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Synthesis and Engineering of Nanostructured Catalysts for Enhanced Hydrogen Evolution Reaction

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General introduction



General Introduction

A new clean energy era is within our reach **[1]**.

Fossil fuels (FFs) continue to dominate the global energy landscape, supplying approximately 82% of the world's primary energy demand according to the 2022 BP Statistical Review of World Energy **[2]**. However, this heavy dependence on coal, oil, and natural gas comes at a substantial environmental cost, as fossil fuels account for nearly 73% of global greenhouse gas (GHG) emissions **[3]**. The continuous rise in these emissions has accelerated climate change, leading to severe environmental, economic, and social consequences worldwide. Consequently, the urgent need to reduce carbon emissions and ensure long-term energy security has driven growing interest in sustainable and clean energy technologies. In this context, the transition from fossil fuel-based systems to renewable and environmentally friendly energy sources has become one of the most critical global priorities for achieving a sustainable future and mitigating the impacts of climate change **[2]**.

At the center of this transition is green hydrogen, a key energy resource whose role is increasingly recognized in building a sustainable future **[4]**.

Hydrogen is widely recognized as an ideal green fuel because it produces zero carbon emissions and has a high combustion energy density **[5]**. Among the various hydrogen production methods, electrochemical water splitting is considered one of the most promising, as it enables hydrogen generation from abundant water resources through the hydrogen evolution reaction (HER) **[6]**, **[7]**, **[8]**. To date, noble metal-based materials are still regarded as the best electrocatalysts for HER; however, their large-scale application remains limited by their low abundance, high cost, and limited stability. Consequently, developing electrocatalysts based on non-precious metals that offer high activity, strong stability, and low cost remains a key challenge in advancing the green hydrogen industry **[9]**.

Transition metal oxides, particularly spinel-type AB_2O_4, are considered promising non-precious catalysts owing to their adjustable electronic structures, wide compositional flexibility, and strong stability in alkaline and neutral environments**[10]**, **[11]**, **[12]**.

Based on these properties, $CoMn_2O_4$ and $ZnMn_2O_4$ were selected as earth-abundant electrocatalysts for the hydrogen evolution reaction (HER), owing to their reported good catalytic activity and stability in alkaline media **[13]**, **[14]**.

In the present study, the materials were prepared by combining two complementary synthesis techniques, namely co-precipitation and ball milling. Co-precipitation is a mild synthesis method that enables the formation of nanoparticles through the precipitation of

insoluble compounds from solutions containing metal cations **[15]**. Ball milling is a mechanochemical technique used to synthesize various materials by grinding solid precursors in milling vessels **[16]**. This process relies on the collision of milling balls, generating frictional forces between the balls and the walls of the vessel, ultimately leading to the reduction of particle size down to the nanoscale **[17]**.

A variety of techniques were used to characterize the prepared materials and investigate their properties, including X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and UV–Visible spectroscopy. The electrochemical performance was evaluated using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). In addition, photocurrent response and Mott–Schottky measurements were performed to study the semiconductor properties. Stability tests and light/dark LSV measurements were also conducted in order to assess the electrochemical and photoelectrochemical performance of the prepared materials.

Among all samples, the $CoMn_2O_4/ZnMn_2O_4$ heterojunction synthesized via ball milling showed the best performance and the most promising results.

Abstract:

Spinel-type materials have attracted significant attention for photo-electrochemical and catalytic energy conversion applications. In this study, $CoMn_2O_4$ and $ZnMn_2O_4$ spinel oxides were synthesized via the co-precipitation method, and $CoMn_2O_4/ZnMn_2O_4$ heterojunction electrodes were fabricated through co-precipitation and ball milling approach. The structural, morphological, optical, and electrochemical properties of the prepared materials were systematically investigated.

X-ray diffraction (XRD) analysis of as-prepared electrodes confirms the formation of the spinel phases, while X-ray fluorescence (XRF) measurement demonstrated their elemental composition. Scanning electron microscopy (SEM) revealed a porous nanostructure with improved interfacial contact between the constituent phases. UV–Visible analysis showed band gap energies of 2.63 eV for $CoMn_2O_4$ and 2.35 eV for $ZnMn_2O_4$, indicating good visible-light absorption.

Electrochemical investigations demonstrated that the $CoMn_2O_4/ZnMn_2O_4$ heterojunction exhibited enhanced charge-transfer properties, larger electrochemically active surface area, and superior hydrogen evolution reaction (HER) activity compared to the pristine spinel oxides. The improved performance was attributed to efficient charge separation and reduced electron–hole recombination at the heterointerface. Among all samples, the ball-milled $CoMn_2O_4/ZnMn_2O_4$ heterojunction showed the best electrochemical performance, highlighting ball milling as a simple and effective strategy for developing high-performance spinel-based materials for sustainable hydrogen production.

