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Galvanic Exchange on Reduced Graphene Oxide. Designing a Multifunctional Two-Dimensional Catalyst Assembly

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Two-dimensional graphene based systems have been used in various applications such as energy storage and conversion, photocatalysis, drug delivery etc. The appeal of graphene lies in its large surface area and high electron mobility. Also discovery of Dirac-fermions and the Quantum Hall effect in graphene have added to the interest in this unique material. Graphene oxide (GO) offers a simple and economical route to process single-few layers of graphene sheets with oxygen containing functional groups. The ability of GO to accept and conduct electrons from semiconductors makes it interesting for various applications.

We have succeeded in anchoring semiconducting titanium dioxide (TiO_2) nano particles and metal nano particles (silver and gold) on the 2-D conductive network of GO. Photogenerated electrons from TiO_2 are transported across GO network to reduce silver ions into silver nanoparticles. These silver nanoparticles are then galvanically exchanged with gold ions forming gold nanoparticles. Such interesting chemical transformation on GO surface demonstrates GO's versatile ability to anchor a wide array of nano-particles. This coupled with GO's unique ability to capture and conduct electrons has been used to contrive a two-dimensional catalyst nanomat (Scheme-1). Using methyl viologen as a probe we elucidate the photocatalytic activity of the Semiconductor-GO-Metal nanoassembly and highlight the mediation of GO in charge transfer processes. These findings pave the way for the development of graphene-based multifunctional composites for photo-catalysis and detect and destroy applications.

Transmission electron microscopy helps us support the spectroscopic data of the above chemical transformations (Figure 1). Various data such as particle size, reciprocal lattice spacings, and elemental analysis via energy-dispersive X-ray spectroscopy (EDX) were gathered from TEM. The quantitative analysis of the EDX spectra indicated that the unreacted silver in the sample to be ~25% and gold to be ~75% (Figure 2). TEM analysis indicates particles are located at different sites and thus the ability of RGO to facilitate spatially separated deposition of TiO_2 and Ag nanoparticles.

The galvanic exchange process was also monitored through the size distribution of Ag nanoparticles deposited on RGO before and after the $AuCl_4^-$ treatment. TEM images used for this analysis are also shown in Figure 3. Reasonably good overlap between the size distribution of Au with that of Ag and NPs further gives credence to our arguments made for the galvanic exchange process. The distribution analysis supports the fact that Ag centers act as nucleation sites for Au NPs.

References:
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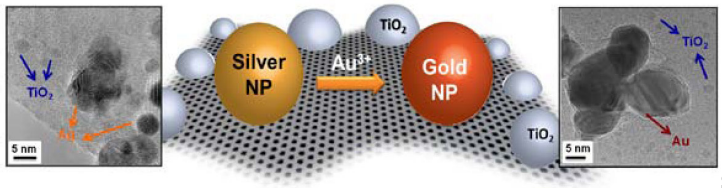

Scheme 1. RGO catalyst mat showing galvanic exchange between silver nano particles and gold ions yielding gold nano particles.

