

Research Article

Cobalt Ferrite Nanocrystallites for Sustainable Hydrogen Production Application

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Cobalt ferrite, CoFe_2O_4 , nanocrystalline films were deposited using electrostatic spray method and explored in sustainable hydrogen production application. Reflection planes in X-ray diffraction pattern confirm CoFe_2O_4 phase. The surface scanning microscopy photoimages reveal an agglomeration of closely-packed CoFe_2O_4 nanoflakes. Concentrated solar-panel, a two-step water splitting process, measurement technique was preferred for measuring the hydrogen generation rate. For about 5 hr sustainable, 440 mL/hr, hydrogen production activity was achieved, confirming the efficient use of cobalt ferrite nanocrystallites film in hydrogen production application.

1. Introduction

Special magnetic and electrical properties, high chemical, and mechanical hardness [1], in modern information technology, have made ferrite films significantly important while designing the electromagnetic devices including the memories [2], sensors [3], and microwaves [4]. In particular, spinel-type ferrites such as MFe_2O_4 where $\text{M} = \text{Co}, \text{Ni}$ are among the most important magnetic materials which have been previously preferred over the past half century [5, 6]. On account of large magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, large magnetostrictive coefficient, chemical stability, and mechanical hardness, which generally are helpful for magnetic recording devices, magneto-optical recording, and electronic devices, cobalt ferrites are nowadays highly in demand. Currently, the well-known established techniques used for fabricating the ferrite films include pulsed laser deposition, rf-magnetron sputtering, electron beam evaporation, metal organic chemical vapour deposition, and molecular beam epitaxy [7–10]. Most of these techniques involve a two step process. In the first step, the desired ferrite material is

synthesized in the bulk form using conventional method, and in the second step, synthesized bulk material is used as a target for irradiation by high power laser, ion/electron beam, or rf source. The resultant plume is then captured on a cold substrate. These techniques require a high power source and/or an ultrahigh vacuum system, making them extremely capital and energy intensive. These techniques are also not suited to obtain conformal coatings on curved substrates. Furthermore, these techniques are inapplicable when the target material is maintained at low-temperatures, as an irradiation would lead to instantaneous decomposition of the target material [11]. There is, therefore, a need to develop simple and inexpensive wet chemical approach for synthesizing ferrite nanostructures on variety of substrates at ambient temperature. Different chemical methods such as ferrite plating [12, 13], sol-gel [14], spin spray ferrite plating [15], and modified ferrite plating [16], spray pyrolysis [17], and the thin liquid film method [18] have been documented in the literature for depositing ferrite nanostructures in the films form. The multicomponent, nanocrystalline, active redox water splitting cobalt ferrite films can be fabricated using electrostatic spray pyrolysis (ESP) electronic method.

Cobalt ferrite films, synthesized using this method, could offer several advantages, for example, synthesis at low temperatures, especially, below 150°C that would be environmentally benign for hydrogen production application [19]. Secondly, available conventional methods such as electrodeposition or normal spray pyrolysis are facing serious large area uniform deposition problem that can be easily solved in ESP method as ESP is a simple chemical synthesis technique in which the high potential field is applied between the substrate and spray nozzle for acceleration.

Chemical synthesis of cobalt ferrite nanocrystalline films using $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is quite known [20, 21]; however, its direct implication in hydrogen production application is quite unknown. Therefore, in the present paper, we report the synthesis of smooth and uniform cobalt ferrite nanocrystallites films using ESP method. Various parameters including the substrate temperature, carrier gas flow rate, solution flow rate, droplet size, nozzle-to-substrate distance, were optimized for acquiring adherent and high quality films. The X-ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy (XPS), the scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques were preferred for the structural elucidation and surface morphological evolution confirmation. Cobalt ferrite films deposited onto a glass substrate were employed for an optical and surface hydrophilicity studies using UV-Vis spectrophotometry and water contact angle techniques, respectively. For an optical absorption measurement, deposited onto glass substrate, Cranx 100 UV-Vis spectrophotometer was preferred. Finally, cobalt ferrite films deposited onto stainless substrate of about $9 \times 9 \text{ cm}^2$ surface area were utilized in hydrogen production activity. During old fashion of hydrogen production, photoelectrochemical (PEC) cell system was used in water splitting process which mainly preferred semiconductor materials photoelectrode, for generating electron-hole pairs [22].

