Progress in Materials Science 88 (2017) 281–324

Contents lists available at ScienceDirect

Progress in Materials Science

journal homepage: www.elsevier.com/locate/pmatsci

Recent progress in chromogenic research of tungsten oxides towards energy-related applications

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ARTICLE INFO

Article history:
Received 16 March 2017
Accepted 6 April 2017
Available online 8 April 2017

Keywords:
Tungsten oxide
Chromism
Synthesis
Energy-related applications
Review

ABSTRACT

This paper summarises the recent research on the chromogenic performance of a unique class of nanomaterials, tungsten oxide (WO_x), and highlights their potential applications in energy-related areas. WO_x exhibits a wealthy range of interesting chromogenic characteristics and has recently shown great potentials towards practical energy-related applications. Recent developments in nano-sized WO_x synthesis have made these potentials even more appealing to engineers, bringing in immense challenges in research and equally tremendous opportunities for applications. The potential smart window/glazing applications for energy saving, the thermochromic coating attractions in solar-thermal conversion, and the highly efficient gas-chromic applications as effective hydrogen sensors during energy generation and transportation, all point to current and future energy-related research areas and demand further efforts to achieve thorough understandings prior to materialisation. Pursuing for understandings of the relationship loop of the chemical composition-physical structure-colouration behaviour of these WO_x-based nanomaterials will be first summarised. The mechanisms for different types of chromism of these materials will then be presented, and factors affecting colouration efficiencies will be analysed. The synthesis, processing and post-treatment techniques associated with their chromogenic performance will be discussed. The current technical challenges and future potentials of this unique WO_x in applications will be discussed throughout the text.
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http://dx.doi.org/10.1016/j.pmatsci.2017.04.003
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1. Introduction

Over the past decade, immense research attentions have been focused on the broad area of sustainability, typically the high capability of energy generation, efficient energy transportation, reduced energy consumption, and friendly impact to environment. A wide range of associated technologies have thus been developed in an effort to fulfil the potentials for different applications in diverse energy-related sectors. For example, research and developments towards reliable and highly sensitive gas sensors [1,2], photocatalysis [3], and solar cells [4,5] in energy generation applications; ion lithium batteries [6] for energy storage, and field emission [7], flat-panel display, optical memory, etc. for low energy consumption devices, have all made significant progresses. As a semiconducting material in bulk form, nanoscale tungsten oxides (WO_x) have emerged as an important candidate for further development due to their unique and wealthy natures. Their excellent chromogenic performances, huge range of compositional combinations and vast crystalline structures from amorphous to different crystallised forms have made them particularly attractive. The chromogenic behaviour of materials is originated from and determined by their optical properties (absorbance, transmittance and reflectance), which allows them to switch between a coloured and a bleached state in response to various external conditions applied. Applying the coloured and bleached states to multifunctional smart devices will lead to improved sensitivities and efficiencies in corresponding energy-related applications. The potentials offered by this unique class of materials are thus significant. Such complexity and promising potentials of the WO_x towards application therefore demand and deserve special research attentions.

Amongst many traditional chromogenic materials, WO_x ($2 \le x \le 3$) have been intensively studied because of their proven potentials for outstanding performance. They exhibit excellent cyclic stability, high Colouration Efficiency (CE), good memory and high contrast ratios, compared with other transition metal oxides [8]. CE is defined as the ratio of change (between transparent and coloured state) of Optical Density (OD) to the inserted charges per unit, which can be expressed as: $CE = \frac{\Delta(OD)}{\Delta Q}$ [9]. A greater CE means a better transmittance variation per unit charge [10]. Four types of WO_x have been reported as attractive colouration media with high stability: pure stoichiometric WO_3 (yellow), non-stoichiometric $W_{20}O_{58}/WO_{2.9}$ (dark blue), $W_{18}O_{49}/WO_{2.72}$ (violet), and WO_2 (chocolate brown) [11]. One basic principle of the colouration process for WO_x is the result of the insertion/extraction of electrons and charges balancing small ions such as H^+, Li^+, K^+ and Na^+. These ions located at the W sites alter the inter-valence of the tungsten ion transition from W^{6+} to W^{5+}. The other principle is the small polaron absorption. The abundant crystalline structures, and especially the almost countless compositional combinations in WO_x, which are all associated with their chromogenic behaviour, make them very unique. Meanwhile, such characteristics bring in immense complexities in their research, in order to achieve deeper understandings and draw a full picture towards applications.

Promoted by the latest nanomaterials advances, chromogenic materials have recently been synthesized into nanoparticles/nanostructures with significantly decreased sizes and properly tuned morphologies. With an appropriate crystalline phase, the nanostructured materials have enhanced the surface to volume ratios, which allow for more surface areas to be involved in reactions [12]. Moreover, the reduced geometrical sizes could shorten the length of ion diffusion paths and make the ion diffusion more effective than those in bulk forms, therefore nanostructures are beneficial for improving the responding time of chromic devices [13]. Thereby, the recent studies of exploring nanomaterials towards advanced chromic devices (such as enhanced durability, fast insertion kinetics, and superior performance) have resulted in new physical and chemical understandings. This leads to another level of challenges and opportunities.

To take advantage of these new achievements, a timely review will allow to keep pace with the rapid developments in this field, and to efficiently develop the WO_x into advanced technologies in emerging research areas. In particular, the wealthy chromogenic characteristics of this class of WO_x materials, offer highly desirable performance as smart or intelligent multifunctional windows/coatings/sensors, which could play an important role in direct energy saving and indirect energy

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