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# Photothermal Conversion Applications of the Transition Metal (Cu, Mn, Co, Cr, and Fe) Oxides with Spinel Structure

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## Abstract

The transition metal (Cu, Mn, Co, Cr, and Fe) oxides with spinel structure can be used as solar absorber materials due to their unique properties. Copper-based spinel ceramic pigments have been successfully prepared by sol-gel combustion method at low temperatures. Subsequently, spinel ceramic pigments have been employed to fabricate selective absorber paint coating by spraying-coating. The paint coating showed good spectral selectivity and thermal stability at low-to-mid temperature region. Spinel ceramic films have also been deposited on metal substrates by one dipping/annealing cycle. Spinel phase for single-layer ceramic film could be achieved at low annealing temperatures, and the single-layer ceramic film showed good spectral selectivity and benign thermal stability. Results presented here show that spinel compounds based on transition metal (Cu, Mn, Co, Cr, and Fe) oxides are promising materials for photothermal conversion applications.

**Keywords:** solar absorber coating, sol-gel combustion, spinel ceramic pigment, sol-gel dip-coating, spinel ceramic film, spectral selectivity

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## 1. Introduction

Spectrally selective absorber coatings have attracted more attention because of the ability of its absorber to convert solar radiation into heat. The high photothermal conversion efficiency is usually dependent on selectivity absorption of the coating, which is required to have a high solar absorbance ( $\alpha_s$ ) in the solar wavelength range (0.3–2.5  $\mu\text{m}$ ) and low

thermal emittance ( $\epsilon_T$ ) in infrared wavelength ranges (2.5–20  $\mu\text{m}$ ) [1]. During the last few decades, the transition metal (Cu, Mn, Co, Cr, and Fe) oxides with spinel structure have attracted significant attention due to their unique properties such as chemical inertness, high corrosion resistance, high mechanical strength, good thermal-shock resistance, and excellent optical and catalytic properties. This makes them very suitable for potential applications ranging from optics, electronics, magnetism, and catalysis to energy conversion and storage [2–4]. Furthermore, the existence of numerous spin-allowed electron transitions between partially filled d-orbitals contributes to their high absorption of radiation across the whole solar radiation spectrum [5]. These features endow these materials with promising application as solar selective absorber in solar-thermal energy conversion systems.

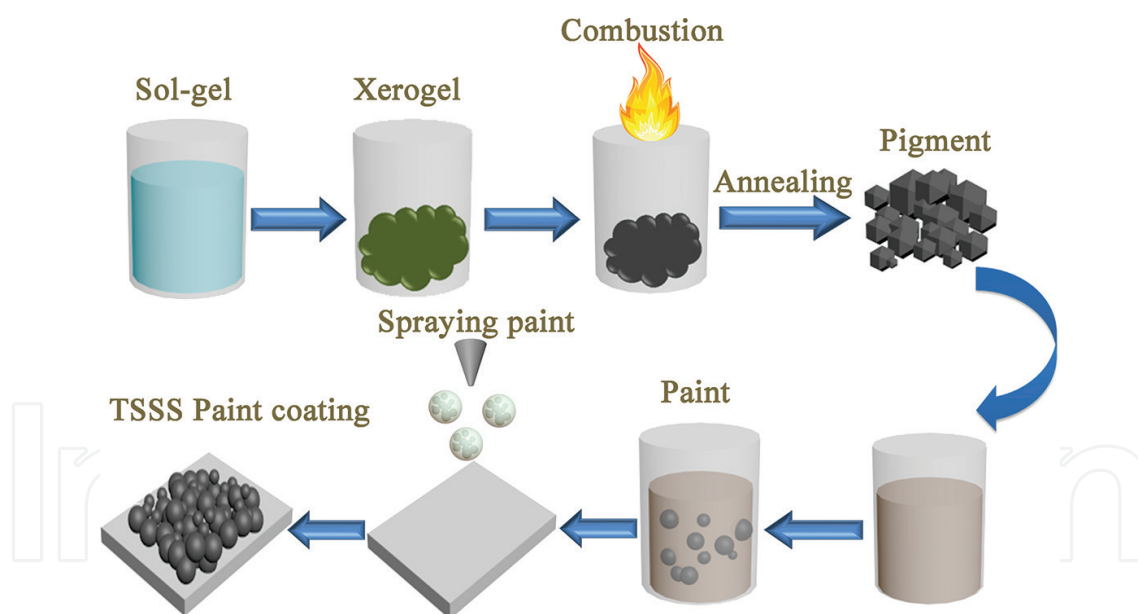
In recent years, several different approaches to the preparation of the spinel ceramic powders have been developed. For example, to prepare the spinel ceramic pigment, techniques of high temperature solid-state reaction, coprecipitation, sol-gel, hydrothermal synthesis, and thermal decomposition have been employed [6–8]. However, it is the major drawback of the above methods that the presence of heterogeneous products and requirement of high temperature and long durations result in tremendous wastage of energy. The sol-gel self-combustion method contributes to synthesize the better chemical homogeneity, small grain size, and high purity powder, which requires relatively low crystallization temperature [9]. In addition, crystallinity, size, and morphology of the particle, surface area, as well as other particular properties of the particles could be directed by tuning reaction parameters such as kinds of fuel, the mole ratio of fuel and oxidizer ratio, kinds and contents of the solvent, and the annealing temperature [10]. The as-prepared spinel ceramic powders are then utilized as solar-absorbing pigments to fabricate thickness-sensitive spectrally selective (TSSS) paint coatings by a convenient and economical spray-coating technology. Spray-coating technique is quick, easily adaptable to different coating solutions, and complex shapes can be coated. This makes it adoptable for an in-line process with minimum of material waste. These advantages with the spray-coating method suggest that this is the technique to prefer when scaling up the process.

