

Hydrogenation/Oxidation Induced Efficient Reversible Color Switching between Methylene Blue and Leuco- methylene Blue

Ya-Nan Liu, Xiao Zhou, Xin Wang, Kuang Liang, Zheng-Kun Yang, Cong-Cong

Shen, M. Imran, Shafaq Sahar and An-Wu Xu *

*Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical
Sciences at Microscale, Department of Chemistry, University of Science and
Technology of China, Hefei 230026, China*

**To whom correspondence should be addressed.*

Email: anwuxu@ustc.edu.cn

1. Experimental section

1.1. Materials

All the chemicals, such as dicyandiamide, potassium chloropalladite (K_2PdCl_4), hydroxyethyl cellulose (HEC) and Methylene Blue (MB) were purchased from commercial sources and used without further purifications. De-ionized water with the specific resistance of $18.25\text{ M}\Omega\cdot\text{cm}$ was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei).

1.2. Synthesis of g- C_3N_4 nanosheets

Graphitic carbon nitride powder was prepared through the polycondensation of dicyandiamide.¹ Typically, the dicyandiamide was heated to $550\text{ }^\circ\text{C}$ within 4 h and held for 4 h in static air. After cooling down to room temperature, the sample was heated at $620\text{ }^\circ\text{C}$ for 2 h in an argon atmosphere. The resultant yellow product was then ground into fine powders with a mortar and pestle and stored at room temperature for further use.

1.3. Synthesis of 2 wt% Pd/g- C_3N_4 catalyst

To synthesize Pd/g- C_3N_4 catalyst, 50 mg g- C_3N_4 was dispersed in 50 mL de-ionized water, then 0.94 mL K_2PdCl_4 aqueous solution (10 mM) was dropped into the mixture under vigorous stirring. After stirring for 24 h at room temperature, the powder was centrifuged, washed with de-ionized water and dried in a vacuum oven at $60\text{ }^\circ\text{C}$ overnight. Then, the powder was subjected to calcination at $250\text{ }^\circ\text{C}$ for 2 h under H_2/Ar (5%/95%) atmosphere. Finally, the resulting product was collected for characterization and further use. The surface of Pd nanoparticles (NPs) is clean since no additional surfactants were added.

1.4. Characterization

The phase structure of the product was characterized by X-ray powder diffraction patterns (XRD) using a Philips X' Pert Pro Super diffractometer with Cu K α radiation

(1.54178 Å), at 40 kV and 200 mA. Inductively-coupled plasma mass spectrometry (ICP–MS) was used to determine the actual Pd content after dissolving sample with a mixture of HCl and HNO₃ (3:1, volume ratio), and was carried out using Plasma mass spectrometer (PlasmaQuad 3). The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were conducted using a JEOL-2010 microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were acquired on a Thermo ESCALAB 250 with an Al Ka ($h\nu = 1486.6$ eV) as the excitation source. The concentration of MB at different time intervals was monitored by the absorption peak at $\lambda = 664$ nm using a Shimadzu UV-2501 spectrophotometer.

1.5 Color switching reactions

An HEC/H₂O stock solution was prepared by dissolving HEC (0.2 g) in H₂O (5 ml) at 60 °C. To prepare the color switching system, Pd/g-C₃N₄ dispersion (0.16 mg·ml⁻¹, 5 mL), MB/H₂O solution (40 ppm, 10 mL), HEC/H₂O stock solution were mixed together and sonicated to form a homogenous solution. Prior to each experiment, the reactor was sealed with a sealing film and continually purged with nitrogen for about 20 min to remove oxygen from the system. The flow of hydrogen and oxygen to the reaction was controlled to maintain at 1 bar. At given time intervals, about 0.5 mL aliquots were sampled, filtered through a 0.22 μm membrane filter to remove the remaining catalyst, then monitored with Shimadzu UV-vis spectrophotometer (Model 2501 PC).