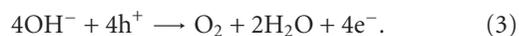
In the relatively new system, silicon solar cell and electrolytic cell are used as active components wherein, for water electrolysis, silicon solar cell provides biasing current to the cathode-anode electrode assembly in an electrolytic cell. The water electrolysis in this system is expected through three steps. The incident solar energy generates electron-hole pairs due to silicon solar cell, in a first step. In a second step, these electron-hole pairs flow through the cathode-anode electrolyte assembly followed by water electrolysis in a third step,



at cathode



and at anode



2. Experimental Details

The ESP technique feasibly facilitates the formation of cobaltite films onto commonly available and inexpensive

glass and stainless steel substrates. These substrates were well cleaned (glass: deionized water, isopropanol, acetone in ultrasonic bath; stainless steel: a zero polishing paper and then ultrasonication) prior to deposition process. For the cobalt ferrite deposition, the aqueous solutions of analytical reagent grade (with 99.99% purity) cobalt acetate dehydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), and iron nitrate nanodehydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were mixed in ethanol and water mixture of 3:1 ratio. Each of the precursor concentration taken in 1:1 volume ratio was 0.2 M. The spraying operation was carried out under an electrostatic potential of 14 kV, at a steady temperature of 150°C by maintaining the substrate-to-spray nozzle distance of 18 cm with spray rate of 15 $\mu\text{L}/\text{min}$. After deposition, the films were annealed at 550°C for 2 h for obtaining cobalt ferrite phase and then used for the structural, morphological, and optical studies and hydrogen production application, respectively. Thickness, measured from the depth profilometer, was close to 100 nm. The X-ray diffractometer (Rigaku, RINT/PMAX 2500) with $\text{Cu-K}\alpha$ radiation wavelength of 1.5406 Å was used for the structural identification. The X-ray source was operated at 40 kV and 100 mA, with a drive axis in 2θ for a scan range from 20 to 80°. Surface morphology and surface topography and average roughness were confirmed from JEOL-JSM 5410 SEM and AFM photoimages, respectively. The sessile drop method was used to measure the contact angle by dropping a microlevel water droplet using fine syringe. The optical absorption measurement of cobaltite film, deposited onto glass substrate, was performed by using Cranx 100 UV-Vis spectrophotometer. The metal contents in cobalt ferrite films were determined by XPS using a Varian FT220s. For hydrogen production measurement, an electrolyser was fabricated with two electrodes (for oxidation and reduction reaction of H_2O). Electrolyte was 1 M NaOH, and Pt counter electrode was for H_2 evolution, and cobalt ferrite film was used for H_2O oxidation. The energy for water splitting can be gained from the photoelectrode located outside of the electrolyser. The areas of photoelectrode and active electrodes were 12.5×12.5 and $9 \times 9 \text{ cm}^2$, respectively. The light intensity was controlled to 100 mW/cm^2 using xenon lamp of 1.5 kW.

3. Results and Discussion

The XRD spectrum of cobalt ferrite film deposited onto glass substrates after annealing at 550°C is shown in Figure 1(a). The XRD spectrum consists of several low intensity peaks. Structure of cobalt ferrite was confirmed after correlating observed XRD peaks to that found in standard JCPDF data card (22-1086). Identical peaks, similar to reported elsewhere [20], were indexed to (220), (311), (400), and (440) diffraction planes. The peak intensity of (311) was relatively higher than others confirming the presence of single cobalt ferrite phase instead of mixed CoO and Fe_2O_3 phases. This higher intensity of (311) plane can be attributed to an annealing effect that boosts the crystallinity and specific orientation of crystallites. Using Scherrer's formula, crystallite size of about 50 nm was calculated. The SEM image