Sol-gel techniques are promising synthesis methods for these spectral selectivity absorber coatings. The optical properties and durability of the spectral selectivity absorber coating can be easily controlled by fine-tuning relevant design parameters such as heating temperature or precursor concentrations in the synthesis process. In light of this, there are many knowledge gaps that need to be filled in the context of technicalities regarding the sol-gel processes and the optical and morphological characteristics of these coatings. The sol-gel processes are a soft chemistry technique where the precursors are generally in the form of a colloidal-based solution that eventually “transforms” into a widespread network of either discrete or continuously linked molecules [11]. Sol-gel techniques facilitate control of coating parameters such as absorber particle size, particle size distribution, homogeneity, chemical composition, and film thickness. The techniques also show good potential for scaling up to an industrial scale [12]. The most significant advantage of sol-gel over other established coating methods is its ability to tailor the microstructure of the deposited film at relatively low temperatures [13].

## 2. Experimental procedures

### 2.1. Synthesis of spinel ceramic pigments and spectrally selective paint coatings

Spinel ceramic pigments were synthesized by sol-gel self-combustion technique. Metal nitrate was first dissolved in an adequate amount of ultrapure water with the appropriate molar ratio. An appropriate amount of citric acid was then added into the prepared aqueous solution to chelate metal ion. After stirring for some time, the polyethylene glycol was added to the solution as an esterifying agent, which took part in chelation reaction. The mixture solution was adjusted to pH = 6.0–4.5 by slowly dropping ammonia and successively stirred to obtain a homogeneous solution. The prepared solution was subsequently heated for the adequate period of time to form the xerogel. Then, the xerogel was ignited in the atmosphere and burned in a self-combustion manner with rapid evolution of a large quantity of fume, yielding voluminous powders. Finally, the as-burned powders were annealed at different temperatures to obtain spinel ceramic pigments. Pigment dispersion was first prepared by mixing the pigments with the commercially corresponding binders and solvent in specific proportions and ground in a ball mill to form paint. Ultimately, the paint was sprayed on metal substrate to obtain paint coatings. A diagram for the sample preparation procedures is shown in **Figure 1**.



