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Unlocking the Potential of Carbon Incorporated Silver-Silver Molybdate Nanowire with Light

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Abstract

We present a novel form of Ag_2MoO_4-based hybrid nanowire (NW) with a few remarkable attributes. Firstly, the NW is embedded and decorated with Ag NPs. Secondly, carbon atoms are intentionally incorporated within the matrix of the NW. Thirdly the hybrid nanowires are created *via* a facile process. Namely, focused laser micropatterning of Ag NPs on GO film as seeding sites and subsequent formation of the hybrid NWs by placing the patterned GO films on heated Mo foil on a hotplate. This unique process resulted in the production of hybrid Ag/Ag_2MoO_4 NWs that emit unique red fluorescence emission. And finally remarkable photodoping effect is observed from a single strand of optically tuned carbon-doped silver nanoparticles embedded silver molybdate nanowire. We demonstrate applications of these hybrid NWs as micro-display and time limiting, logic components for secure transmission of messages.

1. Synthesis

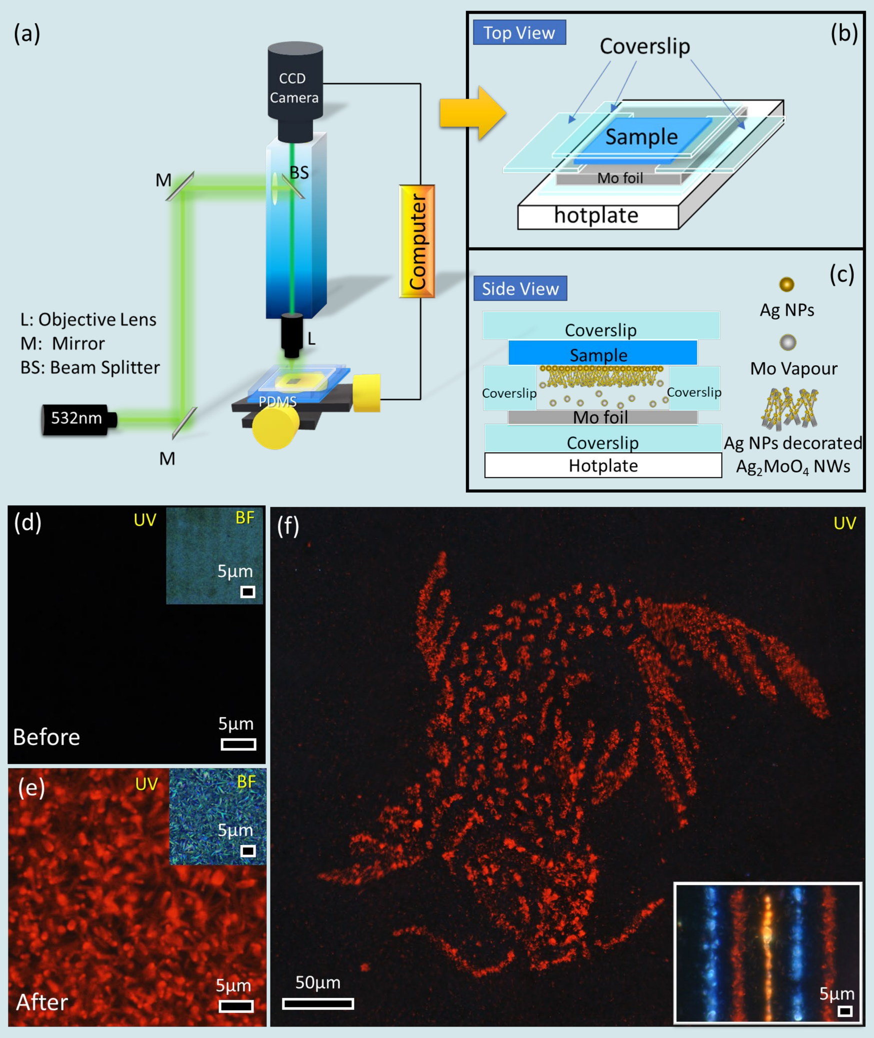


Figure 1. Schematic of the (a) FLB setup, (b) top- and (c) side-view of how the sample and metal source are arranged during the heating process. (d-e) FM of the samples (d) before and (e) after growth of Ag/Ag_2MoO_4 NWs under UV excitation. Inset are the corresponding BF images. (f) FLB patterned micro-art of a *Cyprinus carpio*. Inset of (f) shows a multi-colour display obtained using different materials.