Keywords: $CoMn_2O_4/ZnMn_2O_4$ spinels, Heterojunction, Ball milling, Hydrogen evolution reaction (HER), Electrocatalysis.

Résumé :

Les matériaux de type spinelle suscitent un intérêt croissant pour les applications de conversion photoélectrochimique et catalytique de l'énergie. Dans ce travail, les oxydes spinelles $CoMn_2O_4$ et $ZnMn_2O_4$ ont été synthétisés par la méthode de coprécipitation, puis une hétérojonction $CoMn_2O_4/ZnMn_2O_4$ a été élaborée par broyage mécanique (ball milling). Les propriétés structurales, morphologiques, optiques et électrochimiques des matériaux obtenus ont été étudiées de manière systématique.

Les analyses par diffraction des rayons X (DRX) ont confirmé la formation des phases spinelles et de l'hétérojonction, tandis que la fluorescence X (XRF) a vérifié leur composition élémentaire. Les observations MEB ont révélé une morphologie nanostructurée poreuse ainsi qu'un meilleur contact interfacial entre les phases constitutives. L'analyse UV-Visible a montré des énergies de bande interdite de 2,63 eV pour $CoMn_2O_4$ et de 2,35 eV pour $ZnMn_2O_4$, indiquant une bonne absorption dans le domaine visible.

Les mesures électrochimiques ont démontré que l'hétérojonction $CoMn_2O_4/ZnMn_2O_4$ présente un transfert de charge amélioré, une surface électrochimiquement active plus élevée et une meilleure activité pour la réaction de dégagement de l'hydrogène (HER) par rapport aux oxydes spinelles individuels. Cette amélioration est attribuée à une séparation plus efficace des charges et à une réduction de la recombinaison électron-trou à l'interface de l'hétérojonction.

Parmi tous les échantillons étudiés, l'hétérojonction $CoMn_2O_4/ZnMn_2O_4$ obtenue par broyage mécanique a présenté les meilleures performances électrochimiques, démontrant que le ball milling constitue une méthode simple et efficace pour développer des matériaux spinelles performants destinés à la production durable d'hydrogène.

Mots-clés: Spinels $CoMn_2O_4$ / $ZnMn_2O_4$, Hétérojonction, Ball milling, Réaction HER Électrocatalyse.

الملخص:

تحظى المواد ذات البنية الإسبينيلية باهتمام متزايد في تطبيقات التحويل الكهروضوئي والتحفيز الطاقوي. في هذا العمل، تم تحضير أكاسيد الإسبينيل $CoMn_2O_4$ و $ZnMn_2O_4$باستعمال طريقة الترسيب المشترك، ثم تم تصنيع وصلة غير متجانسة $CoMn_2O_4/ZnMn_2O_4$ بواسطة الطحن الكروي .(Ball Milling) وقد تمت دراسة الخصائص البنيوية والمورفولوجية والبصرية والكهروكيميائية للمواد المحضرة بشكل منهجي.

أكدت تحاليل حيود الأشعة السينية (XRD) تشكل أطوار الإسبينيل والوصلة غير المتجانسة، في حين أكدت تقنية التألق بالأشعة السينية (XRF) التركيب العنصري للعينات. كما أظهرت صور المجهر الإلكتروني الماسح (SEM) بنية نانوية مسامية وتحسنًا في التلامس البيني بين الأطوار المكونة. وبينت دراسة UV-Visible أن فجوة الطاقة بلغت 2.63 إلكترون فولت بالنسبة لـ $CoMn_2O_4$ و2.35 إلكترون فولت بالنسبة لـ$ZnMn_2O_4$ ، مما يدل على قدرة جيدة على امتصاص الضوء المرئي.

أظهرت القياسات الكهروكيميائية أن الوصلة غير المتجانسة $CoMn_2O_4/ZnMn_2O_4$ تمتلك خصائص أفضل لنقل الشحنات، ومساحة سطحية كهروكيميائية فعالة أكبر، ونشاطًا أعلى تجاه تفاعل إنتاج الهيدروجين (HER) مقارنة بالأكاسيد الإسبينيلية المنفردة. ويُعزى هذا التحسن إلى الكفاءة العالية في فصل الشحنات وتقليل إعادة اتحاد أزواج الإلكترون–الفجوة عند الواجهة البينية.

ومن بين جميع العينات المدروسة، أظهرت الوصلة غير المتجانسة $CoMn_2O_4/ZnMn_2O_4$ المحضرة بالطحن الكروي أفضل أداء كهروكيميائي، مما يبرز فعالية هذه الطريقة البسيطة والقابلة للتطبيق في تطوير مواد إسبينيلية عالية الأداء لإنتاج الهيدروجين المستدام.

الكلمات المفتاحية:

الإسبينيلات $CoMn_2O_4$ / $ZnMn_2O_4$ ،وصلة غير متجانسة الطحن الكروي، تفاعل إنتاج الهيدروجين، التحفيز الكهربائي الكيميائي.