**Figure 1.** Spectrally selective paint coatings based on spinel ceramic pigments are fabricated [14].

### 2.2. Synthesis of spinel ceramic film for spectrally selective coatings

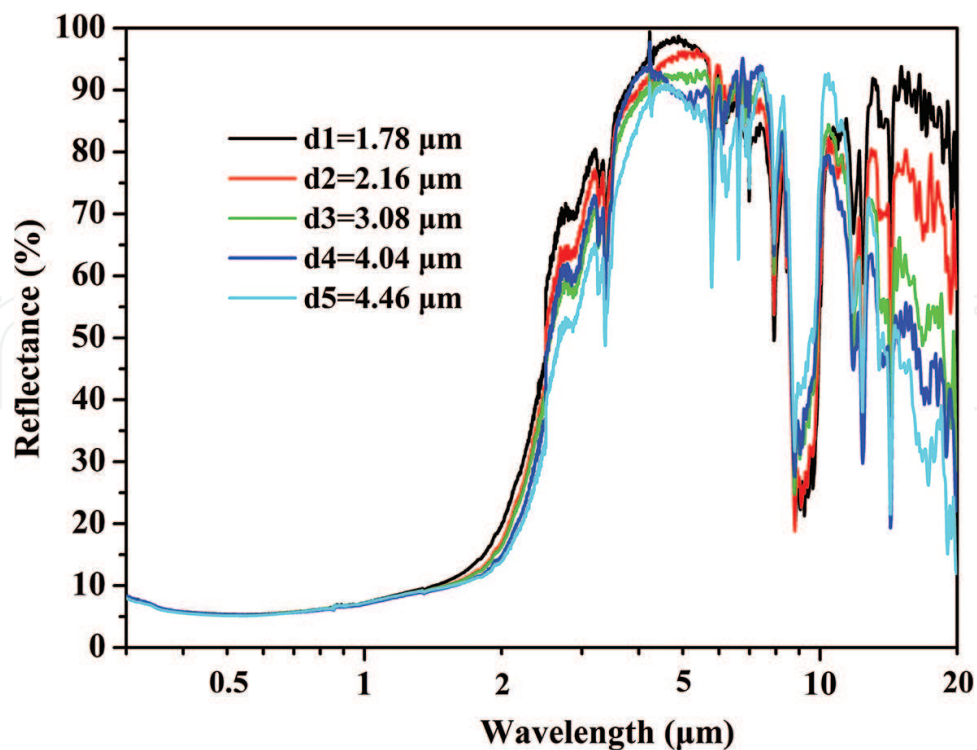
Metallic precursor sol was prepared by dissolving metal nitrates in absolute ethanol with suitable mole ratio of 1:1. This was followed by the addition of the citric acid as chelating agents. After stirring for a period of time, appropriate amount of polyethylene glycol was added

under magnetic stirring. The resulting solution was then used for coating deposited on metallic substrates by soakage method and subsequently heated to obtain xerogel films. The films were then air annealed in an oven at different temperatures.

### 3. Results and discussion

#### 3.1. Spectral selectivity paint coating based on $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ spinel ceramic pigments

$\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$  spinel ceramic pigments have been prepared by a facile and cost-effective sol-gel self-combustion method and annealed at the temperature ranging from 500 to 900°C for 1 h [14]. Ceramic pigments are utilized to fabricate the TSSS paint coatings by means of the convenient and practical spray-coating technique, and TSSS paint coatings based on pigments annealed at 700°C show solar absorbance of  $\alpha_s = 0.914\text{--}0.923$  and thermal emittance of  $\varepsilon_T = 0.244\text{--}0.357$ , which are calculated from the reflectance spectral shown in **Figure 2**. Furthermore, it is seen from reflectance spectral that the absorption edge is shifted toward longer wavelength, which means that the coating becomes thick and both of solar absorbance and thermal emittance are increased. As can be seen from **Figure 3**, the reflectance spectra show the marginal changes after the accelerated thermal test is carried out. Therefore, TSSS paint coating shows the thermal stability at the temperature of 227°C. Meanwhile, TSSS paint coatings exhibit no observable visual changes, and the performance criterion (PC) values reach the qualified requirement.



