Physics Letters A ••• (••••) ••••••

[m5G; v1.261; Prn:23/10/2019; 11:40] P.1 (1-8)



1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

23

24

25

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

61

62

63

64

65

66

Contents lists available at ScienceDirect **Physics Letters A** 

# Au-MoO<sub>x</sub> nanoparticles for LSPR hydrogen detection prepared by a facile anodizing method

M.A. Hosseini, M. Ranjbar\*, M. Sajadi

Department of Physics, Isfahan University of Technology, Isfahan, 8415683111, Iran

ARTICLE INFO ABSTRACT

Article history: 22 Received 8 October 2019 Received in revised form 16 October 2019 Accepted 19 October 2019 Available online xxxx Communicated by M. Wu 26 Kevwords:

Localized surface plasmon resonance Anodizing MoO<sub>x</sub> nanosheets Au NPs Hydrogen sensor

## 1. Introduction

The plasmonic properties exhibited by nanostructured systems have been intensively explored theoretically and experimentally, to be utilized from medical applications to enhanced spectroscopy and sensing [1-4]. Such advances in the plasmonic science are due to the strong optical absorption and scattering as well as the substitution of strong fields into these nanoscale systems [5]. The optical or plasmonic properties of these materials depend strongly on the type of constituent material, the dielectric properties of the environment in which they are located and their shape and size. Perhaps the most widely studied metals so far are gold, silver, and copper nanosystems which typically absorb light in the visible region [6-8]. The infrared region absorption occurs if their longitudinal modes are also activated, in which the shape of the particles must be elongated (nanorods and nanowires) [9].

Besides the noble metal plasmonic materials, in recent years, continuous researches on doped semiconductor materials have been conducted to achieve metal-like behavior and plasmonic resonance absorption at NIR wavelength ranges that are not easily obtainable by traditional noble metal nanoparticles [10-15]. In this category of plasmonic materials, copper sulfides and selenides, as well as molybdenum sulfides and oxides, are a new class of semiconductor plasmonic materials [16-23]. The defect

Corresponding author.

E-mail address: ranjbar@cc.iut.ac.ir (M. Ranjbar).

https://doi.org/10.1016/j.physleta.2019.126079

0375-9601/© 2019 Elsevier B.V. All rights reserved.

Nowadays, the plasmonic properties of defective transition metal oxides, have attracted great attention in the sensing and catalyst applications. The aim of this paper is to fabricate plasmonic Au-MoO<sub>x</sub> nanoparticles (NPs) using a facile anodizing in liquid approach to be used as localized surface plasmon resonance (LSPR) hydrogen sensor. Firstly, dark blue  $MoO_x$  nanosheets with a strong NIR (700-800 nm) LSPR band were obtained. The Au-MoO<sub>x</sub> NPs (Au size=5-7 nm) were then obtained by adding a gold cation into the blue  $MoO_x$  liquid base. Thanks to the catalytic properties of Au NP, this system exhibited LSPR hydrogen sensing ability where the LSPR variations allowed us to detect hydrogen in the 0-3% concentration range with a good linearity and possible many data points.

© 2019 Elsevier B.V. All rights reserved.

in these components is easily controlled by a stoichiometric ratio. By changing this ratio, these materials create a large number of vacancies, causing a large number of charge carriers and creating a quasimetallic behavior of the material. The doped plasmonic semiconductors have presented several advantages over the conventional noble metal plasmonic systems. In particular, plasmon resonance tuning is possible by introducing deficiency or doping leading to increase the carrier concentration at conduction band of semiconductors so as to tune the wavelength at which LSPRs are observed [24,25]. It has been observed that two-dimensional materials can show unique electronic and optical properties when the number of planes is reduced, due to changes in their electronic band structure [26-34]. As a representative, 2D molybdenum oxide nanocrystals emerged recently as a plasmonic martial candidate which have been widely investigated due to their promising potential applications in optical sensors, electrochemical storage devices, photochromic, electrochromic, thermochromic, catalysts and plasmonic [35–40]. The penetration of cations from the first group of the periodic table of elements, especially H<sup>+</sup> and Li<sup>+</sup>, into the Mo oxide lattice creates oxygen vacancies that causes the release of free charge carriers. These carriers exhibit collective plasmonic oscillations in the NIR range [10,41].

In the following, we present a brief review on LSPR of  $MoO_x$ . Intense and tunable LSPR absorption in a wide range was reported for  $MoO_{3-x}$  nanosheets by Cheng et al. [42]. They also found a LSPR based highly efficient hydrogen photo-generation from ammonia borane. Plasmonic MoO<sub>3-x</sub>@MoO<sub>3</sub> two-dimensional nanostructures have been used for surface enhanced Raman scattering

128

129

130

131

132

(SERS) chemical detection with an outstanding sensitivity due to 1 2 enhanced electromagnetic field by the plasmonic properties of 3  $MoO_{3-x}$  core [22]. Solvothermal synthesized  $MoO_{3-x}$  nanosheets with tunable LSPR wavelength and excellent photo-degradation performance has reported by Liu et al. [19]. Li et al. have reported hydrothermally obtained orthorhombic MoO<sub>3-x</sub> nanorods with ex-7 cellent photochromic conversion properties with solar modulation 8 ability due to the LSPR absorption from NIR to visible range suita able for energy saving applications [43]. Pd-MoO<sub>3-x</sub> plasmonic hy-10 brid nanoparticles have been developed for enhanced catalysis of 11 hydrogen evolution from ammonia borane hydrolysis [44].

12 Hydrogen is a clean, renewable energy source that can replace 13 oil in the future [45-48]. On the other hand, hydrogen is highly 14 explosive so its efficient detection is essential for safe and success-15 ful utilization of the hydrogen-based energy. Among the various 16 gas sensor platforms, optical gas sensors based on electromagnetic 17 loss properties are essentially safe, electrical contact free, low-cost 18 and easy to use. In fact, electromagnetic loss in semiconductor has 19 more than one source, which involves loss of inter-band transi-20 tions and loss due to free electrons oscillations. The former usually 21 occurs at higher frequencies, but the absorption at lower frequen-22 cies (such as NIR region) is mostly due to the resonance of free 23 electrons known as plasmonic absorption [24]. Perhaps the most 24 advantageous aspect of plasmonic oscillation is sensitivity to envi-25 ronment dielectric constants and the doping level, which creates 26 an ultra-high sensitivity for sensing any change in environment 27 properties and this is why plasmonic materials have been con-28 sidered for sensing at low concentrations of an analyte. However, 29 the doping level in high-valence metal oxides such as WO<sub>3</sub> and 30 MoO<sub>3</sub> is sensitive to the injection of group I elements known as 31 electrochromic effect, among which, hydrogen is only a gas which 32 is called gasochromic. Due to these advantages, optical hydrogen 33 sensors based on the gasochromic properties of WO<sub>3</sub> [46,49–53] 34 and MoO<sub>3</sub> [23,54–56] nanostructures have been investigated. How-35 ever, the LSPR features of hydrogen-doped  $WO_3$  or  $MoO_3$  have not 36 been addressed in these papers, and this has been attempted to 37 be described on the basis of small polaron or inter-band transition 38 models.

