



## Communication

# New strategy to incorporate nano-particle sized water oxidation catalyst into dye-sensitized photoelectrochemical cell for water splitting<sup>☆</sup>

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## ABSTRACT

In order to develop a new strategy to deposit nano-particle sized water oxidation catalyst based on earth abundant element to the photoanode in a photoelectrochemical cell for water splitting,  $\text{Co}_3\text{O}_4$  as water oxidation catalyst was prepared and subsequently modified by 3-aminopropyltriethoxysilane. The amino functionalized  $\text{Co}_3\text{O}_4$  catalyst was carefully characterized and then integrated to the ruthenium dye sensitized photoelectrode through fast Schiff base reaction. Cyclic voltammetry experiments in the dark confirmed that the modified  $\text{Co}_3\text{O}_4$  catalyst was still active toward water oxidation, which could be initiated by oxidation of the ruthenium photosensitizer. Under visible light irradiation, incorporation of the modified  $\text{Co}_3\text{O}_4$  catalyst resulted in dramatic enhancement of the transient photocurrent density for the photoanode, which was 8 times higher than that of without  $\text{Co}_3\text{O}_4$  catalyst.

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Conversion of solar energy into hydrogen via visible light-driven water splitting represents a bridge towards a renewable-energy future [1]. Dye-sensitized photoelectrochemical cells (DS-PECs) for water splitting have attracted worldwide attention since they can produce hydrogen without any accumulated byproduct, making hydrogen generation and utilization to be cyclic [2,3]. The photoanode in a DS-PEC device is assembled by molecular dyes and water oxidation catalysts co-deposited onto a mesoporous  $\text{TiO}_2$  electrode. The dye sensitizer absorbs visible light and injects an electron into the conduction band of  $\text{TiO}_2$ , resulting in a strong oxidant to initiate the water oxidation through electron transfer from the water oxidation catalyst(s), in which most of the cases, ruthenium and iridium based catalysts are employed dominantly [3–5]. Although excellent performances have been achieved using catalysts based on ruthenium complexes [6], the development of efficient catalyst based on earth-abundant first row transition metal elements is still appealing in the long term.

Cobalt based water oxidation catalysts such as organic cobalt complexes [7–10], inorganic polyoxometalate cobalt [11],  $\text{Co}_3\text{O}_4$  [12,13] and  $\text{CoO}_x$  analogues [14–16] have been demonstrated to be potential candidates, among which nano-particle sized  $\text{Co}_3\text{O}_4$  is more promising from a viewpoint of easy preparation as well

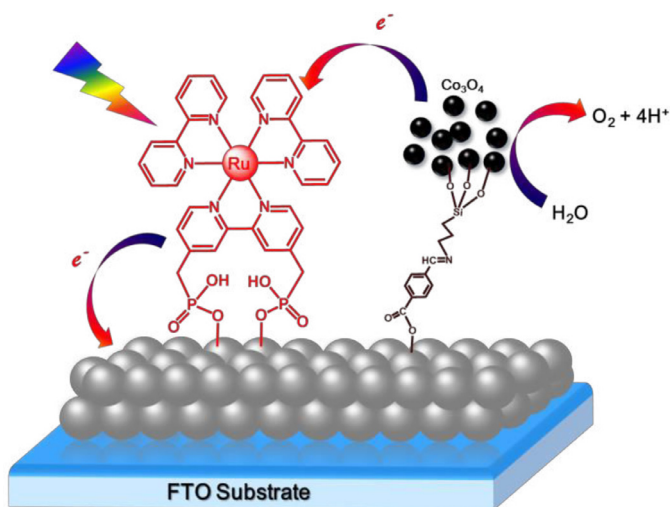
as good stability. Recently, light-driven water oxidation catalyzed by  $\text{Co}_3\text{O}_4$  nano-particles (NPs) has been successfully initiated by  $\text{Ru}(\text{bpy})_3^{2+}$  photosensitizer in the presence of sacrificial electron acceptor, in which the catalytic activity of  $\text{Co}_3\text{O}_4$  could be improved by narrowing the particle sizes [13]. Since the large surface of  $\text{Co}_3\text{O}_4$  NPs can provide sites for chemical modification, it is possible to develop strategies to incorporate  $\text{Co}_3\text{O}_4$  catalyst into the ruthenium dye-sensitized  $\text{TiO}_2$  photoanodes for light-driven water splitting, but has, as far as we know, never been explored. In contrast to the reported strategies that dye molecules were attached to the nano-particle sized catalyst as stabilizers [17,18], stepwise co-sensitization was adopted since remarkable performances have been achieved by molecular components co-sensitized on the  $\text{TiO}_2$  electrode [6]. Herein, we describe the surface modification of  $\text{Co}_3\text{O}_4$  NPs with 3-aminopropyltriethoxysilane (3-APTES) and integration of the amino functionalized catalyst into ruthenium dye (**RuP**)-sensitized  $\text{TiO}_2$  photoanode through Schiff base reaction (Scheme 1).