**Figure 2.** Reflectance spectra of paint coatings with different thickness based on spinel ceramic pigments [14].

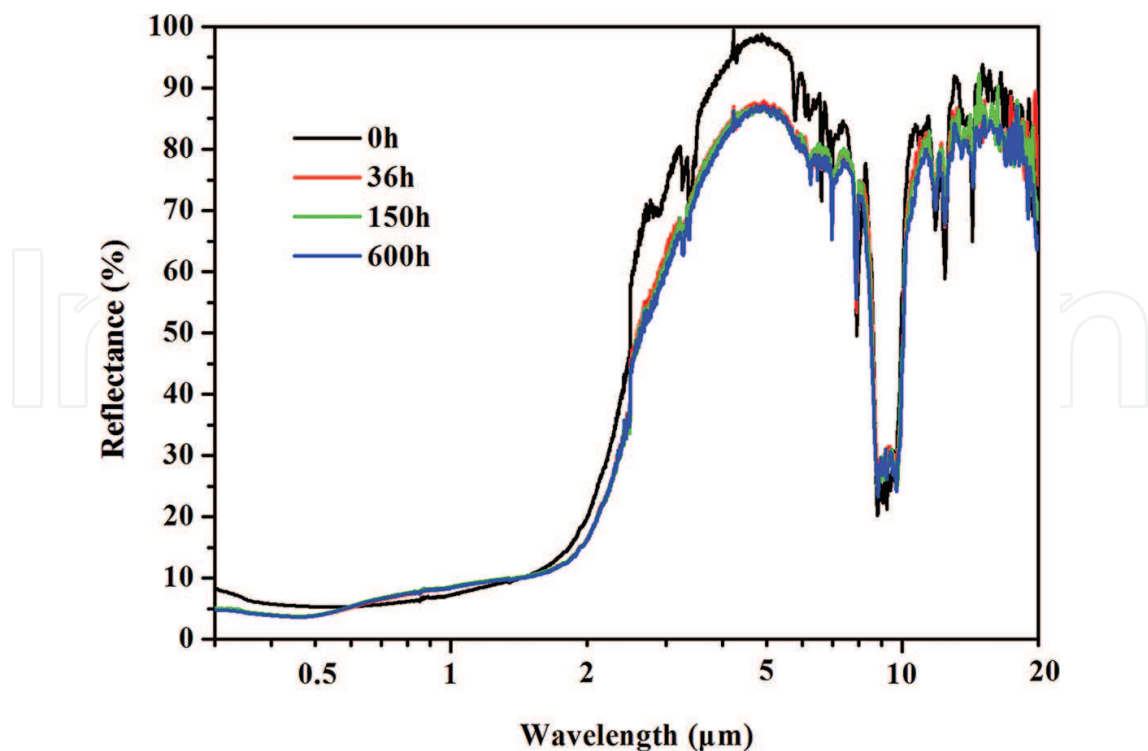
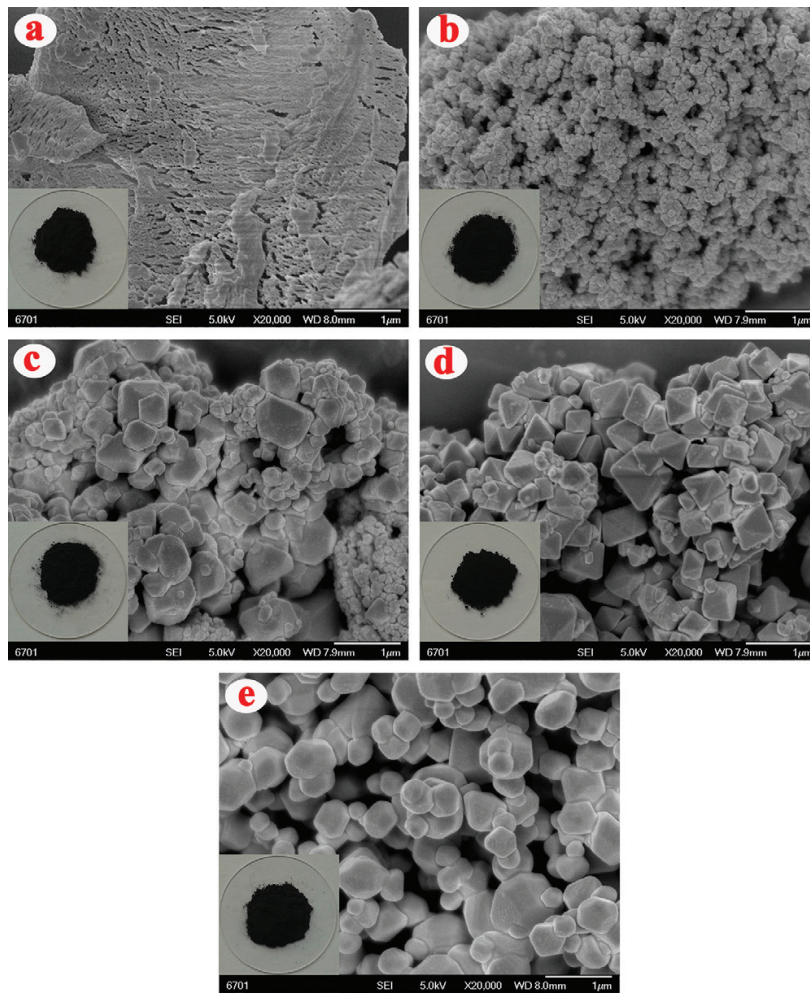


Figure 3. Reflectance spectra of paint coating subjected to thermal stability test [14].

