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Atomic Plane-Selective Deposition of Gold Nanoparticles on Metal Oxide Crystals Exploiting Preferential Adsorption of Additives

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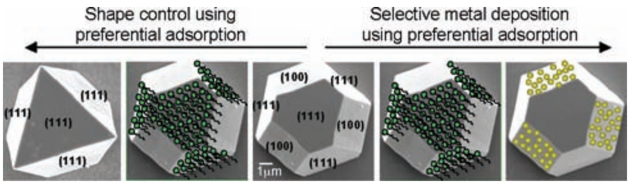
Semiconductor−metal composite materials are used as catalysts and electrodes for a broad range of applications.[1−4] The semiconductor−metal interactions can depend significantly on their interfacial structures. Therefore, understanding and manipulating the semiconductor/metal interfacial structures are critical to enhance desired properties of the composite materials. In particular, the ability to selectively place metal particles/catalysts on certain crystallographic planes of semiconductor crystals in polycrystalline electrodes is of special interest in that it can allow us to understand anisotropic (i.e., atomic plane-dependent) interactions between the metal and the semiconductor surfaces without needing a single crystal semiconductor substrate. Based on this understanding, the interface of a semiconductor electrode can be tailored to maximize preferred semiconductor−metal interactions.

In this paper we report a simple solution-based chemical method to deposit gold nanoparticles on selective crystallographic planes of semiconductor crystals (i.e., Cu_2O and ZnO) using anisotropic interactions between additives and inorganic surfaces. Certain additives introduced to the growth medium of inorganic crystals are known to adsorb on specific crystallographic planes of the crystal more strongly than others.[5−10] Such preferential adsorption of additives hinders the inorganic growth perpendicular to the bound plane and can alter the final crystal shape (Scheme 1, left).

We postulated that the additives that preferentially adsorb on a certain semiconductor surface could also be utilized for selectively inhibiting metal deposition on these planes (Scheme 1, right). Since the adsorption of additives is achieved in situ during metal deposition, this method does not require any chemical or physical treatment before and after metal deposition,[11] significantly simplifying the procedure for selective metal deposition.

Scheme 1. Utilization of Preferential Adsorption of Additives for Shape Control (Left) and for Atomic Plane-Selective Metal Deposition (Right)



Previously, we reported that the preferential adsorption of sodium dodecyl sulfate (SDS) on {111} planes of Cu_2O crystals can be utilized to obtain octahedral crystal shapes.[6,7] To probe the possibility of using the same phenomenon for selectively inhibiting gold nucleation on the {111} planes of Cu_2O crystals, micrometer size Cu_2O crystals were first electrochemically deposited on indium tin oxide (ITO) substrates with three different shapes, cubic, octahedral, and truncated octahedral (Supporting Information).

Gold particles were placed on these Cu_2O crystals via electrodeposition by using Cu_2O crystals on ITO as the working electrode. The counter electrode was platinum foil and the reference electrode was a double junction Ag/AgCl electrode in 4 M KCl /4 M KNO_3. A 0.1 mM $AuCl_3$ aqueous solution was used as a plating solution, and deposition was carried out potentiostatically at $E = -0.1$ V at room temperature (see Supporting Information for the X-ray diffraction (XRD) pattern of the resulting Cu_2O/Au electrodes).