39 Recently, we have reported palladium modified MoO<sub>3</sub> nano-40 sheets [56-58] and observed an excellent ability towards optical 41 hydrogen detection. We have discovered there that the defective 42 MoO<sub>x</sub> nanosheets could serve as a mild reductant to convert pal-43 ladium salt to Pd NPs. In fact, high density oxygen vacancies at 44 edge-site of two-dimensional MoO<sub>x</sub> are responsible for reduction 45 without need to any extra reducing agents or stabilizing molecules 46 [20]. As we reported previously, through the redox reaction, the 47 blue  $MoO_{3-x}$  turns colorless because of oxidation. The resultant 48 was a colorless solution containing colloids of Pd-MoO<sub>3</sub> NPs. Pd 49 NPs have LSPR most often in the soft UV region. Therefore, sub-50 stituting palladium by a material with visible LSPR may emerge 51 catalytic behavior based on LSPR.

52 As another hydrogen catalyst, small gold NPs have extraordi-53 nary stability against oxidation in the aqueous environment and 54 is a visible range plasmonic material whose presence in solu-55 tion can be traced by UV-Vis optical absorption spectra without 56 any potential of interference [59]. Although MoO<sub>3</sub> nanostructures 57 have been proven to be capable of detecting different gas emis-58 sion due to their absorption properties, the presence of plasmonic 59 gold nanoparticles is expected to promote optical detection abil-60 ity due to enhanced local electric intensity  $(|E|^2)$  in the vicinity of 61 particles.

<sup>62</sup> In this study, we successfully fabricated Au-MoO<sub>x</sub> nanoparticles <sup>63</sup> by a synthetic facile rout; preparing  $MoO_x$  nanosheets by anodiz-<sup>64</sup> ing method and simply adding a gold aqueous salt. Besides the <sup>65</sup> mechanical and liquid-phase exfoliation approaches [60–62], elec-<sup>66</sup> trochemical oxidation (anodizing) of transition metals in aqueous electrolyte and ambient conditions is an alternative novel strategy to synthesize colloidal 2D-metal oxides NPs which is less considered up to now [63]. Accordingly, the main contribution of this paper is first to provide a facile way to make  $MOO_x$  nanosheets based on the anodizing method and to use their reductant ability to convert gold salt to gold nanoparticles. The Au-MoO<sub>x</sub> colloidal nanoparticles are then examined as plasmonic hydrogen gas sensors. We characterized the obtained Au-MoO<sub>x</sub> by different conventional techniques including, XRD, TEM, XPS and UV-Vis spectrometry.

## 2. Experimental

### 2.1. Sample preparation

Fig. 1 shows schematic representation of the anodizing process, adding gold salt solution followed by Au nanoparticle formation and hydrogen exposure to the obtained  $Au-MoO_x$  samples. The spectral variation of samples is also depicted. The  $MoO_x$  NPs were fabricated via an electrochemical anodizing method. In this process, two molybdenum probes were put into a 0.02 M HCl electrolyte, spaced 1 cm apart from each other. By applying a 30 V DC bias voltage for 5 min, the anode begins to corrode electrochemically, and the resultant oxide particles are released into the electrolyte.  $[AuCl_4]^-$  (10<sup>-4</sup> mM) aqueous solution was prepared by dissolving 0.039 g hydrogen tetrachloroaurate (III) hydrate (99.9%, metals basis, Au 49% min., Alfa Aesar) in 1000 ml DI water and 0.1 ml HCl. To prepare different molar ratios of Au:Mo in samples including 2.5:100, 3.25:100, 5:100 and 10:100, aqueous solutions of [AuCl4]<sup>-</sup> were added drop by drop into the colloidal blue molybdenum oxide, and as a result, the blue color turned to a stable pink/purple color. To better investigate the spectral shifts we came to the conclusion that it is better to fix the amount of gold in the solution and adjust the molybdenum value. Samples of different molar ratios named as S<sub>2.5</sub>, S<sub>3.25</sub>, S<sub>5</sub> and S<sub>10</sub>.

# 2.2. Sample characterizations

X-ray powder diffraction (XRD) was performed on Phillips XPERT with Cu-K $\alpha$  radiation to characterize the crystalline structure of our samples. The morphology and size distribution of the samples were determined by TEM imaging using Philips Holland model CM120 TEM instrument. The XPS analyses carried out using an ESCA/AES system (CHA, Specs model EA10 plus) and the binding energy of carbon (284.8 eV) was used for calibration energy scales. We measured the optical absorptions in the UV–Vis-NIR region using Perkin Elmer spectrophotometer (Lambda 25) in 200–1100 nm wavelength range. The cumulative absorption of samples was calculated by simply summation of optical absorption in 400–1100 nm wavelength range. Gas sensing was investigated by injecting an H<sub>2</sub>/Ar mixture of gas into a sealed glass vessel containing 10 ml of Au-MoO<sub>3</sub> colloidal solutions and rested for 10 min prior to UV–Vis spectrometry to verify the LSPR response.

## 3. Results and discussion

## 3.1. Structure and morphology

The XRD patterns of the initial  $MOO_x$  NPs and the Au-MoO\_x 126 NPs in samples  $S_{10}$  and  $S_{2.5}$  are shown in Fig. 2(a). The diffraction pattern of the pristine  $MOO_x$  drop-casted colloids is not of 127 high spectral quality but the diffraction peaks, close to crystalline 129 phases of  $MOO_x$ , can be detected. This suggests that the molybdenum oxide particles are two-dimensional so that there is weak 131 diffraction for them in the accuracy range of our XRD instrument. 132

67

68

69

Please cite this article in press as: M.A. Hosseini et al., Au-MoO<sub>x</sub> nanoparticles for LSPR hydrogen detection prepared by a facile anodizing method, Phys. Lett. A (2019), https://doi.org/10.1016/j.physleta.2019.126079

M.A. Hosseini et al. / Physics Letters A ••• (••••) •••••

JID:PLA AID:126079 /SCO Doctopic: Nanoscience



Fig. 1. Schematic representation of the experimental procedure. Deep blue defective MoO<sub>x</sub> colloidal nanosheets were prepared by a facile anodizing of Mo metal sheets in diluted HCl electrolyte. An [AuCl4]- solution is added to the obtained MoOx, where [AuCl4]- is converted to gold NPs with appearing an LSPR peak at 530 nm. At the same time, the initial blue color of the liquid diminishes as a result of  $MOO_x$  oxidation. Upon hydrogen exposure (<3%), the Au-MoO<sub>x</sub> solution turns again the deep blue color, LSPR peak appears around 750 nm in which the peak position and intensity depend on H<sub>2</sub> concentration. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.) 



