

Metal-enhanced chemiluminescence from chromium, copper, nickel, and zinc nanodeposits: Evidence for a second enhancement mechanism in metal-enhanced fluorescence

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Over the past decade metal-fluorophore interactions, metal-enhanced fluorescence, have attracted significant research attention, with the technology now becoming common place in life science applications. In this paper, we address the underlying mechanisms of metal-enhanced fluorescence (MEF) and experimentally show using chemiluminescence solutions that MEF is indeed underpinned by two complimentary mechanisms, consistent with the recent reports by Geddes and co-workers [Zhang *et al.*, *J. Phys. Chem. C* **113**, 12095 (2009)] and their enhanced fluorescence hypothesis. © 2010 American Institute of Physics. [doi:10.1063/1.3492849]

Chemiluminescence is widely used throughout the scientific and medical communities as an analytical tool.^{1–4} It offers simplicity, reduced background interference, and does not require optical filters or an excitation source. Chemiluminescent-based detection is limited by the availability of probes, the need for reagents to chemically induce electronically excited states, and the quantum efficiency of chemiluminescent solutions. Bioassays relying on chemiluminescent detection would clearly benefit from an increased overall brightness.

Our laboratory has developed a technology that has been shown to increase the overall brightness of chemiluminescent and fluorescence based detection systems.^{5–8} In our previous paper,⁵ we observed metal-enhanced chemiluminescence (MEC) on silver coated nanoparticulate slides and showed that MEC is mechanistically similar to the closely related phenomenon, metal-enhanced fluorescence (MEF), Fig. 1. MEF has been observed from several metals, including Cr, Cu, Ni, Sn, Fe, and Zn.^{9–12} Subsequently, in this paper we likewise explore thin nanoparticle coatings of Cr, Cu, Ni, and Zn for applications in MEC.

The Cr, Cu, Ni, and Zn were vapor deposited onto glass slides using an Edwards Auto 306 vapor deposition unit. The Chemiluminescence was detected with an Ocean Optics HR2000+fluorometer from the top chemiluminescence side of the films. To demonstrate MEC, 60 μ l of green chemiluminescent solution (acridan oxalate system⁵) was sandwiched between a 1" \times 1" glass and metal coated slide or two glass slides (control sample) containing no metal. Each set of slides consisted of three metal coated slides of different thicknesses (e.g., 1 nm Cr, 4 nm Cr, and 10 nm Cr) and an identical control glass sample which contained no metallic nanoparticles.

When determining the chemiluminescence enhancement factors (i.e., MEC), the emissions were measured between 8.5 and 10.5 min after the solution was activated to avoid measuring during the initial steep chemiluminescence decay,

where measurement errors were deemed to occur [Fig. 4(a)]. During a 1–2 min measurement window, each sample and control in a set was measured three times and spatially averaged. The enhancement factors for each sample thickness were calculated by dividing the average emission intensity of the metal coated slide by that of the control.

The data shows that the metal coated slides increased the chemiluminescence emission with the spectrum of both the control and sample being very similar (Fig. 2, left). These results support our previous MEC conclusions in that MEC increases the brightness but does not change the emission profile of the chromophore, consistent with our mirror dipole concept.^{5,6}

The mechanism for MEC has been reported, as being very similar to MEF (Fig. 3).⁷ The main difference is that MEF is externally excited, pumped by a light source, while chemiluminescence is chemically excited.^{5,6} In recent reports of MEF,^{5,13} it has been reported that both an electric field enhanced absorption and a plasmon coupling component are the two underlying mechanisms which cooperatively contribute to the observed enhanced emission intensities. For MEC, only a plasmon coupling component is present as no external light source is used for chemiluminescence.¹⁵ We have subsequently questioned whether the four new surfaces would support this previous hypothesis obtained with silver nanoparticles. By allowing the chemiluminescence solutions on metal to run to completion, which depletes only the oxidiz-

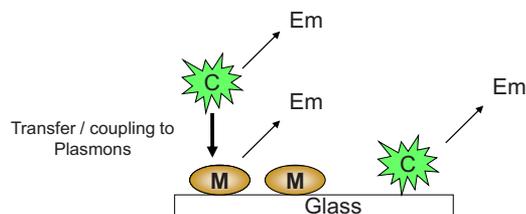


FIG. 1. (Color online) Cartoon depicting our current interpretation of MEC. Solution chemically excited states induce surface metal mirror dipoles in the near field, which radiate the coupled quanta in the far field as enhanced chemiluminescence. C—chemiluminescence species, M—metal, and Em—emission.