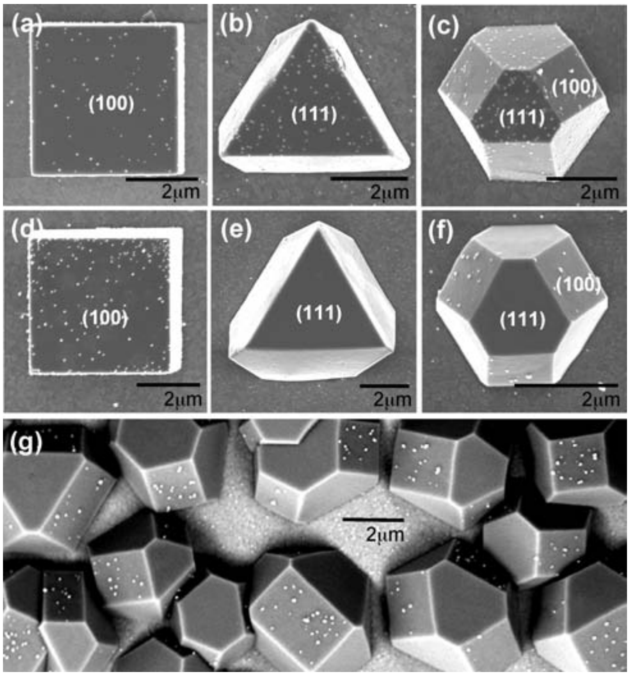


Figure 1. SEM images of Au particles deposited on Cu_2O crystals without (a−c) and with SDS (d−g). All truncated octahedral crystals in (g) consistently show no Au deposited on {111} planes. Additional low magnification SEM images showing Cu_2O/Au crystals with and without plane selectivity can be found in the Supporting Information.

SEM images of cubic, octahedral, and truncated octahedral Cu_2O crystals after 15 s of gold deposition show that gold nanoparticles were formed on both {100} and {111} planes (Figure 1a−c). To observe the effect of SDS on gold deposition, the same deposition was carried out after 0.2 M SDS was introduced to the plating solution. For the ITO electrode containing only cubic crystals, gold deposition occurred on all {100} planes (Figure 1d), which was expected as SDS does not adsorb strongly on {100} planes of Cu_2O.[6] However, for the ITO substrate composed of only octahedral crystals, no gold deposition was observed on the Cu_2O surfaces (Figure 1e), which indicates that the adsorption of SDS on the {111} planes can effectively inhibit the nucleation of gold on these planes. The selective blocking of gold deposition on {111} planes of Cu_2O is best demonstrated by gold deposition on truncated octahedral Cu_2O crystals that contain both {100} and {111} planes. Figure 1f

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and g unambiguously show that gold particles were selectively deposited on {100} planes. To determine the extent of the deposition selectivity, we examined 273 {100} planes and 372 {111} planes contained on 100 discrete truncated octahedral Cu_2O/Au crystals prepared with SDS. The average number of Au particles found on {100} and {111} planes were 11.36 and 0.04, respectively. This clearly confirmed the selectivity of gold deposition on {100} planes achieved by the preferential adsorption of SDS.

The minimum amount of SDS required to selectively hinder gold deposition on {111} Cu_2O planes was 0.2 M. This SDS concentration is similar to the SDS concentration that is necessary to grow Cu_2O crystals with uniform octahedral shapes.[6] When the SDS concentration is decreased below this value, gold particles started to form also on the {111} planes. The selectivity of gold deposition can also be removed when the driving force for gold nucleation is increased by applying a more negative potential ($E < -0.2$ V) or by increasing the concentration of Au^{3+} ions (>0.1 mM), which increases the overpotential for gold deposition.

To demonstrate the general applicability of this method, selective gold deposition on ZnO was also investigated. ZnO has the hexagonal wurtzite structure and can be grown as hexagonal rods by electrodeposition, which have {0001} and {01−10} planes as the end and the side facets of the rods, respectively. When Cl^- ions are added to the plating solution, they adsorb on the polar {0001} planes and alter ZnO crystal shapes from hexagonal rods to hexagonal plates (Supporting Information).[8−10]

We probed the possibility of using the preferential adsorption of Cl^- ions on {0001} planes of ZnO rods for selective deposition of gold on {01−10} planes. Gold particles were placed on ZnO rods via photochemical deposition, which utilizes photoexcited electrons in the conduction band of ZnO for the reduction of Au^{3+} ions (Supporting Information).[12]