Fig. 2. (a) XRD patterns of nanoparticles in different colloidal solutions including the initial blue MoO<sub>x</sub>, sample S<sub>10</sub> and sample S<sub>2.5</sub> and TEM images and size distribution histograms of NPs in (b) initial blue MoO<sub>x</sub>, (c) sample S<sub>10</sub> and (d) sample S<sub>2.5</sub>. The inside of part (b) indicated a TEM image with more clarity showing the two dimensional nature of the  $MoO_x$  NPs.

Please cite this article in press as: M.A. Hosseini et al., Au-MoO<sub>x</sub> nanoparticles for LSPR hydrogen detection prepared by a facile anodizing method, Phys. Lett. A (2019), https://doi.org/10.1016/j.physleta.2019.126079

1

2

3

4

5

6

7

8

9

10

11

12 13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

40



38 Fig. 3. XPS core level spectra of (a) Mo3d of pristine blue  $MoO_x$  colloids, (b) Mo3d of sample  $S_{2.5}$  and (c) Au4f of  $S_{2.5}$ . 39

41 As a result of the addition of certain amounts of [AuCl<sub>4</sub>]= droplets to the blue colloidal liquid, the diffraction peaks of fcc 42 gold (JCPDS No. 00-004-0784), with considerable intensity, appear 43 in the patterns of samples  $S_{10}$  and  $S_{2.5}$ . Therefore, the plasmonic 44 blue MoO<sub>x</sub> colloids could successfully convert the gold salt into 45 46 metallic gold at room temperature. The intensity of diffraction peaks in samples  $S_{10}$  and  $S_{2.5}$  are high compared to the back-47 ground noise and the diffraction peaks related to molybdenum 48 oxide were not detectable. The crystallite size of Au nanoparticles 49 50 in S10 and S2.5 were calculated by using Williamson-.Hall equation 51 of 8, and 12 nm, respectively.

The NPs in the obtained colloidal samples were further char-52 acterized by TEM. Fig. 2(b-d) shows representative TEM images 53 54 and corresponding size distribution histograms of the initial blue 55  $MoO_x$ , sample  $S_{10}$  and  $S_{2.5}$ , respectively. The initial  $MoO_x$  pre-56 pared by anodizing process involves two-dimensional nanopar-57 ticles with an average lateral size of about 60 nm. The inside TEM image shows the two dimensional nature of the nanoparti-58 59 cles more clearly. The weak and wide XRD peaks for this sample 60 can be attributed to this ultra-small thickness. These particles are 61 polyhederal in shape indicating their crystallinity. In the TEM im-62 ages and corresponding size distribution histograms of samples S<sub>10</sub> 63 and S<sub>2.5</sub>, one can recognize formation of gold nanoparticles in the 64 range of 5-7 nm with a narrow size distribution. The dimensions 65 of these particles were found to be approximately in the same 66 range in all the samples. This difference in particle size compared

89

90

94

95

99

100

101

102

to XRD results is probably because the TEM imaging was measured from a specific area of the colloidal system that did not include all the particle size distribution.

TEM clearly shows the plasmonic  $MoO_x$  nanosheets easily convert [AuCl4]<sup>-</sup> to Au NPs with an average domination smaller than 10 nm. In addition to strong local field enhancement due to their plasmonic property, this range of size provides a good catalytic property for Au NPs to decompose H<sub>2</sub> molecules into H atoms in any gas detection processes [64,65].

### 3.2. X-ray photoelectron spectroscopy

XPS was used to clarify the surface elemental composition variation as a result of adding gold salt solution. Fig. 3 represents typical Mo3d high-resolution spectra for the pristine blue  $MoO_x$ and sample  $S_{2.5}$ . For the pristine blue  $MoO_x$  nanosheets, Mo3d peak is well decomposed into two doublets at (235.7, 232.6 eV) positions related to Mo<sup>6+</sup> states and (234.7, 231.6 eV) for Mo<sup>5+</sup> state [44] whose peak area corresponds to 74% and 26% counterparts for Mo<sup>6+</sup> and Mo<sup>5+</sup>, respectively. The significant percentage of 5+ states originates form defects such as oxygen vacancy and confirms the defective nature of the blue  $MoO_x$  nanosheets. The oxygenvacancy defects induce localized electrons that lead to plasmon absorption in the visible and NIR region [29,30,66-68]. For sample  $S_{2.5}$ , the Mo3d peak is narrower than the blue MoO<sub>x</sub> indicating 91 92 a less multivalent contribution of Mo oxidation states. It could be deconvoluted into Mo<sup>6+</sup> (235.9, 232.7 eV) and Mo<sup>5+</sup> (234.7, 232.0 93 eV)states with 88 and 12%, respectively. Losing Mo<sup>5+</sup> peak contribution confirms partial conversion of 5+ states to 6+ as a result 96 of an oxidation reaction [67]. The small energy transfer to higher 97 binding energy in S<sub>2.5</sub> comparing to blue MoO<sub>x</sub> can be related to 98 the oxidation of molybdenum as a result of combination with gold precursor.

The Au core level typical spectrum has one doublet with peaks at 83.4 and 87 eV which is attributed to Au  $4f_{7/2}$  and Au  $4f_{5/2}$ , respectively, characteristic of metallic gold in agreement with the results of XRD. No part of gold ion (Au<sup>3+</sup>) could be found as the peak is narrow (FWHM about 1.17 eV). According to the XPS results, the proposed reaction mechanism can be simply expressed as:

$$Mo^{5+} \to Mo^{6+} + e^- \tag{1}$$

$$\mathrm{Au}^{3+} + 3e^- \rightarrow \mathrm{Au}^0$$

# 3.3. LSPR hydrogen sensing

A

To examine the LSPR response of our Au-MoO<sub>x</sub> colloidal solutions towards hydrogen detection, their optical absorption spectra were recorded in the UV-Vis region, 10 min after injection various hydrogen concentrations (from 0.1 to 3%) into the sealed containers containing certain volume of samples S<sub>2.5</sub>, S<sub>3.25</sub>, S<sub>5</sub> and  $S_{10}$  (Fig. 4(a-d)). For further interpretations, we also plotted LSPR wavelength and cumulative absorption as a function of gas concentration as shown in Fig. 5(a, b). Comparing the overall spectra in Fig. 4(a) to Fig. 4(c) reveals that increasing the Au:Mo ratio leads to a notable blue shift in the  $MoO_x$  LSPR band. This suggests that a higher Au fraction is translated into a greater hydrogen dissociation rate, increased defect doping level and increase in carrier concentration, leading to a spectral blue shift. However, from Fig. 4(d) representing a NIR LSPR-free spectrum, one can see that to have a detectable LSPR band, Au relative concentration should not exceed an optimum range (5:100 in our experimental conditions).