Laser assisted selective seeding of Ag NPs on GO film for the growth of hybrid Ag/Ag_2MoO_4 NWs on hotplate.

2. Characterisation – SEM, TEM

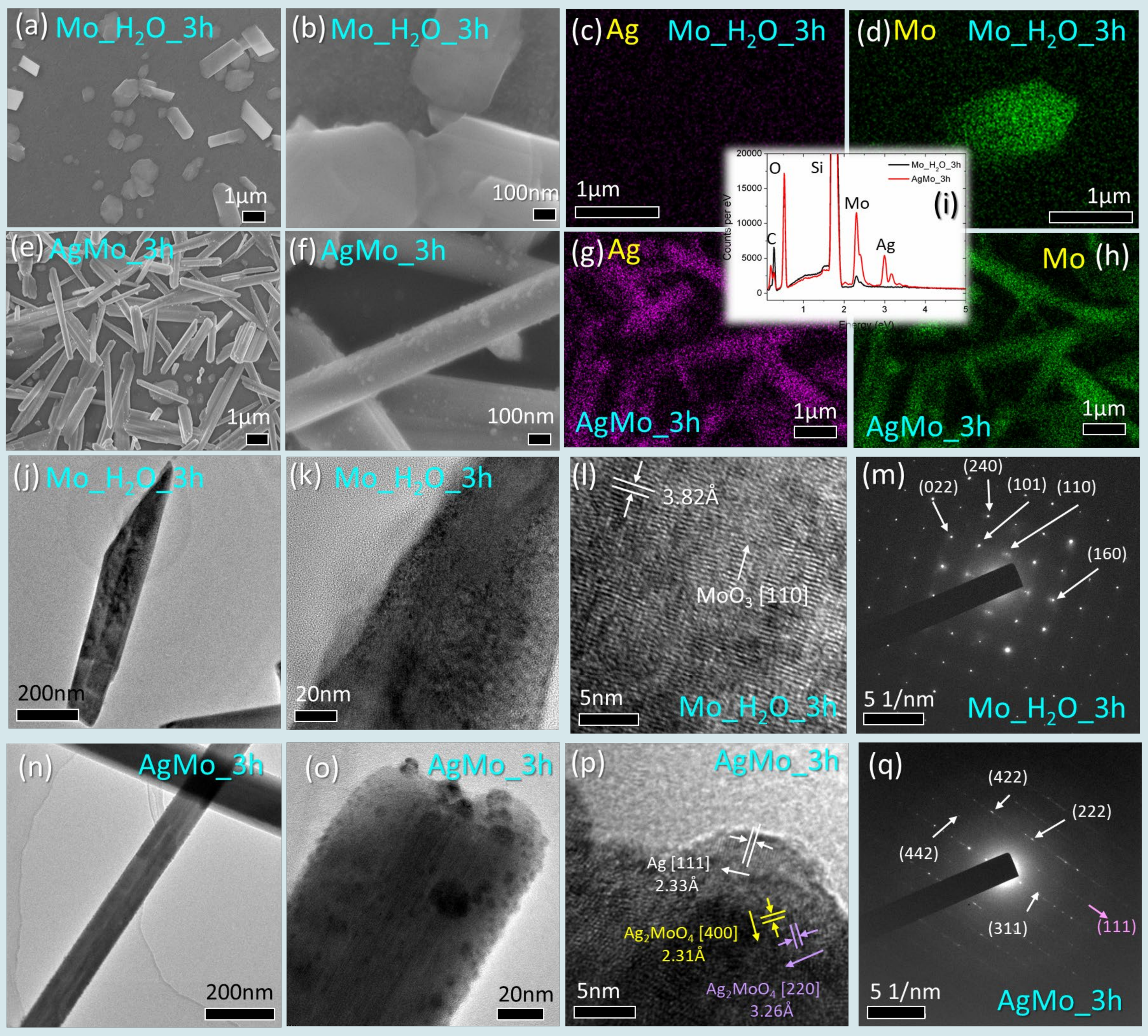


Figure 2. (a,b,e,f) SEM of (a,b) MoO_3 nanobelts and (e,f) Ag/Ag_2MoO_4 NWs. (c,d,g,h) EDX elemental map of (c,g) Ag and (d,h) Mo from (c,d) MoO_3 nanobelts and (g,h) Ag/Ag_2MoO_4 NWs. Inset is the corresponding