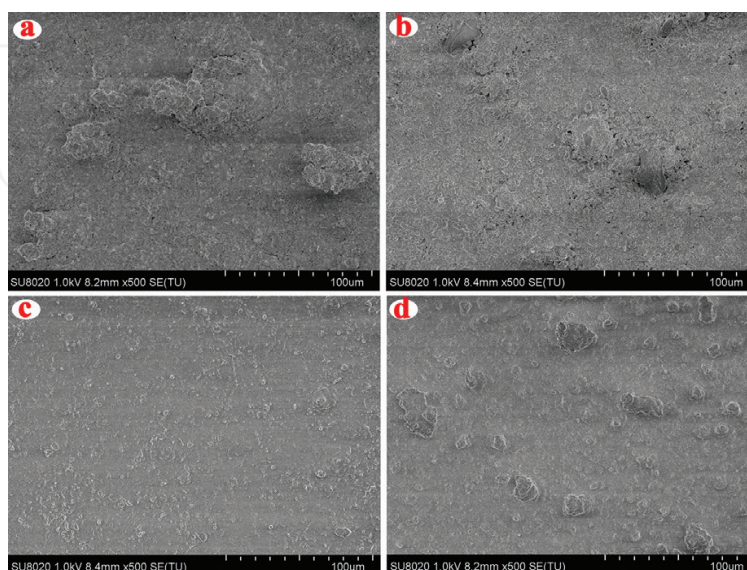
### 3.2. Spectral selectivity paint coating based on $\text{CuCr}_2\text{O}_4$ spinel ceramic pigments

Single-phase  $\text{CuCr}_2\text{O}_4$  spinel crystals are obtained after heat treatment of the as-burned powder at a low temperature ( $600^\circ\text{C}$ ) for 1 h, and the average crystallite size, morphology, and crystallinity of the  $\text{CuCr}_2\text{O}_4$  are greatly influenced by the annealing temperature. It can be seen from SEM images (Figure 4) that the as-burned powder has numerous voids and pores embedding into lamella. Increasing the annealing temperature, there are obvious flat face and clear edge appearing on the particles. Particles take on regular octahedron-shaped morphology and perfection of crystals at the annealing temperature of  $800^\circ\text{C}$  [15]. Comparison of TSSS paint coating based on metal oxide powder, the as-burned powder, and  $\text{CuCr}_2\text{O}_4$  spinel ceramic pigments as solar absorber pigments shows that TSSS paint coatings based on the spinel ceramic pigment exhibit the relative high solar selective absorption. The SEM representative morphologies of the similar thickness TSSS paint coatings ((a) sample A3 based on  $\text{CuO}$  and  $\text{Cr}_2\text{O}_3$ , (b) sample B4 based on as-burned pigment, (c) sample C4 based on pigment annealed at  $600^\circ\text{C}$ , and (d) sample D2 based on pigments annealed at  $800^\circ\text{C}$ ) are shown in Figure 5. It can be observed that the surface morphologies of all samples exhibit microscale bumps and protrusions, which are brought about particles agglomeration. For the TSSS paint coating, pigment particle agglomeration in the resin can cause uneven distribution and formation of clusters. The corresponding 3D surface profile images of samples are coincident with the surface morphologies shown by the SEM images. Water contact angles exhibited on sample surface can testify the different surface roughness (Figure 6). Furthermore, the TSSS paint coatings based on the spinel ceramic pigment show low surface roughness value and good hydrophobicity.





**Figure 4.** FE-SEM images and corresponding (inset) photographs of the powders: (a) the as-burned powder and powders annealed at (b) 600°C, (c) 700°C, (d) 800°C, and (e) 900°C for 1 h [15].



**Figure 5.** SEM images of paint coatings for (a) the sample A3, (b) the sample B4, (c) the sample C4, and (d) the sample D2 [15].