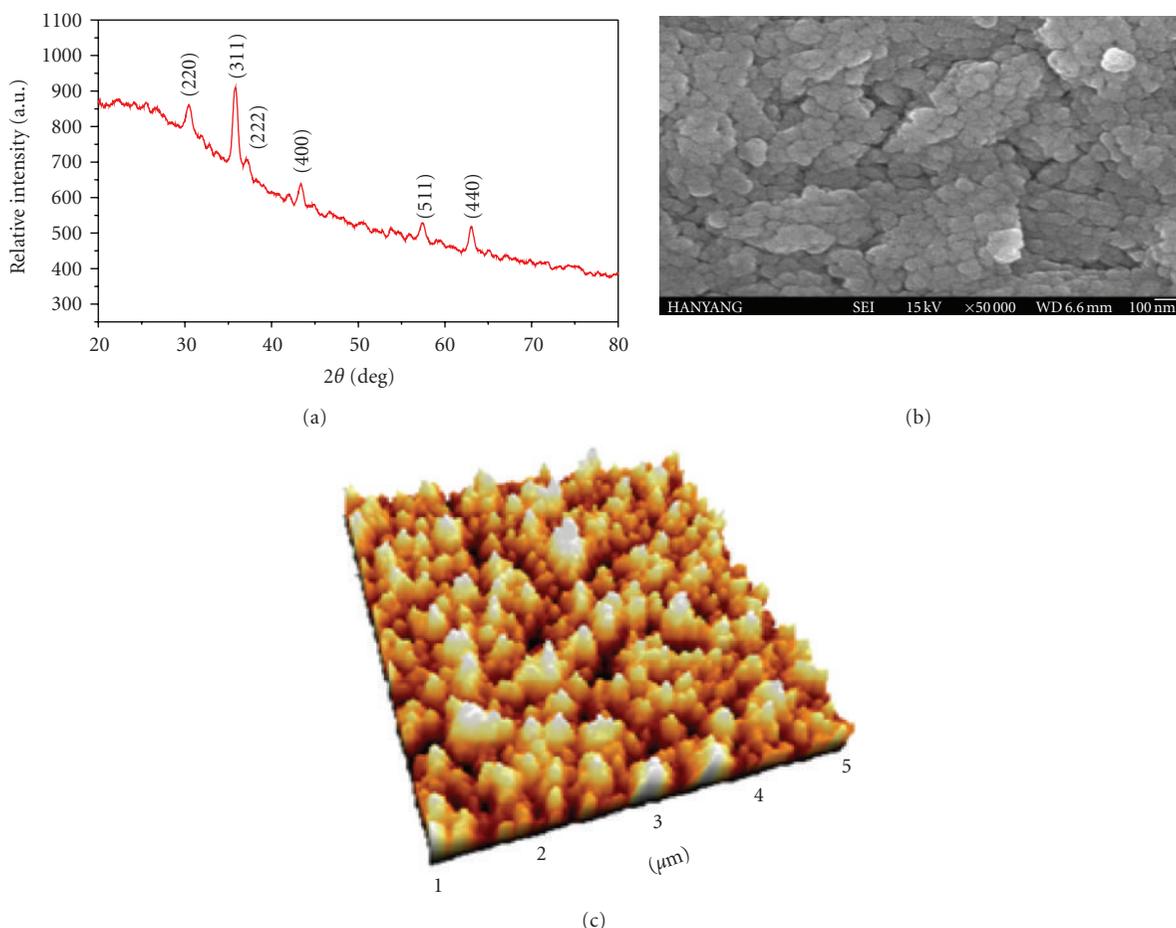


FIGURE 1: (a) Normalized XRD pattern, (b) SEM, and (c) 3D AFM image confirming the structural identification with spherical crystallites evolution of cobalt ferrite.

of cobalt ferrite film is presented in Figure 1(b). Within the scanned surface area, aggregated-type uniform coverage of cobalt ferrite nanoflakes was obtained which was free from the surface cracks or voids. It was found that these nanoflakes were made up of several oval-type elongated crystallites separated by fine and sharp grain boundaries. Each of these crystallites was 60–80 nm in width. However, due to their interpenetrating behaviour, it was difficult for us to measure exact individuals height. Similar type of morphology was also reported by others [21, 23]. We expect enhanced redox reactions, due to the large surface area of these nanoparticles, can be advantageous in hydrogen production activity application. The 3D surface topography image, scanned using noncontact mode of AFM, is presented in Figure 1(c). From 3D AFM image oval-type grain texture, which was actually missing in SEM image, was confirmed.