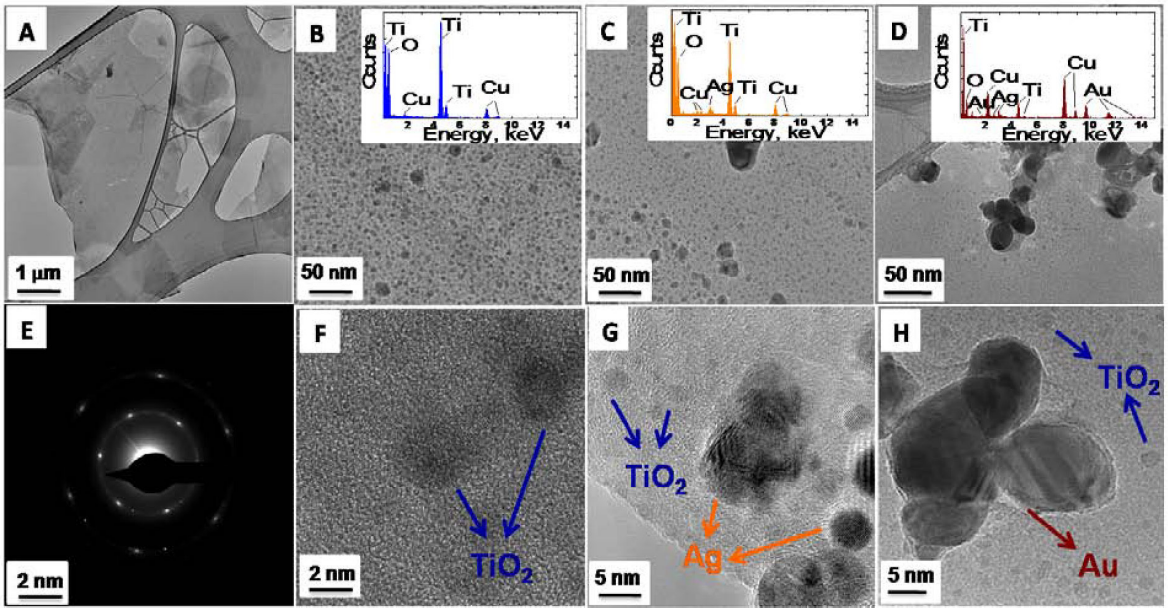

Figure 1. TEM images of **(A)** Bare RGO sheets, **(B)** TiO_2 particles anchored on RGO sheets, **(C)** TiO_2 and Ag particles and **(D)** TiO_2 and Au particles anchored on RGO sheets. Insets of B-D show elemental analysis via energy-dispersive X-ray spectroscopy supporting the presence of respective particles on RGO **(E)** Diffraction pattern of graphene. HRTEM images **(F)** TiO_2 particles anchored on RGO sheets, **(G)** TiO_2 and Ag particles and **(H)** TiO_2 and Au particles anchored on RGO sheets. Samples were prepared by dropcasting 50µl of the respective dispersions and drying over holey carbon grid.

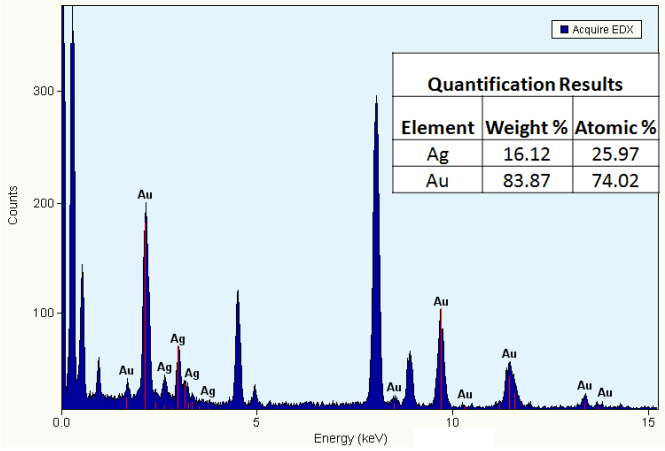

Figure 2. Elemental analysis via energy-dispersive X-ray spectroscopy showing the presence of Ag and Au particles on RGO. Inset showing the quantitative distribution of Ag and Au elements in the sample.

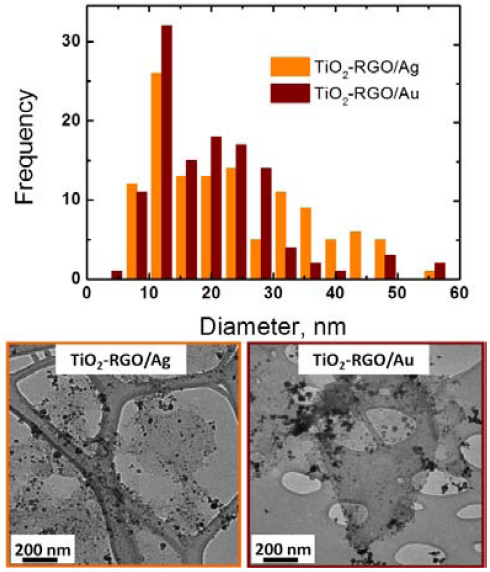

Figure 3. Size distribution of Ag and Au NPs on TiO_2-RGO. Also shown are TEM images of TiO_2-RGO/Ag and TiO_2-RGO/Au composites used for size distribution analysis.

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