spectrum obtained from both samples. TEM, HRTEM and SAED images of (j-m) MoO_3 nanobelts and (n-q) Ag/Ag_2MoO_4 nanowires.

SEM → importance of having Ag as the seeding agent to initiate the growth of hybrid Ag/Ag_2MoO_4 NWs.

HRTEM → successful creation of Ag embedded and decorated Ag_2MoO_4 NWs.

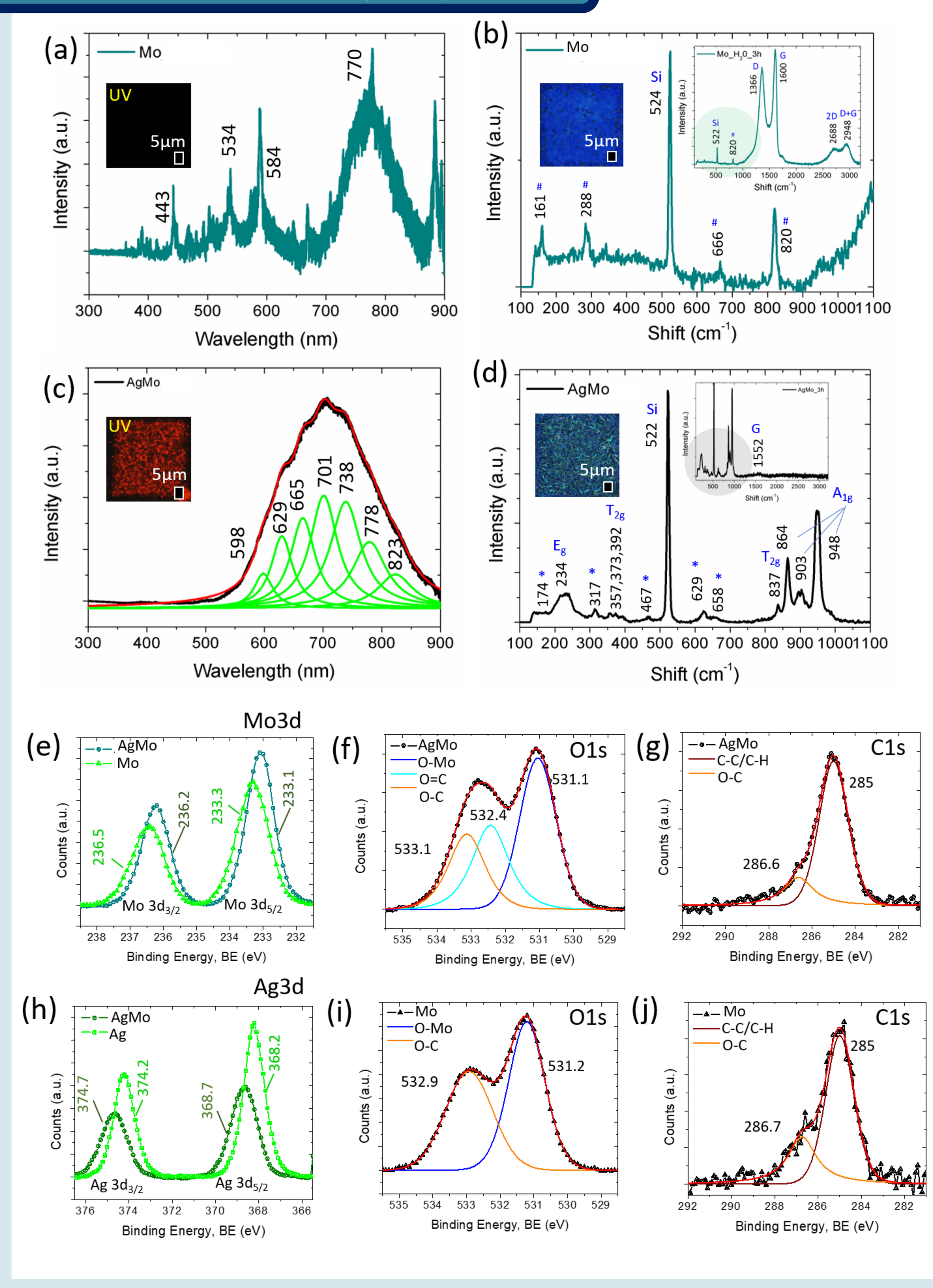
3. Characterisation – Raman, Photoluminescence (PL), XPS