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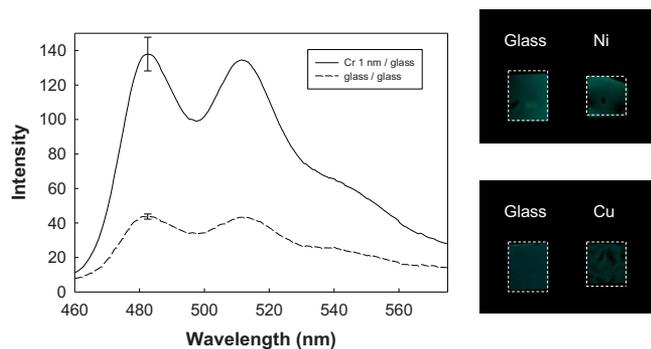


FIG. 2. (Color online) Chemiluminescence emission spectra in a Cr metal/glass sandwich and from a glass/glass sandwich (control sample), left. True color photographs showing the chemiluminescence intensity from between glass/glass and sheet metal/glass sandwiches, right.

ing agent and not the fluorophore, external laser line excitation would be expected to show further luminescent enhancements, with the introduction of an additional electric field component. Figure 3 shows the enhancement factors observed relative to a glass-glass control sample for both chemiluminescence and laser excited depleted chemiluminescence solution. As expected, additional enhancements were observed for Cr, Cu, and Zn nanoparticles, with less pronounced changes for Ni nanoparticles. These findings are consistent with our observations for MEC from silver nanoparticles and indeed our mechanistic description of the MEC phenomenon,¹⁵ i.e., that it originates solely from a plasmon coupling and emission mechanism.

Figures 3(a) and 3(b) also show that the thinner the coatings of Cr and Cu the greater the enhancement of MEC and for the case of exciting depleted solutions, MEF. While a

10 nm coating of Cr and Cu showed MEC, there was no enhancement of the MEF at that thickness. 1 nm of Ni coating enhanced the emission in both MEC and MEF, but the thicker coatings of Ni effectively quenched emission [Fig. 3(c)]. While the enhancement factors for MEF of Zn followed the same decreasing trend as the other metals, the enhancement factor of the MEC increased from 3 nm of Zn coating to 4 nm before decreasing at 5 nm. It is important to note that different thicknesses of Zn available were 3, 4, and 5 nm, whereas the thicknesses of Cr, Cu, and Ni were 1, 4, and 10 nm. The small difference in the thicknesses of the Zn samples is likely the reason that the decreasing trend in Zn is not as obvious as in the other metals, and was due to the availability of metallic nanodeposits at that time. For all metal substrates, the enhancements were observed to decrease as a function of increased film thickness, consistent with our previous reports from silver nanoparticles^{5,6} and due to the fact that localized confined resonances are required in MEF and MEC,⁵ i.e., the coupled quanta is not delocalized or propagating.

Lastly, given the widespread use of ions to catalyze chemiluminescent solutions,¹⁶ we undertook several control experiments to ascertain whether Cr, Cu, Ni, or Zn thermally evaporated nanoparticles could also catalyze the chemiluminescent reaction and additionally contribute to the increased emission.¹⁶ This, at first, seemed unlikely as the thicker coatings of metals provided for the smallest emission enhancements (Fig. 3). Subsequently, to determine the decay rates, two experimental systems were built side by side so the glass/metal sandwich and the glass/glass sandwich could be measured simultaneously. Eight minutes after activating the solutions, 60 μ l of chemiluminescent solution was used for