Figure 2(a) shows the contact angle measurement photo-image recorded with CCD camera. Surface wettability, an important parameter that enables to know the surface interaction of the metal oxide with given electrolyte, was important measurement during this study. The surface of cobalt ferrite was hydrophilic as water contact angle was less than 90° . Water-droplet was spread equally in all directions instead of forming hilly-like dome once water

droplet fixed on it [24]. In the present case, cobalt ferrite film showed hydrophilic surface with $41 (\pm 2)^\circ$ contact angle measurement. Hydrophilic cobalt ferrite could be useful for increasing the redox reactions due to relatively strong interfacial contact between the nanoparticles electrode and electrolyte [25]. The optical absorbance spectrum as a function of the photon energy in the wavelength range of 350–800 nm for cobalt ferrite film deposited onto glass substrate is shown in Figure 2(b). The band gap energy was estimated by using Tauc relation [26]. The film exhibited a strong band edge around 400 nm.

The overall chemical stoichiometry of cobalt ferrite in film was obtained from the XPS analysis. In the XPS analysis, the samples are generally exposed to the monochromatic X-radiation and the properties of the inner shell electrons are probed. Figures 3(a), 3(b), and 3(c) present the XPS spectra of synthesized cobalt ferrite film for Co 2p, Fe 2p and O 1s core levels. The film was composed of Co, Fe, and O with corresponding binding energies of 779.18 (Co 2p_{3/2}), 794.60 (Co 2p_{1/2}), 710.40 (Fe 2p_{3/2}), 723.96 (Fe 2p_{1/2}), and 529.61 eV (O 1s), respectively, and the values presented here belong to Co²⁺, Fe³⁺, and O²⁻. The analysis of the Co 2p, Fe 2p, and O 1s peaks offered Co:Fe and Fe:O atomic ratios close to 1:2 and 1:2, respectively, as expected for

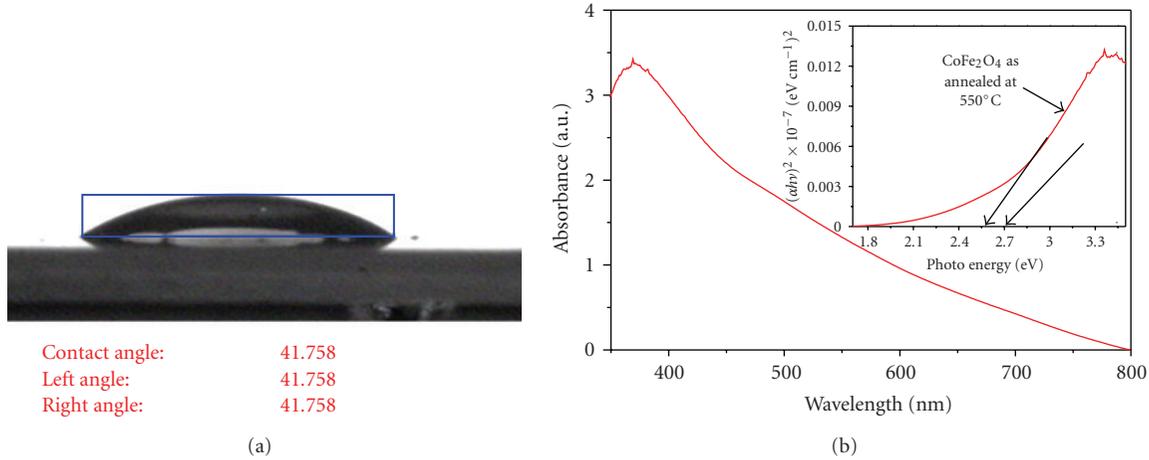
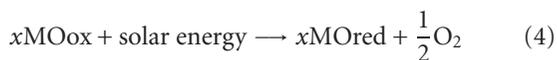


FIGURE 2: (a) Measurement of water contact angle, (b) Uv-Vis spectrum, and then corresponding direct band gap (inset, free arrow indicates the bulk band gap energy).