Figure 3. (a,c) PL and (b, d) Raman spectrum of (a,b) MoO_3 nanobelts and (c,d) Ag/Ag_2MoO_4 NWs. Insets are the (a,c) FM and (b,d) BF images of the respective samples. Inset in (b, d) also show 100-3200 cm^{-1} scan of the respective samples. High resolution XPS scans of (e) Mo 3d, (f, i) O 1s, (g, j) C 1s and (h) Ag 3d of Ag NPs catalysts, MoO_3 nanobelts and Ag/Ag_2MoO_4 NWs.

PL
→ Strong broadband fluorescence centred at ~ 700 nm.

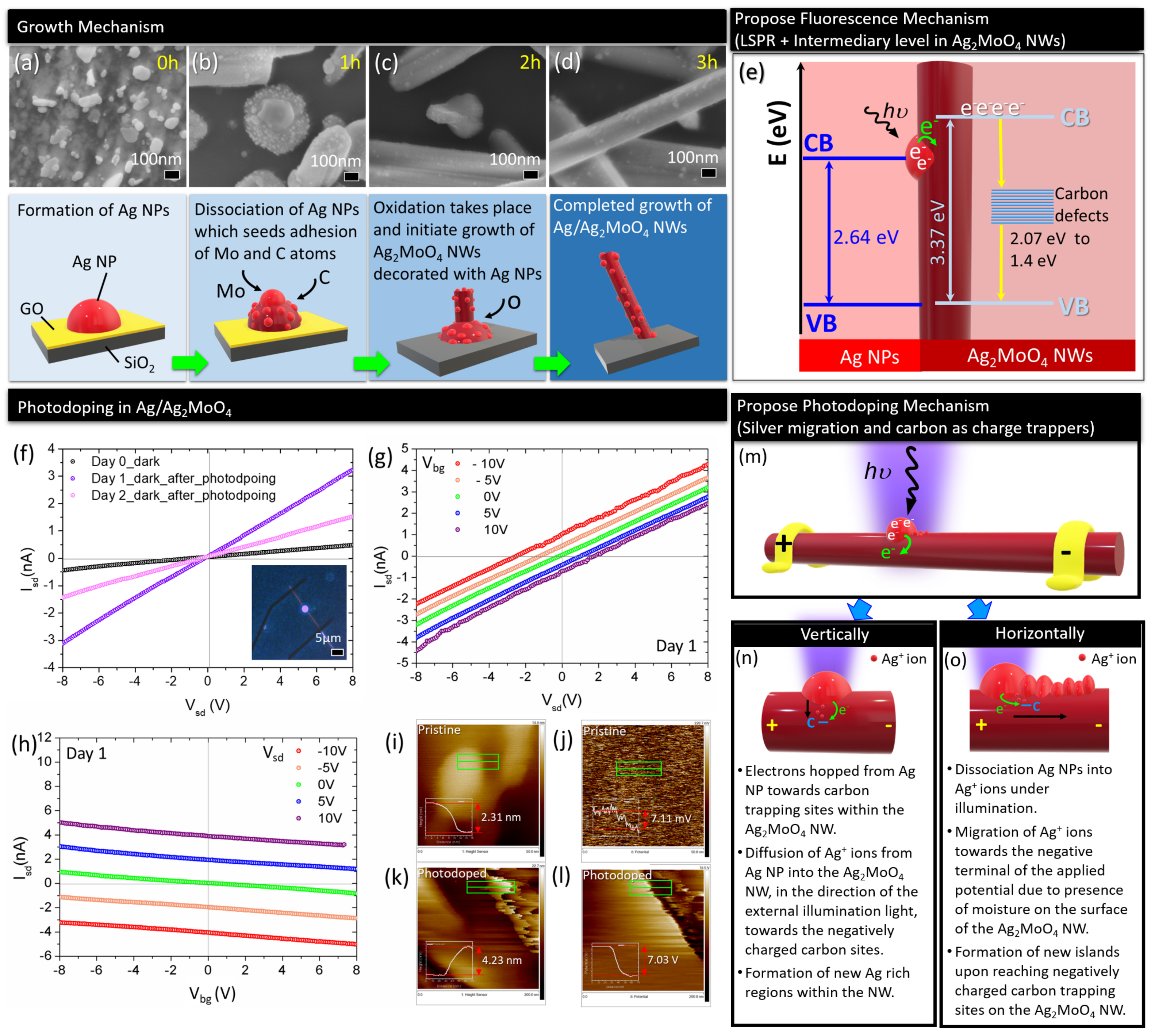
Raman
→ Substantial amount of carbon from the GO film is incorporated into the NWs, with some remanence found along the surface of the NWs, contributing to surface defects.