On the other hand, in the each individual sample, it seems that LSPR peak undergoes a red shift with hydrogen concentra-132 tion (Fig. 5(a)). This is likely due to a slight decrease in the carrier



**Fig. 4.** Optical absorption spectra of different Au-MoO<sub>x</sub> samples: (a)  $S_{2,5}$ , (b)  $S_{3,25}$ , (d)  $S_5$  and (e)  $S_{10}$  after exposing different  $H_2$  concentration (0-3%).

density n, as a result of lattice expansion due to hydrogen inter-calation. Moreover, any change in the dielectric constant of the medium may also be another reason which was not possible for us to evaluate. The plot of cumulative absorption vs. gas concen-tration (Fig. 5(b)) reveals an overall increasing trend for all the samples with a possible linearity trend depending on Au:Mo ratio. In the 0-3% H<sub>2</sub> concentration range of interest, the best linear-ity behavior is observed for sample S5, suggesting the Au:Mo ratio play role in the detection range of an LSPR sensor. Low Au content is not sufficient for effective hydrogen catalysis and high content leads to a small relative intensity of  $MoO_x$  LSPR in the spectra so an optimum mixing ratio is required. It is worth noting that LSPR wavelength and intensity saturate for above 4% concentration thereby this kind of sensing platform works well in the low con-centration limits with possible many data points.



[m5G; v1.261; Prn:23/10/2019; 11:40] P.5 (1-8)

Fig. 5. (a) the MoO<sub>x</sub> plasmonic peak position verse H<sub>2</sub> concentration, (b) The cumulative absorption of different samples verse gas concentration.

To explain LSPR property of our sample Drude-Lorentz model is suitable. According to this model, the plasmonic resonance frequency is proportional to the square root of the free carrier concentration (n) [38]:

$$\nu_p = \sqrt{\frac{ne^2}{\varepsilon_0 m_e}} \tag{2}$$

According to this relation, it can be found that the plasmon frequency,  $\omega_p$ , is highly sensitive to the charge carrier concentration (or doping level).

To have a visual detector, its color must change in the presence of a chemical agent. For the obtained  $Au-MoO_x$  samples, hydrogenation causes the purple colloidal solutions of gold NPs to return a deep blue color analogous to the pristine sample. This visual optical switching reflects the good catalytic dissociation of hydrogen in the presence of fine Au NPs as well as the application potential of these solutions as visual hydrogen indicator. To have a suitable LSPR response for sensing applications, however, the free carrier concentration (n) and hence the LSPR frequency of the plasmonic substance, should be a specific function of analyte concentration.

Au NPs are expected to do two different functions in the liquidbased hydrogen detection; Due to their high catalytic activity, they could dissociate hydrogen molecules to proton/electron pairs and enable them to diffuse into the  $MoO_x$  structure, an alternative to Pt and Pd catalysts. In addition to the catalytic function, co-localization of light energy and hydrogen in the vicinity of Au-MoO<sub>x</sub> NPs, they can promote the gas-surface interactions over the  $MoO_x$  surface via a light-matter coupling leading to an enhanced charge transfer mechanism.

As noted above, the wavelength (frequency) of LSPR absorption depends on the concentration of charge carriers and thus on the

1

2

3

5

6

7

8

9

10

11

12

13

14

15

16

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48



**Fig. 6.** (a) Optical absorption spectra of samples  $S_5$  through spontaneously bleaching process in ambient air after exposing to 3% hydrogen. The photographic images before and after bleaching process are also shown. (b) The time variation of absorption at  $\lambda_{LSPR} = 760$  nm during the bleaching.

17 concentration of oxygen defects in metal oxide systems. These de-18 fects arise from the injection of hydrogen. So with a higher H:Mo 19 ratio injected a higher the blue-shift is expected. We claim that 20 the Au:Mo ratio further increases the amount of hydrogen injec-21 tions and thus increases the amount of blue-shift, as our results 22 show. The absorption intensity, however, depends on the molar 23 concentration of plasmonic  $MoO_x$  in the solution. The reason for 24 the non-increase in the intensity with increasing Au:Mo is that we 25 adjusted the amount of gold in all the solution constant and de-26 crease the Mo molar ratio to obtain samples with higher Au:Mo 27 ratios. This is why the intensity of absorption does not change with 28 increasing gold ratio. On the basis of the wavelength shift, the in-29 crease in the ratio of gold shows a greater shift (with the exception 30 of sample S<sub>10</sub> where its Mo concentration is low so that no LSPR 31 peak appears) so the increase in gold can be associated with an 32 increase in blue-shift based sensitivity. 33

The reversibility of a gas sensor is of great importance for its applicability. To investigate the reversibility of our LSPR colloidal solutions, we exposed the sample S<sub>5</sub> to the ambient air of the laboratory after interacting with 3% hydrogen. As shown in Fig. 6(a), it is observed that over time, the optical absorption decreases spontaneously so that the LSPR peak of MoO<sub>x</sub> disappeared and the gold absorption peak appeared again. The color of the samples also turned gradually from blue to pink (Fig. 6(a)). Although the recovery time measure at  $\lambda = 760$  nm is estimated to be around 300 min (Fig. 6(b)), we expect this trend to increase more rapidly if the colored solution is heated and pure oxygen is bubbled.

# 4. Conclusion

49 In this research work,  $MoO_x$  nanoparticles were first made by 50 anodizing oxidation of molybdenum metal probes into an acidic 51 electrolyte. This is a very simple, inexpensive and mass-produced 52 method. The resulting solution was blue, had a NIR LSPR absorp-53 tion band, and was known as a material for gold salt reduction and 54 creation of fine gold nanoparticles. The creation of gold nanoparti-55 cles was accompanied by more and more oxidation of MoO<sub>x</sub>, which 56 eventually resulted in a purple color substituted the initial blue 57 color, appearing of gold LSPR absorption, and decreasing adsorp-58 tion of MoO<sub>x</sub> LSPR. This two-phase colloidal solution has thereafter 59 shown considerable potential for detecting hydrogen gas based on 60 LSPR absorption and shift. In this functionality, an increase in the 61 concentration of hydrogen injecting gas resulted in a re-growth 62 of the molybdenum NIR LSPR peak, while a significant plasmonic 63 shift was observed. Overall, it was shown that the system could 64 65 provide desirable sensitivity at H<sub>2</sub> concentrations below 3%, which 66 is below the hydrogen explosion limit as well as reversibility.