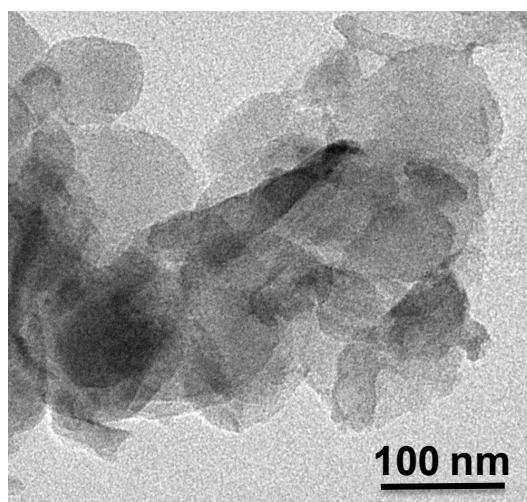


Fig. S1 The TEM image of pure g-C₃N₄.

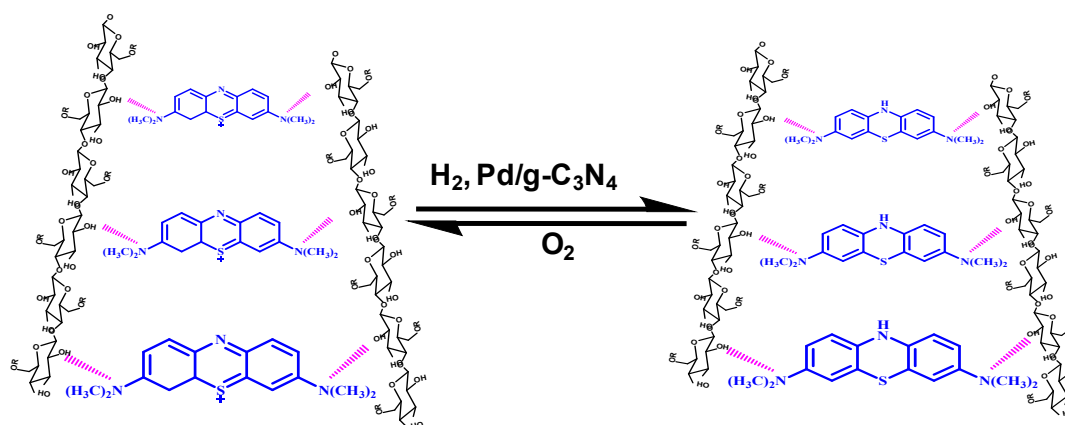


Fig. S2 The stabilizing effect of HEC in color switching reaction.

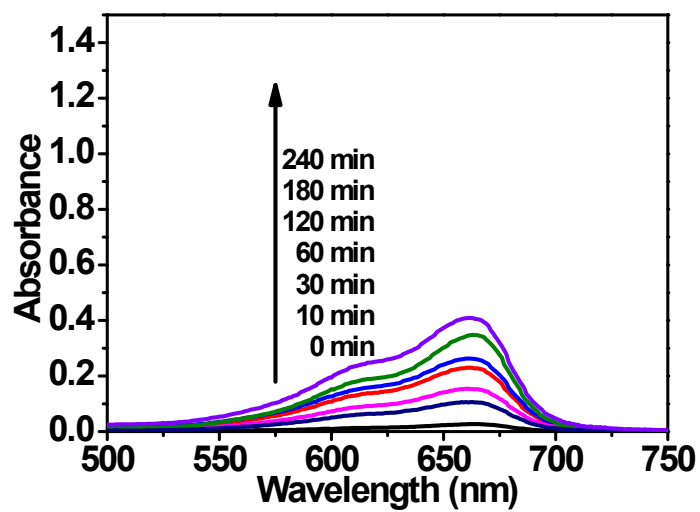


Fig. S3 UV/Vis spectra of the recoloration process in the absence of catalyst under 1 bar O₂ at room temperature.

References

1. Y. Y. Kang, Y. Q. Yang, L. C. Yin, X. D. Kang, G. Liu and H. M. Cheng, *Adv. Mater.*, 2015, **27**, 4572-4577.