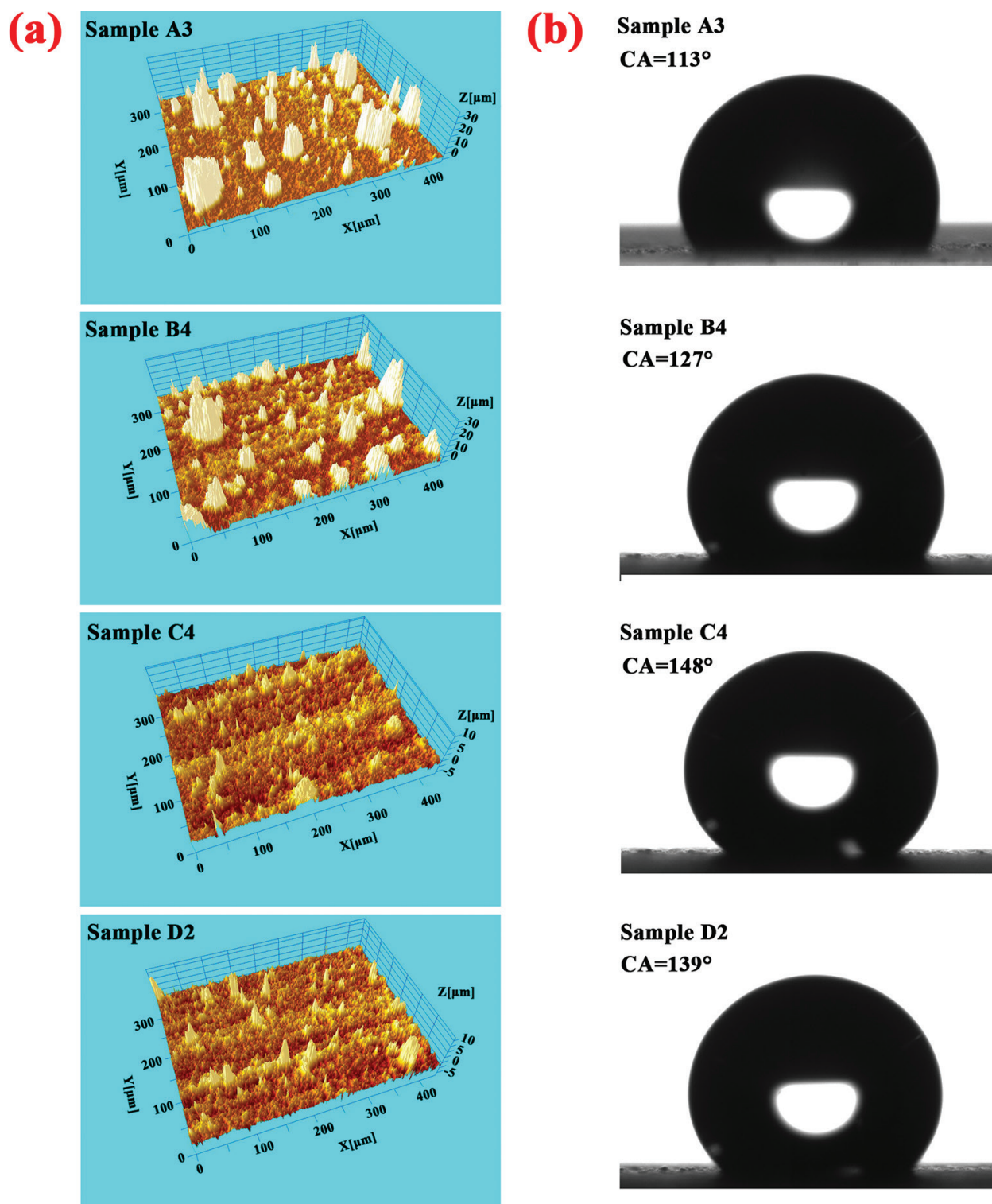


Figure 6. (a) 3D surface roughness profiles of samples and (b) images of water droplet on samples [15].