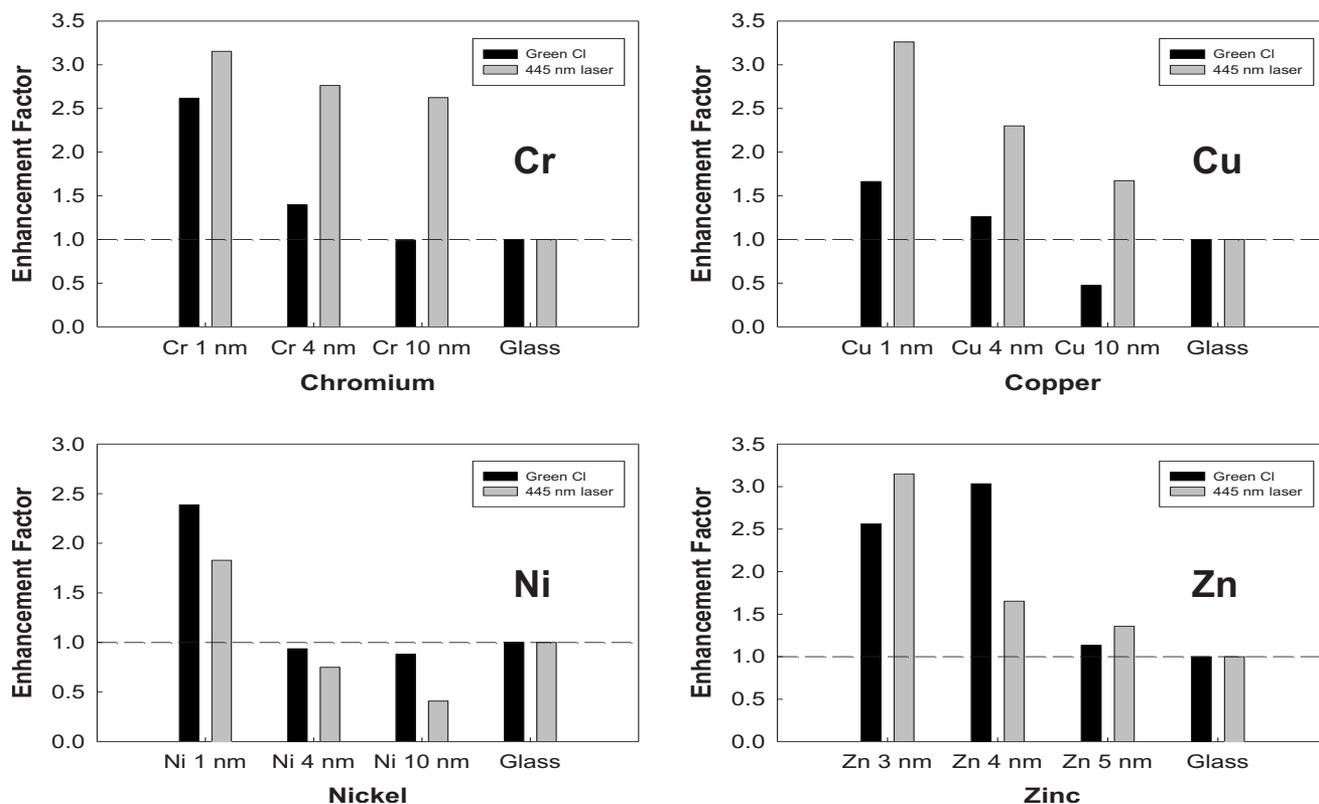
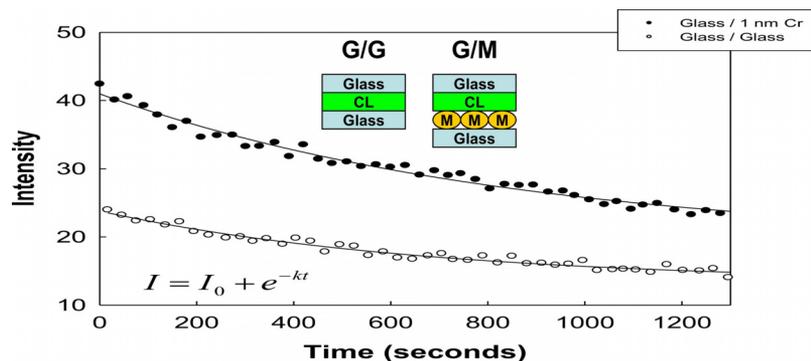


FIG. 3. Enhancement factor vs metal deposition thickness for four metals for both a green chemiluminescence solution and the same solution after reaction completion and subsequent optical excitation at $\lambda_{ex}=473$ nm.



Samples	k (S ⁻¹)	Error (1 std)	R ²
Cr Control (glass/glass)	0.0015	0.0002	0.97
Cr (1 nm)/glass	0.0012	0.0001	0.98
Cu Control (glass/glass)	0.0017	0.0001	0.99
Cu (1 nm)/glass	0.0012	7.97 × 10 ⁻⁵	0.99
Ni Control (glass/glass)	0.0015	0.0001	0.98
Ni (2nm)/glass	0.0014	0.0003	0.94
Zn Control (glass/glass)	0.0010	0.0002	0.97

FIG. 4. (Color online) Green Chemiluminescence intensity decay vs Time (top) with the glass/glass and metal/glass sample geometry inserts and the tabulated first order decay kinetics for various metal and glass sandwiches (bottom).

both the sample and control, and the emission at 512 nm was measured every 20 s for 22 min.

The results in Fig. 4 show the rates of decay of Cr, Cu, Ni, and Zn were all comparable to their respective glass/glass controls which contained no metal, and thus the metals were deemed to have minimal if any catalytic influence on the far-field luminescence. These findings support our previous findings from particulate silvered films⁵ and continuous surfaces^{13–15} where the metals were found to have minimal to no catalytic effect, the metal present in the zero state as compared to ionic films.

In summary, this paper describes MEC from Cr, Cu, Ni, and Zn nanoparticulate films similar to trends observed for MEF using the same metals. The enhanced chemiluminescence signatures observed were at best between two to three-fold larger than the control sample, suggesting the downstream use of nanoparticulate films in applications of chemiluminescence. Finally, surface plasmon coupling and indeed enhancement has been shown to be effective up to 20 nm from the surface.⁸ Given that the solution thickness between the slides was approximately 1000 nm, only 2% of the solution was thought to be within the interaction distance.⁵ This implies that the near-field MEC enhancement was 50-fold greater, approximately 200 times that of the glass control sample.

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