### Acknowledgement

The authors would like to thank the Iranian National Science Foundation (INSF) for their financial support.

### References

- [1] M. Gao, X. Zheng, I. Khan, H. Cai, J. Lan, J. Liu, J. Wang, J. Wu, S. Huang, S. Li, J. Kang, Resonant light absorption and plasmon tunability of lateral triangular Au nanoprisms array, Phys. Lett. A 383 (2019) 125881, https://doi.org/10.1016/ j.physleta.2019.125881.
- [2] M. Hu, J. Chen, Z.Y. Li, L. Au, G.V. Hartland, X. Li, M. Marquez, Y. Xia, Gold nanostructures: engineering their plasmonic properties for biomedical applications, Chem. Soc. Rev. 35 (2006) 1084–1094, https://doi.org/10.1039/b517615h.
- [3] P. Bhatia, S.S. Verma, M.M. Sinha, Tuning the optical properties of Fe-Au coreshell nanoparticles with spherical and spheroidal nanostructures, Phys. Lett. A 383 (2019) 2542–2550, https://doi.org/10.1016/j.physleta.2019.05.009.
- [4] M. Singh, S.K. Raghuwanshi, T. Srinivas, Nanophotonic on-chip hybrid plasmonic electro-optic modulator with phase change materials, Phys. Lett. A 383 (2019) 3196–3199, https://doi.org/10.1016/j.physleta.2019.07.004.
- [5] P.K. Jain, K.S. Lee, I.H. El-Sayed, M.A. El-Sayed, Calculated absorption and scattering properties of gold nanoparticles of different size, shape, and composition: applications in biological imaging and biomedicine, J. Phys. Chem. B 110 (2006) 7238–7248, https://doi.org/10.1021/jp0571700.
- [6] L. He, M.D. Musick, S.R. Nicewarner, F.G. Salinas, S.J. Benkovic, M.J. Natan, C.D. Keating, Colloidal Au-enhanced surface plasmon resonance for ultrasensitive detection of DNA hybridization, J. Am. Chem. Soc. 122 (2000) 9071–9077, https://doi.org/10.1021/ja001215b.
- [7] C.M. Cobley, S.E. Skrabalak, D.J. Campbell, Y. Xia, Shape-controlled synthesis of silver nanoparticles for plasmonic and sensing applications, Plasmonics 4 (2009) 171–179, https://doi.org/10.1007/s11468-009-9088-0.
- [8] G.H. Chan, J. Zhao, E.M. Hicks, G.C. Schatz, R.P. Van Duyne, Plasmonic properties of copper nanoparticles fabricated by nanosphere lithography, Nano Lett. 7 (2007) 1947–1952, https://doi.org/10.1021/nl070648a.
- [9] T.K. Sau, C.J. Murphy, Seeded high yield synthesis of short Au nanorods in aqueous solution, Langmuir 20 (2004) 6414–6420, https://doi.org/10.1021/ la049463z.
- [10] H. Cheng, M. Wen, X. Ma, Y. Kuwahara, K. Mori, Y. Dai, B. Huang, H. Yamashita, Hydrogen doped metal oxide semiconductors with exceptional and tunable localized surface plasmon resonances, J. Am. Chem. Soc. 138 (2016) 9316–9324, https://doi.org/10.1021/jacs.6b05396.
- [11] H.H. Afify, S.A. Hassan, A. Abouelsayed, S.E. Demian, H.A. Zayed, Coloration of molybdenum oxide thin films synthesized by spray pyrolysis technique, Thin Solid Films 623 (2017) 40–47, https://doi.org/10.1016/j.tsf.2016.12.033.
- [12] M.M.Y.A. Alsaif, M.R. Field, B.J. Murdoch, T. Daeneke, K. Latham, A.F. Chrimes, A.S. Zoolfakar, S.P. Russo, J.Z. Ou, K. Kalantar-Zadeh, Substoichiometric twodimensional molybdenum oxide flakes: a plasmonic gas sensing platform, Nanoscale 6 (2014) 12780–12791, https://doi.org/10.1039/c4nr03073g.
- [13] K. Manthiram, A.P. Alivisatos, Tunable localized surface plasmon resonances in tungsten oxide nanocrystals, J. Am. Chem. Soc. 134 (2012) 3995–3998, https:// doi.org/10.1021/ja211363w.
- [14] N. Li, X. Cao, Y. Li, T. Chang, S. Long, Y. Zhou, G. Sun, L. Ge, P. Jin, A plasmonic non-stoichiometric  $WO_{3-x}$  homojunction with stabilizing surface plasmonic resonance for selective photochromic modulation, Chem. Commun. 54 (2018) 5241–5244, https://doi.org/10.1039/c8cc02211a.
- [15] S.D. Lounis, E.L. Runnerstrom, A. Llordés, D.J. Milliron, Defect chemistry and plasmon physics of colloidal metal oxide nanocrystals, J. Phys. Chem. Lett. 5 (2014) 1564–1574, https://doi.org/10.1021/jz500440e.

127

128

129

130

131

132

Please cite this article in press as: M.A. Hosseini et al., Au-MoO<sub>x</sub> nanoparticles for LSPR hydrogen detection prepared by a facile anodizing method, Phys. Lett. A (2019), https://doi.org/10.1016/j.physleta.2019.126079