The SEM and back scattered electron (BSE) images show that when 0.1 mM $Au(CH_3COO)_3$ ethanol solution was used as the deposition solution, gold particles were formed on both {0001} and {01−10} planes (Figure 2a). In BSE images, gold particles appear as brighter spots due to the higher electron density of gold than zinc oxide, which can clearly distinguish gold particles from other features on the ZnO surfaces. When the concentration of $Au(CH_3COO)_3$ was reduced to 0.05 mM, the nucleation density of gold on both {0001} and {01−10} planes was equally and nonselectively decreased, resulting in deposition of less gold particles on both planes (Figure 2b). This indicates that there is no intrinsic atomic plane-dependent selectivity of ZnO for Au deposition. When Cl^- ions were introduced to the deposition solution by using 0.05 mM $AuCl_3$ ethanol solution as the Au^{3+} source instead of 0.05 mM $Au(CH_3COO)_3$, no gold particles were deposited on {0001} planes although the nucleation density on {01−10} planes was significantly increased (Figure 2c). This indicates that the adsorption of Cl^- ions on {0001} planes is responsible for the selectivity of gold deposition achieved. When we examined 119 ZnO/Au crystals prepared from this condition, we found only four {0001} planes with one gold particle while the rest did not contain any. The rare exceptions observed were most likely due to the imperfection (e.g., pits, cracks) of the {0001} planes in these crystals.

In summary, we developed a simple solution-based chemical route for atomic plane-selective metal deposition by utilizing preferential adsorption of additives as an in situ generated mask to protect certain planes of oxide crystals from metal deposition. In this study, we demonstrated selective gold deposition on Cu_2O and ZnO crystals as examples, but the same strategy can be used as a general route for selective or asymmetric deposition of a broader range of catalysts (e.g., oxides and chalcogenides) on various crystalline surfaces. The method described here may make it possible to design highly structured composite architectures that contain multiple catalysts with different functions on specific locations of the semiconductor surfaces.

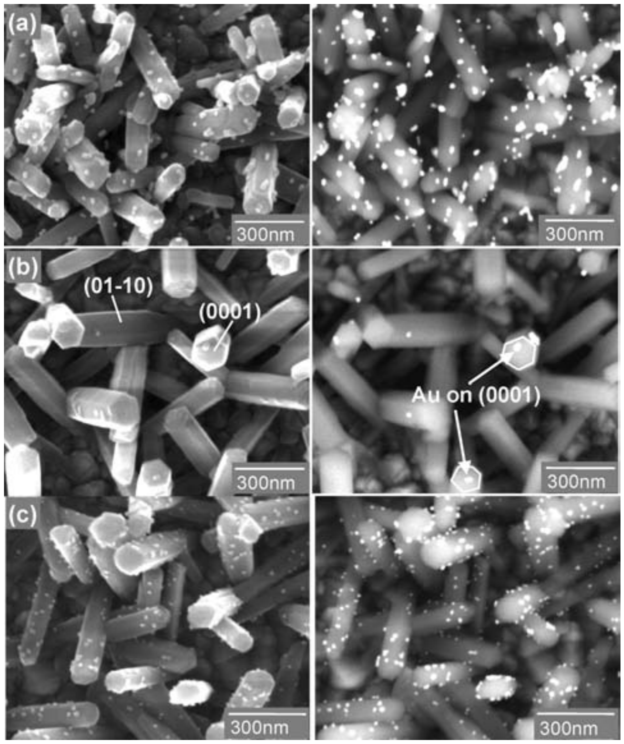

Figure 2. SEM of Au photochemically deposited on ZnO rods in (a) 0.1 mM $Au(CH_3COO)_3$, (b) 0.05 mM $Au(CH_3COO)_3$, and (c) 0.05 mM $AuCl_3$ ethanol solution. The corresponding BSE images are shown in the right column. An enlarged Figure 2 and an SEM image showing the selective Au deposition on ZnO crystals with wider {0001} planes can be found in the Supporting Information.

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Supporting Information Available: Experimental section, SEM of Cu_2O and ZnO crystals before Au deposition, low magnification SEM of Cu_2O/Au and ZnO/Au composite crystals, and XRD of Cu_2O/Au crystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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