. Kang, K. Zhu, N. R. Neale and A. J. Frank, *Chem. Commun.*, 2011, **47**, 10419−10421.

24 I. Barceló, E. Guillén, T. Lana-Villarreal and R. Gómez, *J. Phys. Chem. C*, 2013, **117**, 22509−22517.

25 F. Wang, W.-G. Wang, H.-Y. Wang, G. Si, C.-H. Tung and L.-Z. Wu, *ACS Catal.*, 2012, **2**, 407−416.

26 F. Wen and C. Li, *Acc. Chem. Res.*, 2013, **46**, 2355−2364.

27 P. D. Tran, L. H. Wong, J. Barber and J. S. C. Loo, *Energy Environ. Sci.*, 2012, **5**, 5902−5918.

28 J. Ran, J. Zhang, J. Yu, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2014, **43**, 7787−7812.

29 M. Wang, K. Han, S. Zhang and L. Sun, *Coord. Chem. Rev.*, 2015, **287**, 1−14.

30 T. Nann, S. K. Ibrahim, P.-M. Woi, S. Xu, J. Ziegler and C. J. Pickett, *Angew. Chem. Int. Ed.*, 2010, **49**, 1574−1577.

31 F. Lakadamyali and E. Reisner, *Chem. Commun.*, 2011, **47**, 1695−1697.

32 F. Lakadamyali, M. Kato, N. M. Muresan and E. Reisner, *Angew. Chem. Int. Ed.*, 2012, **51**, 9381−9384.

33 F. Lakadamyali, A. Reynal, M. Kato, J. R. Durrant and E. Reisner, *Chem. Eur. J.*, 2012, **18**, 15464−15475.

34 J. Huang, K. L. Mulfort, P. Du and L. X. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 16472−16475.

35 E. S. Andreiadis, P.-A. Jacques, P. D. Tran, A. Leyris, M. Chavarot-Kerlidou, B. Jousselme, M. Matheron, J. Pécaut, S. Palacin, M. Fontecave and V. Artero, *Nat. Chem.*, 2013, **5**, 48−53.

36 N. M. Muresan, J. Willkomm, D. Mersch, Y. Vaynzof and E. Reisner, *Angew. Chem. Int. Ed.*, 2012, **51**, 12749−12753.

37 Y. B. Zhang and Z. G. Guo, *Chem. Commun.*, 2014, **50**, 3443−3446.

38 J. Huang, D. Stockwell, Z. Q. Huang, D. L. Mohler and T. Q. Lian, *J. Am. Chem. Soc.*, 2008, **130**, 5632−5633.

39 S. Powar, T. Daeneke, M. T. Ma, D. Fu, N. W. Duffy, G. Götz, M. Weidelener, A. Mishra, P. Bäuerle, L. Spiccia and U. Bach, *Angew. Chem. Int. Ed.*, 2013, **52**, 602–605.

40 B. C. Das, S. K. Batabyal and A. J. Pal, *Adv. Mater.*, 2007, **19**, 4172–4176.

41 W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.*, 2003, **15**, 2854−2860.

42 C. N. Valdez, J. L. Dempsey, B. S. Brunschwig, J. R. Winkler and H. B. Gray, *Proc. Natl. Acad. Sci. USA*, 2012, **109**, 15589–15593.

43 E. Anxolabéhère-Mallart, C. Costentin, M. Fournier, S. Nowak, M. Robert and J.-M. Savéant, *J. Am. Chem. Soc.*, 2012, **134**, 6104–6107.

44 K. Zheng, K. Zídek, M. Abdellah, W. Zhang, P. Chabera and N. Lenngren, *J. Phys. Chem. C*, 2014, **118**, 18462−18471.

45 C. Gimbert-Surinach, J. Albero, T. Stoll, J. Fortage, M.-N. Collomb, A. Deronzier, E. Palomares and A. Llobet, *J. Am. Chem. Soc.*, 2014, **136**, 7655−7661.