2

#### M.A. Hosseini et al. / Physics Letters A ••• (••••) ••••••

5

71

72

73

74

75

76

77

78

79

80

81

82

83

84

85

86

87

88

89

90

91

92

93

94

95

96

97

98

99

100

101

102

103

104

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

125

126

127

128

129

130

131

132

- [16] Y. Zhao, H. Pan, Y. Lou, X. Qiu, J. Zhu, C. Burda, Plasmonic Cu<sub>2-x</sub>S nanocrystals: optical and structural properties of copper-deficient copper(1) sulfides, J. Am. Chem. Soc. 131 (2009) 4253–4261, https://doi.org/10.1021/ja805655b.
- Chem. Soc. 131 (2009) 4253-4261, https://doi.org/10.1021/ja805655b.
   [17] I. Kriegel, C. Jiang, J. Rodríguez-Fernández, R.D. Schaller, D.V. Talapin, E. Da
   Como, J. Feldmann, Tuning the excitonic and plasmonic properties of copper
   chalcogenide nanocrystals, J. Am. Chem. Soc. 134 (2012) 1583-1590, https://
   doi.org/10.1021/ja207798g.
- [18] S. Haupt, Z. Malik, B. Ehrenberg, Comparative kinetics of damage to the plasma and mitochondrial membranes by intra-cellularly synthesized and externallyprovided photosensitizers using multi-color FACS, Photochem. Photobiol. Sci. 13 (2014) 38–47, https://doi.org/10.1039/c3pp50189b.
- [19] Q. Liu, Y. Wu, J. Zhang, K. Chen, C. Huang, H. Chen, X. Qiu, Plasmonic MoO3-x nanosheets with tunable oxygen vacancies as efficient visible light responsive photocatalyst, Appl. Surf. Sci. 490 (2019) 395–402, https://doi.org/10.1016/j. apsusc.2019.06.099.
   [13] [20] O. Yin, L. Tan, O. Lang, X. Ke, L. Bai, K. Guo, S. Bai, Plasmonic molybde-
- [20] Q. Yin, L. Tan, Q. Lang, X. Ke, L. Bai, K. Guo, R. Qiao, S. Bai, Plasmonic molybdenum oxide nanosheets supported silver nanocubes for enhanced near-infrared antibacterial activity: synergism of photothermal effect, silver release and photocatalytic reactions, Appl. Catal. B, Environ. 224 (2018) 671–680, https:// doi.org/10.1016/j.apcatb.2017.11.024.
- [21] S.H. Lee, H. Nishi, T. Tatsuma, Plasmonic behaviour and plasmon-induced charge separation of nanostructured MoO<sub>3-x</sub> under near infrared irradiation, Nanoscale 10 (2018) 2841–2847, https://doi.org/10.1039/c7nr09477a.
- [22] X. Tan, L. Wang, C. Cheng, X. Yan, B. Shen, J. Zhang, Plasmonic MoO<sub>3-x</sub>@MoO<sub>3</sub>
   nanosheets for highly sensitive SERS detection through nanoshell-isolated electromagnetic enhancement, Chem. Commun. 52 (2016) 2893–2896, https://doi.org/10.1039/c5cc10020h.
- [23] M.A. Hosseini, M. Ranjbar, Plasmonic Au-MoO<sub>3</sub> colloidal nanoparticles by reduction of HAuCl<sub>4</sub> by blue MoO<sub>x</sub> nanosheets and observation of the gasochromic property, Plasmonics 13 (2018) 1897–1906, https://doi.org/10. 1007/s11468-018-0704-8.
   [26] INTERCENTION OF CALL AND ADDRESS AND AD
- [24] P.R. West, S. Ishii, G.V. Naik, N.K. Emani, V.M. Shalaev, A. Boltasseva, Searching
   for better plasmonic materials, Laser Photonics Rev. 4 (2010) 795–808, https://
   doi.org/10.1002/lpor.200900055.
- [25] X. Liu, M.T. Swihart, Heavily-doped colloidal semiconductor and metal oxide nanocrystals: an emerging new class of plasmonic nanomaterials, Chem. Soc. Rev. 43 (2014) 3908–3920, https://doi.org/10.1039/c3cs60417a.
- [26] H. Zhang, T. Wang, J. Wang, H. Liu, T.D. Dao, M. Li, G. Liu, X. Meng, K. Chang,
   L. Shi, T. Nagao, J. Ye, Surface-plasmon-enhanced photodriven CO<sub>2</sub> reduction
   catalyzed by metal-organic-framework-derived iron nanoparticles encapsulated
   by ultrathin carbon layers, Adv. Mater. 28 (2016) 3703–3710, https://doi.org/
   10.1002/adma.201505187.
- [27] G. Liu, P. Li, G. Zhao, X. Wang, J. Kong, H. Liu, H. Zhang, K. Chang, X. Meng, T. Kako, J. Ye, Promoting active species generation by plasmon-induced hotelectron excitation for efficient electrocatalytic oxygen evolution, J. Am. Chem. Soc. 138 (2016) 9128–9136, https://doi.org/10.1021/jacs.6b05190.
   [28] D. L. J. Liu, Y. C. Kata, M. T. Kata, M. Kata, J. Ka
- [28] H. Zhang, L. Yu, T. Chen, W. Zhou, X.W. (David) Lou, Surface modulation of hierarchical MoS<sub>2</sub> nanosheets by Ni single atoms for enhanced electrocatalytic hydrogen evolution, Adv. Funct. Mater. 28 (2018) 1807086, https://doi.org/10.
   1002/adfm.201807086.
- 42 [29] M. Xu, T. Liang, M. Shi, H. Chen, Graphene-like two-dimensional materials, Chem. Rev. 113 (2013) 3766–3798, https://doi.org/10.1021/cr300263a.
- G.R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y. Son,
  M.S. Strano, V.R. Cooper, L. Liang, S.G. Louie, E. Ringe, W. Zhou, S.S. Kim, R.R.
  Naik, B.G. Sumpter, H. Terrones, F. Xia, Y. Wang, J. Zhu, D. Akinwande, N.
  Alem, J.A. Schuller, R.E. Schaak, M. Terrones, J.A. Robinson, Recent advances in
  two-dimensional materials beyond graphene, ACS Nano 9 (2015) 11509–11539, https://doi.org/10.1021/acsnano.5b05556.
- [31] P. Miró, M. Audiffred, T. Heine, An atlas of two-dimensional materials, Chem.
   Soc. Rev. 43 (2014) 6537–6554, https://doi.org/10.1039/c4cs00102h.
- [32] F. Xia, Two-dimensional material photonics, in: CLEO Sci. Innov. CLEO-SI 2015, 2015, p. 2267.
- [33] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, Nat. Nanotechnol. 7 (2012) 699–712, https://doi.org/10.1038/nnano.2012.193.
- [34] D. Deng, K.S. Novoselov, Q. Fu, N. Zheng, Z. Tian, X. Bao, Catalysis with twodimensional materials and their heterostructures, Nat. Nanotechnol. 11 (2016) 218–230, https://doi.org/10.1038/nnano.2015.340.
- [35] K. Zhou, W. Zhou, X. Liu, Y. Sang, S. Ji, W. Li, J. Lu, L. Li, W. Niu, H. Liu, S. Chen, Ultrathin MoO<sub>3</sub> nanocrystalsself-assembled on graphene nanosheets via oxygen bonding as supercapacitor electrodes of high capacitance and long cycle life, Nano Energy 12 (2015) 510–520, https://doi.org/10.1016/j.nanoen.2015.01.
   [00] 107.
- [36] S.J. Xiao, X.J. Zhao, P.P. Hu, Z.J. Chu, C.Z. Huang, L. Zhang, Highly photoluminescent molybdenum oxide quantum dots: one-pot synthesis and application in 2, 4,6-trinitrotoluene determination, ACS Appl. Mater. Interfaces 8 (2016)
   8184–8191, https://doi.org/10.1021/acsami.5b11316.
- [37] R. Li, H. An, W. Huang, Y. He, Molybdenum oxide nanosheets meet ascorbic acid: tunable surface plasmon resonance and visual colorimetric detection at room temperature, Sens. Actuators B, Chem. 259 (2018) 59–63, https://doi.org/10.1016/j.snb.2017.12.058.