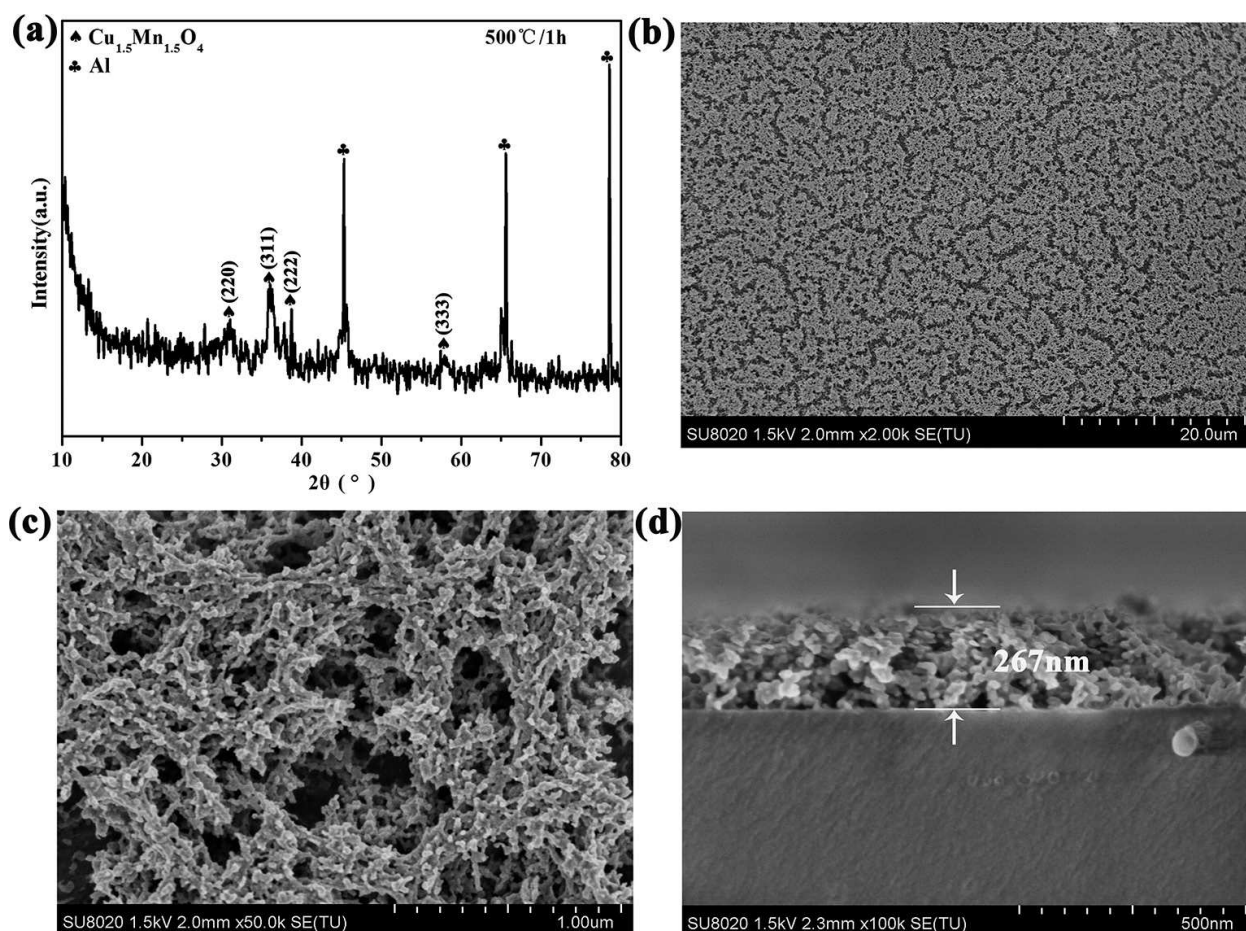
### 3.3. Spectral selectivity absorber coating based on $\text{CuMnO}_x$ spinel ceramic film

Spray-coating technique is quick, low-cost, easily adaptable to different coating solutions, and suitable for the establishment of a large-scale process, and there is a minimum of material waste. But as paint coatings are comparatively thicker and the organic binders also absorb in the thermal



IR range, these coatings usually suffer from the higher thermal emittance ( $\epsilon_{100} > 0.2$ ) [16]. Hence, the preparation and investigation of the spinel thin films by sol-gel route have attracted considerable attention. There is a great demand for low-cost and environmentally friendly techniques for synthesizing high-quality spectral selectivity absorber coatings. Such coatings are capable of absorbing most of the incoming solar radiation (high solar absorbance) without losing much of the thermal energy through reradiation from heated surface (low thermal emittance) [17].