All reagents used were reagent grade without further purification. The photosensitizer  $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CH}_2\text{PO}_3\text{H}_2)\text{bpy})](\text{PF}_6)_2$  (**RuP**) was synthesized according to the literature [19]. Nano-structured  $\text{Co}_3\text{O}_4$  was prepared according to the published procedure with minor modification [13]. Typically, 0.5 g of cobalt(II) acetate tetrahydrate was dissolved in 2 mL of water followed by addition of 23 mL of ethanol. The reaction solution was stirred at 45 °C for 10 min before aqueous ammonia (3.2 mL, 28%) was added dropwise. The reaction mixture was heated at 80 °C under

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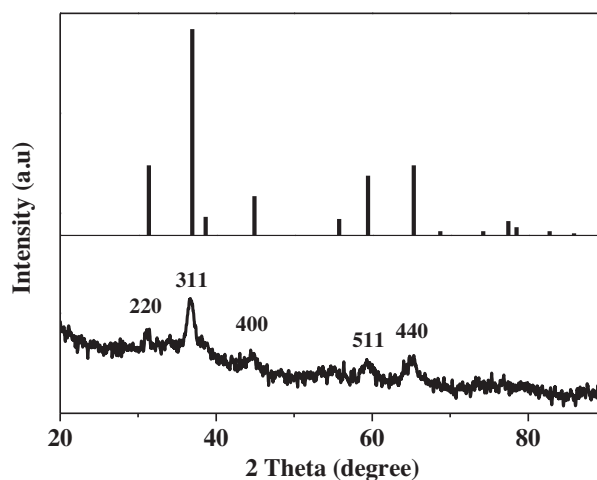
**Scheme 1.** Schematic illustration of the  $\text{TiO}_2$  electrode co-sensitized by RuP and surface modified  $\text{Co}_3\text{O}_4$  NPs.

magnetic stirring for 3 h and then cooled to room temperature, which became turbid immediately upon addition of acetone (100 mL). The precipitate of brownness  $\text{Co}_3\text{O}_4$  was obtained by centrifugation at 4500 rpm for 20 min. The crude product was re-dispersed in 12 mL of methanol followed by addition of acetone (120 mL) and then centrifugation (4500 rpm, 20 min). The above dispersion–centrifugation wash was repeated for two times until the supernatant liquid was almost colorless. The organic solvent residue was removed under vacuum to obtain  $\text{Co}_3\text{O}_4$  NPs powder.

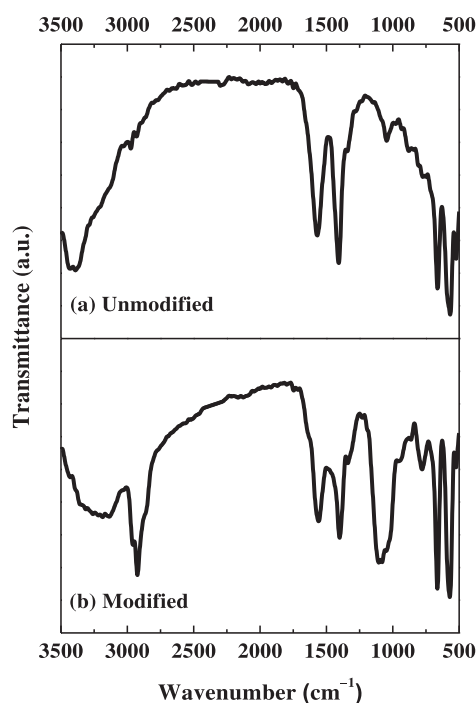
In a typical surface modification procedure, 100 mg of  $\text{Co}_3\text{O}_4$  NPs powder was dispersed in 20 mL of methanol by ultrasonication. The dispersion was degassed by bubbling with  $\text{N}_2$  for 15 min before 360 mg of 3-aminopropyltriethoxysilane was added dropwise. The reaction mixture was stirred at room temperature for 12 h under  $\text{N}_2$ . Solvent was removed by rotary evaporation to obtain the crude product, which was washed two times with  $\text{CH}_2\text{Cl}_2$  to get rid of the excess 3-aminopropyltriethoxysilane by centrifugation (10,000 rpm, 10 min). The  $\text{CH}_2\text{Cl}_2$  residue was removed under vacuum to obtain the amino-functionalized  $\text{Co}_3\text{O}_4$  NPs that was stored under  $\text{N}_2$ .