- [39] S. Pandey, A.K. Sharma, K.H. Sharma, Y. Nerthigan, M.S. Khan, D.R. Hang, H.F. Wu, Rapid naked eye detection of alkaline phosphatase using A-MoO<sub>3-x</sub> nanoflakes, Sens. Actuators B, Chem. 254 (2018) 514–518, https://doi.org/10.1016/j. snb.2017.06.123.
- [40] M.B. Sreedhara, H.S.S.R. Matte, A. Govindaraj, C.N.R. Rao, Synthesis, characterization, and properties of few-layer MoO<sub>3</sub>, Asian J. Chem. 8 (2013) 2430–2435, https://doi.org/10.1002/asia.201300470.
- [41] W. Liu, Q. Xu, W. Cui, C. Zhu, Y. Qi, CO<sub>2</sub>-assisted fabrication of two-dimensional amorphous molybdenum oxide nanosheets for enhanced plasmon resonances, Angew. Chem., Int. Ed. Engl. 56 (2017) 1600–1604, https://doi.org/10.1002/anie. 201610708.
- [42] S.K. Konda, A. Chen, Palladium based nanomaterials for enhanced hydrogen spillover and storage, Mater. Today 19 (2016) 100–108, https://doi.org/10.1016/ j.mattod.2015.08.002.
- [43] N. Li, Y. Li, G. Sun, Y. Zhou, S. Ji, H. Yao, X. Cao, S. Bao, P. Jin, Enhanced photochromic modulation efficiency: a novel plasmonic molybdenum oxide hybrid, Nanoscale 9 (2017) 8298–8304, https://doi.org/10.1039/c7nr02763j.
- [44] H. Cheng, X. Qian, Y. Kuwahara, K. Mori, H. Yamashita, A plasmonic molybdenum oxide hybrid with reversible tunability for visible-light-enhanced catalytic reactions, Adv. Mater. 27 (2015) 4616–4621, https://doi.org/10.1002/ adma.201501172.
- [45] C. Wadell, S. Syrenova, C. Langhammer, Nanoplasmonic hydrogen sensing, in: Plasmon. Met. Nanostructures Their Opt. Prop. XII, vol. 9163, 2014, 916310.
- [46] S.S. Kalanur, J. Heo, I.H. Yoo, H. Seo, 2-D WO<sub>3</sub> decorated with Pd for rapid gasochromic and electrical hydrogen sensing, Int. J. Hydrog. Energy 42 (2017) 16901–16908, https://doi.org/10.1016/j.ijhydene.2017.05.172.
- [47] H. Gu, Z. Wang, Y. Hu, Hydrogen gas sensors based on semiconductor oxide nanostructures, Sens. (Switzerland) 12 (2012) 5517–5550, https://doi.org/10. 3390/s120505517.
- [48] S.S. Kalanur, Y.A. Lee, H. Seo, Eye-readable gasochromic and optical hydrogen gas sensor based on CuS-Pd, RSC Adv. 5 (2015) 9028–9034, https://doi.org/10. 1039/c4ra11067f.
- [49] H. Takahashi, S. Okazaki, Y. Nishijinia, T. Arakawa, Optimization of hydrogen sensing performance of Pt/WO<sub>3</sub> gasochromic film fabricated by sol-gel method, Sens. Mater. 29 (2017) 1259–1268, https://doi.org/10.18494/SAM.2017.1585.
- [50] S. Okazaki, S. Johjima, Temperature dependence and degradation of gasochromic response behavior in hydrogen sensing with Pt/WO<sub>3</sub> thin film, Thin Solid Films 558 (2014) 411–415, https://doi.org/10.1016/j.tsf.2014.02.080.
- [51] M.H. Yaacob, M. Breedon, K. Kalantar-zadeh, W. Wlodarski, Y. Li, Comparative study of the gasochromic performance of Pd/WO<sub>3</sub> and Pt/WO<sub>3</sub> nanotextured thin films for low concentration hydrogen sensing, in: 2009 IEEE Sensors, IEEE, 2009, pp. 304–307.
- W.C. Hsu, C.C. Chan, C.H. Peng, C.C. Chang, Hydrogen sensing characteristics of an electrodeposited WO<sub>3</sub> thin film gasochromic sensor activated by Pt catalyst, Thin Solid Films 516 (2007) 407–411, https://doi.org/10.1016/j.tsf.2007.07.055.
- [53] M. Chen, L. Zou, Z. Zhang, J. Shen, D. Li, Q. Zong, G. Gao, G. Wu, J. Shen, Z. Zhang, Tandem gasochromic-Pd-WO<sub>3</sub>/graphene/Si device for room-temperature high-performance optoelectronic hydrogen sensors, Carbon 130 (2018) 281–287, https://doi.org/10.1016/j.carbon.2018.01.013.
- [54] S.S. Kalanur, I.H. Yoo, H. Seo, Pd on MoO<sub>3</sub> nanoplates as small-polaron-resonant eye-readable gasochromic and electrical hydrogen sensor, Sens. Actuators B, Chem. 247 (2017) 357–365, https://doi.org/10.1016/j.snb.2017.03.033.
- [55] C.C. Chang, J.Y. Luo, T.K. Chen, K.W. Yeh, T.W. Huang, C.H. Hsu, W.H. Chao, C.T. Ke, P.C. Hsu, M.J. Wang, M.K. Wu, Pulsed laser deposition of (MoO<sub>3</sub>)<sub>1-x</sub>(V<sub>2</sub>O<sub>5</sub>)<sub>x</sub> thin films: preparation, characterization and gasochromic studies, Thin Solid Films 519 (2010) 1552–1557, https://doi.org/10.1016/j.tsf.2010.09.003.
- [56] F. Delalat, M. Ranjbar, H. Salamati, Blue colloidal nanoparticles of molybdenum oxide by simple anodizing method: decolorization by PdCl<sub>2</sub> and observation of in-liquid gasochromic coloration, Sol. Energy Mater. Sol. Cells 144 (2016) 165–172, https://doi.org/10.1016/j.solmat.2015.08.038.
- [57] A.R. Shafieyan, M. Ranjbar, P. Kameli, Localized surface plasmon resonance H<sub>2</sub> detection by MoO<sub>3</sub> colloidal nanoparticles fabricated by the flame synthesis method, Int. J. Hydrog. Energy 44 (2019) 18628–18638, https://doi.org/10.1016/ j.ijhydene.2019.05.171.
- [58] M.A. Hosseini, M. Ranjbar, A.R. Shafieyan, flame synthesis of MoO<sub>3</sub> films and their flame reduction to MoO<sub>3-x</sub> films for NIR-shielding applications, Surf. Rev. Lett. (2019) 1950110, https://doi.org/10.1142/S0218625X19501105.
- [59] N. Tahmasebi, S.M. Mahdavi, Synthesis and optical properties of Au decorated colloidal tungsten oxide nanoparticles, Appl. Surf. Sci. 355 (2015) 884–890, https://doi.org/10.1016/j.apsusc.2015.07.181.
- [60] A.J. Molina-Mendoza, J.L. Lado, J.O. Island, M.A. Niño, L. Aballe, M. Foerster, F.Y. Bruno, A. López-Moreno, L. Vaquero-Garzon, H.S.J. Van Der Zant, G. Rubio-Bollinger, N. Agraït, E.M. Pérez, J. Fernández-Rossier, A. Castellanos-Gomez, Centimeter-scale synthesis of ultrathin layered MoO<sub>3</sub> by van der Waals epitaxy, Chem. Mater. 28 (2016) 4042–4051, https://doi.org/10.1021/acs.chemmater. 6b01505.