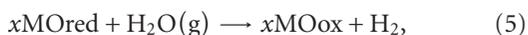
the stoichiometric composition of cobalt ferrite. The XPS measurement results were consistent to XRD observations, confirming the formation of single phase cobalt ferrite rather than mixed phases of CoO and Fe₂O₃. These observations suggest that annealing step played a key role during the process growth of cobalt ferrite nanoflakes. The nucleus of cobalt ferrite could be created by Co ions with the Fe³⁺ and O²⁻ on the surface of Fe₂O₄ as the Fe²⁺ could be easily interchanged into the Fe₂O₄ lattice by only electron transfer, Fe³⁺ might gather near the cobalt ferrite nucleus and became part of the ferrite lattice [27]. This could result the formation of Fe²⁺ rich phase left in the Fe₂O₄ among the reactions of the H₂O/CoFe₂O₄ system. To satisfy electronic neutrality, this Fe²⁺ rich phase could hold few O²⁻, so called as a cation-excess magnetite.

The cation-excess magnetite has the ability for sufficient water splitting in which some Fe²⁺ get oxidized to Fe³⁺ for H₂O/CoFe₂O₄ reaction operation. The production of pure hydrogen is based on splitting and regeneration rates. In general, the regeneration rate is temperature dependent. The most advantageous way to get such high temperature is exploitation of the photon energy of the sun which reduces the environmental utilization of polluting gases that does not cause immense and impact on the energetic and economics [3, 28]. The water-splitting process can produce H₂ gas, which is a promising solar fuel, and has the advantages that H₂ and O₂ gases can be separately recovered due to the two separated steps of the H₂ generation step and the O₂ releasing step. The two-step water-splitting processes that uses metal oxides, MO_{red}/MO_{ox}, as a redox pair utilizing the concentrated solar heat, can be presented using the following oxygen and hydrogen production steps:

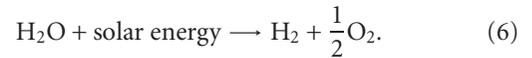
O₂ generation



H₂ generation



where MO_{red} and MO_{ox} denote the reduced and oxidized states, respectively. The net reaction is



Iron oxides have a higher possibility for utilization in the two-step water-splitting system, as they are oxides with different oxidation states [29]. The practical operating temperature for the O₂ releasing step of the cobalt ferrite was quite unknown. Lowering the operating temperature for the O₂ generation step was an important step for the practical production of solar hydrogen. While the gas phase (Co, O₂) formation from CoO by the solar thermochemical process has been extensively studied [30, 31], but that from the CoFe₂O₄ phase has not yet been reported. In Figure 3(d), the amount of hydrogen production rate (L/hr) with time showed the stability of the system wherein the water-splitting conversion was totally depending upon product characteristics. Cobalt ferrite film synthesized on stainless steel substrate using electrostatic spray pyrolysis showed comparable water-splitting activity when compared with zinc ferrite films (450 mL/hr) [32]. Water splitting rate, that is, hydrogen production rate was almost the same during the total time span. It is noteworthy that there was no chemical dissociation or degradation of photoanode, cobalt ferrite electrode during the oxidation-reduction process, which, in fact, was advantageous in long-run hydrogen production application due to good chemical stability of cobalt ferrite electrode.

4. Conclusions

In summary, the present work deals with an electrostatic synthesis of cobalt ferrite films and its sustainable hydrogen production application. Cobalt ferrite films, deposited onto both conducting steel and glass substrates, were uniform and free from the pinholes or cracks. Films obtained onto glass substrates were examined for structural, morphological, optical, and surface wettability characteristics whereas those