Mesoporous  $\text{TiO}_2$  film was deposited to FTO substrate with active area of  $1\text{ cm}^2$  according to the reported procedure [20]. The  $\text{TiO}_2$  electrode was first immersed into aqueous solution of RuP (0.15 mM) for 12 h at room temperature in the dark and rinsed with water and ethanol. This dye sensitized  $\text{TiO}_2$  electrode was then dipped into ethanolic solution of 4-formylbenzoic acid for 2 h. The electrode was rinsed with ethanol to get rid of excess 4-formylbenzoic acid. Finally, the electrode was immersed in methanolic solution of amino-functionalized  $\text{Co}_3\text{O}_4$  at  $40\text{ }^\circ\text{C}$  for another 1 h to get the desired photoanode.

Scanning electron microscope (SEM) image and energy dispersive spectrometer (EDS) was analyzed by Hitachi SU8000 instrument. The X-ray powder diffraction (XRD) measurement was performed with  $\text{Cu K}\alpha$  radiation by a Shimadzu XRD-6000 X-ray diffraction instrument. FT-IR spectra were measured on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer. Electrochemistry measurements were recorded using a CHI-660E electrochemical potentiostat at a scan rate of 50 mV/s. CV experiments were carried out in a three-electrode cell under argon. The working electrode was the photoanode, and the auxiliary electrode was a platinum wire. The reference electrode was  $\text{Ag}|\text{AgCl}$  (sat. KCl) electrode. The potentials versus NHE discussed in CV section were calibrated



**Fig. 1.** X-ray powder diffraction pattern of the prepared  $\text{Co}_3\text{O}_4$  NPs.



**Fig. 2.** FT-IR spectra of the prepared  $\text{Co}_3\text{O}_4$  NPs before (a) and after (b) surface modification with 3-APTES.

using  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  as a reference with  $E_{1/2}(\text{Ru}^{\text{III}}/\text{II})=1.26\text{ V}$ . A phosphate buffer solution at pH 6.8 was used as electrolyte, which was degassed by bubbling with dry argon for 15 min before measurement.

The prepared  $\text{Co}_3\text{O}_4$  NPs were first characterized by XRD and FT-IR spectroscopy (Fig. 1). It can be observed that all diffraction peaks are in good agreement with characteristic peaks of the standard (JCPDS-ICDD no. 42-1467), corresponding to spinel phase  $\text{Co}_3\text{O}_4$  (Fig. 1). The most prominent diffraction peak at  $37.6^\circ$  can be attributed to the crystal plane (311). The particle size is calculated to be 8.9 nm according to the Scherrer equation:  $d=K\lambda/\beta\cos\theta$ . In the FT-IR spectrum shown in Fig. 2(a), the characteristic absorption bands at  $665\text{ cm}^{-1}$  and  $577\text{ cm}^{-1}$  can be ascribed to the  $\nu(\text{Co}-\text{O})$  of spinel phase cobalt oxide, which is consistent with the result from XRD patterns. Moreover, the existing of hydroxyl groups on the surfaces of the prepared  $\text{Co}_3\text{O}_4$  NPs is confirmed by the absorption bands for  $\nu(\text{OH})$  at  $3380\text{ cm}^{-1}$  and  $1560\text{ cm}^{-1}$ , providing

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