Please cite this article in press as: M.A. Hosseini et al., Au-MoO<sub>x</sub> nanoparticles for LSPR hydrogen detection prepared by a facile anodizing method, Phys. Lett. A (2019), https://doi.org/10.1016/j.physleta.2019.126079

[61] I.A. de Castro, R.S. Datta, J.Z. Ou, A. Castellanos-Gomez, S. Sriram, T. Daeneke, K. Kalantar-zadeh, Molybdenum oxides - from fundamentals to functionality, Adv. Mater. 29 (2017) 1-31, https://doi.org/10.1002/adma.201701619.

[62] F. Rahman, T. Ahmed, S. Walia, E. Mayes, S. Sriram, M. Bhaskaran, S. Balendhran, Two-dimensional MoO3 via a top-down chemical thinning route, 2D Mater. 4 (2017) 035008, https://doi.org/10.1088/2053-1583/aa79d5.

- [63] Y. Tang, P. Wee, Y. Lai, X. Wang, D. Gong, P.D. Kanhere, T.T. Lim, Z. Dong, Z. Chen, Hierarchical TiO2 nanoflakes and nanoparticles hybrid structure for improved photocatalytic activity, J. Phys. Chem. C 116 (2012) 2772-2780, https:// doi.org/10.1021/jp210479a.
- [64] M.Z. Ahmad, A.Z. Sadek, M.H. Yaacob, D.P. Anderson, G. Matthews, V.B. Golovko, W. Wlodarski, Optical characterisation of nanostructured Au/WO3 thin films for sensing hydrogen at low concentrations, Sens. Actuators B, Chem. 179 (2013) 125-130, https://doi.org/10.1016/j.snb.2012.09.102.
- [65] T.D. Tran, M.T.T. Nguyen, H.V. Le, D.N. Nguyen, Q.D. Truong, P.D. Tran, Gold nanoparticles as an outstanding catalyst for the hydrogen evolution reaction, Chem. Commun. 54 (2018) 3363-3366, https://doi.org/10.1039/c8cc00038g.
- [66] J. Shi, Y. Kuwahara, M. Wen, M. Navlani-García, K. Mori, T. An, H. Yamashita, Room-temperature and aqueous-phase synthesis of plasmonic molybdenum oxide nanoparticles for visible-light-enhanced hydrogen generation, Asian J. Chem. 11 (2016) 2377-2381, https://doi.org/10.1002/asia.201600771.

[67] H. Bai, F. Ye, Q. Lv, G. Xi, J. Li, H. Yang, C. Wan, An in situ and general preparation strategy for hybrid metal/semiconductor nanostructures with enhanced solar energy utilization efficiency, J. Mater. Chem. A 3 (2015) 14550-14555, https://doi.org/10.1039/c5ta03612g.

[68] A. Agrawal, S.H. Cho, O. Zandi, S. Ghosh, R.W. Johns, D.J. Milliron, Localized surface plasmon resonance in semiconductor nanocrystals, Chem. Rev. 118 (2018) 3121-3207, https://doi.org/10.1021/acs.chemrev.7b00613.

Please cite this article in press as: M.A. Hosseini et al., Au-MoO<sub>x</sub> nanoparticles for LSPR hydrogen detection prepared by a facile anodizing method, Phys. Lett. A (2019), https://doi.org/10.1016/j.physleta.2019.126079

JID:PLA AID:126079 /SCO Doctopic: Nanoscience

1 2	Sponsor names	67 68
3	Do not correct this page. Please mark corrections to sponsor names and grant numbers in the main text.	69
4	INCE country-Iran grante-	70
5	<b>INSF</b> , country-fran, grunts-	71
6		72
7 8		73
9		75
10		76
11		77
12 13		78 79
14		80
15		81
16		82
17 18		83 84
19		85
20		86
21		87
22		88
23 24		89 90
25		91
26		92
27		93
28 29		94 95
30		96
31		97
32		98
33		99 100
34 35		100
36		102
37		103
38		104
39 40		105
41		107
42		108
43		109
45		111
46		112
47		113
48 49		114 115
		116
51		117
52		118
53		119
э4 55		120
56		122
57		123
58		124
59 60		125
61		127
62		128
63		129
64 65		130 131
66		132

# Highlights

- Blue colloidal MoO<sub>x</sub> nanoparticles were prepared by a facile anodizing method.
- A strong NIR localized surface plasmon resonance were observed.
- $\bullet$  The LSPR NPs showed good ability for  $[AuCl_4]^-$  salt conversion to Au nanoparticles.
- The obtained Au-MoO<sub>x</sub> nanosystems was showed a good LSPR hydrogen sensing.
- By monitoring the NIR LSPR band, it was possible to detect hydrogen in the 0–3% concentration range.