The term spinel refers to a group of minerals, which crystallize in a cubic (isometric) crystal structure. Kaluza et al. [18] have succeeded in synthesizing  $\text{CuFeMnO}_4$  black film spinel solar absorber coating using sol-gel dip-coating and heat treatment at  $500^\circ\text{C}$ . Mn-acetate tetrahydrate, Cu-chloride, and Fe-chloride hexahydrate precursors are used in a molar ratio of 3:3:1, respectively. To protect the spinel from corrosion, a 3-aminopropyltriethoxysilane (3-APTES) silica precursor is added to the Cu, Mn, and Fe sol precursors with a molar ratio of (Mn-Cu-Fe): silica = 1:1. Analytical results show that the films consist of two layers: the lower is amorphous  $\text{SiO}_2$ , and the upper is a spinel having the composition of  $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$ . The films exhibit solar absorbance values of around  $\alpha_s = 0.6$  and thermal emittance values of  $\epsilon = 0.29\text{--}0.39$ . Copper-cobalt oxide thin coatings have been deposited on highly infrared-reflecting aluminum substrate via a four-dipping/annealing-cycle sol-gel dip-coating route [19]. Nevertheless, the high annealing temperature and long annealing time would severely wreck the mechanical strength of aluminum substrate. Furthermore, the low solar absorptance ( $\alpha_s = 0.834$ ) was merely obtained. He and Chen [5] added a complexing agent and an esterifying agent to fabricate the precursor sol, and thus  $\text{CuCoMnO}_x$  coatings were deposited on aluminum substrate with a  $\alpha_s$  value up to 0.93. Mahallawy et al. [17] also successfully synthesized  $\text{CuCoMnO}_x$  coatings on aluminum and copper substrates by sol-gel dip-coating method.  $\text{CuMnO}_x$  monolayer coating,  $\text{CuMnO}_x/\text{SiO}_2$  two-layer coating, and  $\text{CuMnSiO}_x/\text{CuMnSiO}_x/\text{SiO}_2$  three-layer coating have been fabricated [20], which provide good design strategies for ceramic spectral selectivity (CSS) coatings.  $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ -based CSS coating is deposited on aluminum substrate using sol-gel dip-coating method from a stable metal nitrate precursor sol [21]. The Chelating agent citric acid, acting as a reducing agent simultaneously in the exothermic redox reaction, lowered the annealing temperature required by the formation of crystalline  $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ . By optimizing the withdrawal rates and annealing temperatures, coating with optical parameter values as good as  $\alpha_s = 0.876$  and  $\epsilon_{100} = 0.057$  is achieved after only one dipping/annealing cycle. Furthermore, the recycling experiment should be implemented to certify the reproducibility and stability of the metallic precursor sol. After reserved for 20 days, the precursor sol was deposited on aluminum substrate to obtain the CSS coating. **Figure 7** shows the typical x-ray diffraction (XRD) patterns and field emission scanning electron microscopy (FE-SEM) images of the CSS coating, which is deposited at 120 mm/min and annealed at  $500^\circ\text{C}$  for 1 h after recycling experiment. As can be seen from the XRD diffraction spectra, the diffraction peaks of the sample at  $2\theta$  values of  $30.46^\circ$ ,  $35.85^\circ$ ,  $37.52^\circ$ , and  $57.82^\circ$  correspond to (2 2 0), (3 1 1), (2 2 2), and (3 3 3) crystal planes of cubic spinel structure  $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ . The morphology of  $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$  coating indicates the presence of jagged and uneven pores, which can be attributed to the liberation of abundant  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{NO}_2$ , and other  $\text{NO}_x$  during the heat treating process. One interesting thing worthy to discuss is that the pores are conducive to enhance solar absorber of the CSS coatings. The pores look like light traps where the reflected light can be refracted consecutively and enters into the absorber layer again.



**Figure 7.** The XRD patterns and FE-SEM images of the solar selective absorber coating deposited on aluminum substrate after recycling experiment [21].

## 4. Conclusions

Black-colored transition metal oxides with spinel structure are easy to synthesize via sol-gel methods, and most of them show the high spectral selectivity and thermal stability. However, most of the coatings based on those materials are relatively lower spectral selectivity than the commercial absorber surfaces. More explorations on precursor's combinations, absorber stack configuration and compositions, as well as the application of superior antireflection layer are needed to improve their spectral selectivity. Furthermore, there are still problems associated with the reproducibility of the sol, and few studies have been done on this type of absorber coatings using sol-gel methods. Some problems such as the border effect and the heterogeneity of the film, which have a negative effect on the practical application of spinel films, arise when sol-gel dip-coating method is used for large-scale deposition. The use of highly soluble raw materials and the avoidance of compounds that easily settle in precursor's preparation are the robust ways to solve the reproducibility problem. Additionally, other pertinent factors such as the thickness of silica (especially if used as a matrix), abrasion, corrosion resistance, and the durability of the spinel absorber film should also be examined more extensively in future research.

## Author details

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