XPS
→ In Mo3d scan, absence of peak at 229.7 eV implies that Ag NPs in the hybrid system is relatively stable.
→ The lack of peaks at the 228.8 eV and 228.5 eV shows that there are no MoC formation in the hybrid material.



4. Mechanisms and Application

Figure 4. SEM images of Ag NPs patterned GO samples taken at (a) 0h, (b) 1h, (c) 2h and (d) 3h of growth in the presence of Mo foil. Below the SEM images are models illustrating the growth process. (e) Proposed mechanism for the observed red florescence from the Ag/Ag_2MoO_4 NWs. (f) I_{sd}-V_{sd} of single Ag/Ag_2MoO_4 NW before (Day0), one day (Day1) and two days (Day2) after photodoping with 325 nm focused laser beam. (g) I_{sd}-V_{sd} of Day 1 sample with back gate, V_{bg}. (h) I_{sd}-V_{bg} with applied V_{sd} ranging from -10V to 10V. (i-l) KPFM images of Ag NP on the NW (i, j) before and (k,l) after photodoping measurement. (m-o) Proposed mechanism for photodoping effect.



Growth mechanism
→ Laser -> reduce Ag^+ to Ag NPs -> Mo (from Mo foil) and C (from GO) vapour agglomerate at Ag NPs -> saturation, oxidation, dissociation of Ag NPs into Ag island to be embedded/decorated on Ag_2MoO_4 NWs.

Fluorescence mechanism
→ LSPR + carbon incorporated intermediary levels within the optical bandgap of Ag_2MoO_4 NWs.

Photodoping effect
→ Dissociation & diffusion of Ag NPs into Ag clusters -> Ag rich hetero-layer within the Ag_2MoO_4 NW

Conclusion

- Synthesis of carbon-infused Ag/Ag_2MoO_4 NWs with exceptional red fluorescing optical property.
- External illumination, applied potential & moisture on the highly dynamical Ag NPs -> the photodoping phenomenon detected.
- Gate tunable volatile nature of Ag NPs -> application for time-restricted transmission of sensitive information.

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