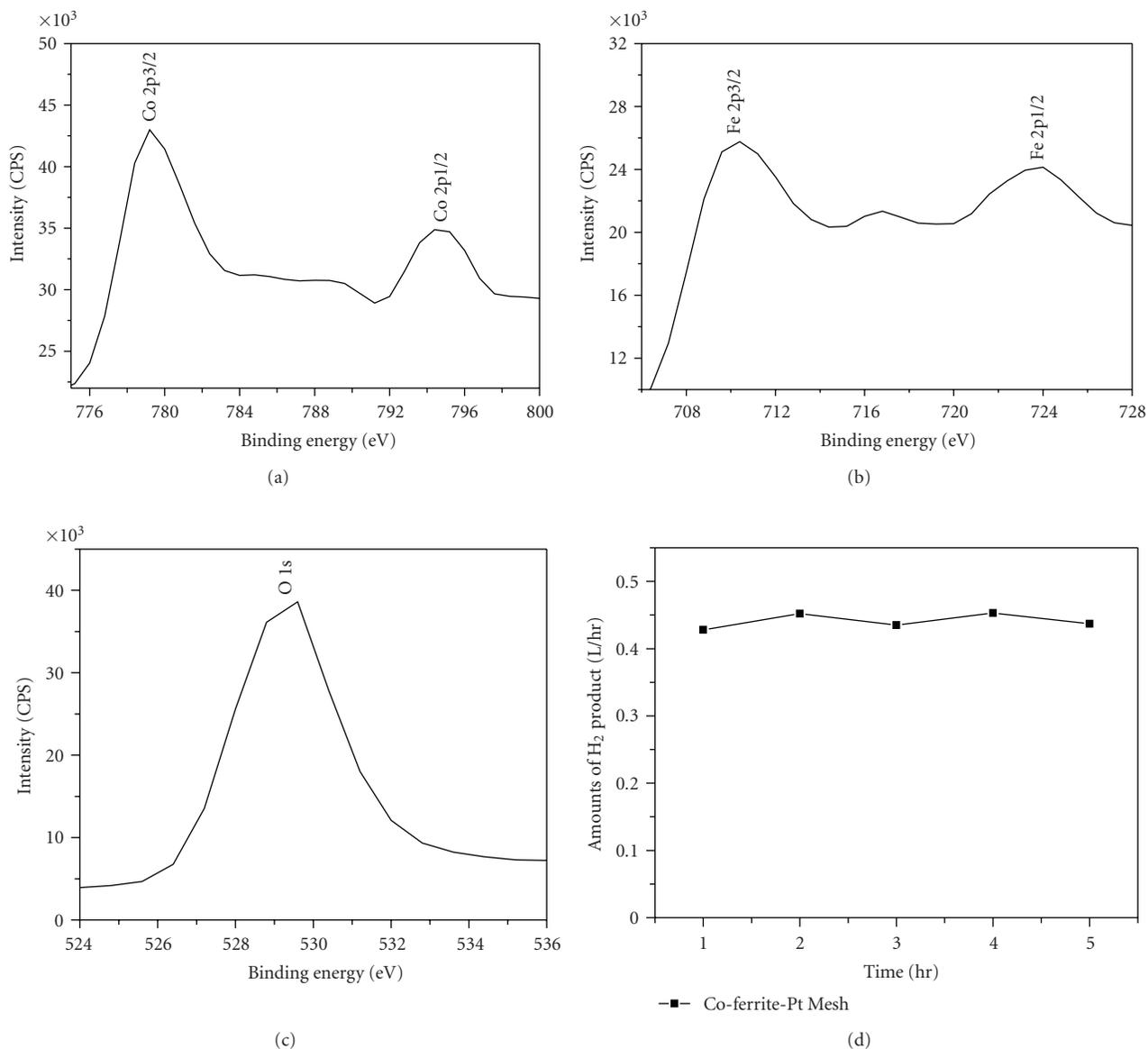


FIGURE 3: The XPS spectra of (a) Co 2p, (b) Fe 2p, (c) O 1s core levels, and (d) quantitative measurement of hydrogen production rate using cobaltite films.

onto stainless steel were used for hydrogen production activity application. The XRD and XPS measurements proved the formation of single phase of CoFe_2O_4 instead of mixed phased. The SEM image showed agglomeration of closely packed nanoflakes with a direct band gap energy of 2.57 eV and water contact angle of $41 (\pm 2)^\circ$. Finally, about 440 mL/hr hydrogen generation activity for more than 5 hr was obtained.

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